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TO KATE
For Understanding

CO-ORDINATION CHEMISTRY OF VINYLPYRIDINE POLYMERS

Ian Burchette, B.A., M.Sc.

A Thesis submitted for the degree of Doctor of Philosophy

The University of Aston in Birmingham

January 1982

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SUMMARY

Preparations of polymeric derivatives of 4-Vinylpyridine, in finely divided from, using 'suspension' polymerisation methods are described. These products have formed the basis of experiments dealing in a quantitative manner with reaction and absorption of first row transition metal ions from solution by the macromolecular ligands. The possibility that these polymers may selectively absorb some ions is investigated and some comparative experiments are described. The results of variation in reaction conditions are reported. In particular, attention is focussed on reaction of mixtures of Cobalt (II), Nickel (II) and Copper (II) with the polymers. The possibility that pH and anion dependance occurs in these reactions is considered.

The structures of the metal ion containing polymeric products from the absorption experiments have been investigated using electron spin resonance, nuclear magnetic measurements and elemental analyses. The results have been compared with those for analogues prepared from the monomer (4-vinylpyridine) and from the polymers (poly(4-vinylpyridine) and poly(4-vinylpyridine-N-oxide)) by reaction in solution.

A novel approach to preparation of selective polymers, which may have wider application, is described for poly(4-vinylpyridine).

Vinylpyridine polymers
Co-ordination chemistry

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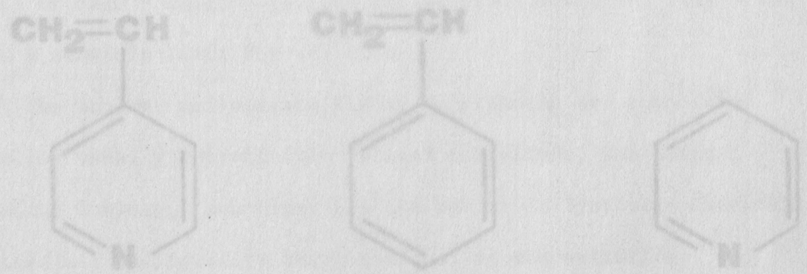
CHAPTER I

INTRODUCTION



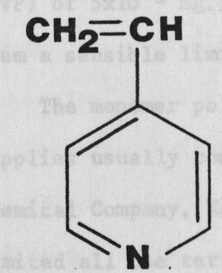
4-Vinylpyridine Styrene Pyridine

I. INTRODUCTION

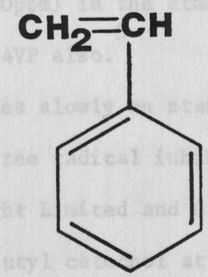
This report describes the work which has been carried out in a study of reactions of monomer 4-vinylpyridine (4VP) and related polymers with some of the first row Transition Metal cations. The study resulted from interest shown by the industrial manufacturers of the monomer, Croda Synthetic Chemicals Limited, in finding new outlets for their product. An initial brief study by an undergraduate project student indicated that further investigation might prove fruitful.[1] The initial aims of this project then were to discover if poly(4-vinylpyridine) or related polymers could selectively absorb some Transition Metal ions from their aqueous mixtures and to examine the structure of the metal containing polymers produced.

I.1 The Monomer

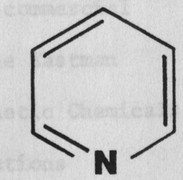
4-Vinylpyridine (4VP) is a heterocydic aromatic vinyl monomer it combines some characteristics of styrene with some of those of Pyridine, as might be expected



4-Vinylpyridine



Styrene



Pyridine

The presence of the vinyl bond enables polymerisation to occur by free radical, catonic or anionic reaction mechanisms as for styrene and causes the monomer to be much less soluble in water than is Pyridine itself. The presence of the pyridyl unit containing the Nitrogen atom bearing a lone pair of electrons in an sp^2 hybridized orbital allows 4VP to behave just as pyridine does in reactions with Transition Metal (TM) cations, that is as an electron donating ligand. Larkworthy and Agnew have prepared a number of complexes of TM cations having 4VP as ligand.[2-4]

Freshly distilled 4VP is a clear colourless liquid under normal conditions but quickly discolours on exposure to the atmosphere. Physiologically it is an extremely unpleasant substance and severe irritation quickly results from skin contact. Prolonged exposure to the vapour which also causes irritation of the skin, as well as of the eyes and respiratory tract, must be avoided. More severe allergies to this monomer can develop in some individuals. Though no figures for the toxicity of 4VP are directly available a Soviet study has suggested a maximum permissable level for 2-Vinylpyridine (2VP) of 5×10^{-3} mg.l^{-1} (40ppm) in the atmosphere and this would seem a sensible limit for 4VP also.[5]

The monomer polymerises slowly on standing and commercial supplies usually contain free radical inhibitors, the Eastman Chemical Company, Koch-Light Limited and Croda Synthetic Chemicals Limited all use tertiary butyl catechol at concentrations of about 0.1% by weight on the monomer. 4VP is hygroscopic at room temperature and drying is an important part of the purification procedure. As normally supplied the monomer has a red or brown discolouration caused by reaction with atmospheric oxygen, this

is removed by distillation under reduced pressure of nitrogen to give the pure water clear monomer.

I.2 Polymerisation of 4-Vinylpyridine

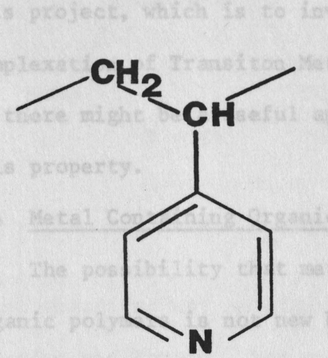
Numerous methods for the polymerisation of Vinylpyridines have been described, free radical, anionic and cationic initiation reactions all being successful. Anionic polymerisation of 2VP and 4VP can be carried out in much the same way as for styrene,[6] 'living polymers' can be prepared by reaction of the monomers with Sodium/Napthalene complexes allowing construction of block copolymers as well as the homopolymers.[7] Attempts to prepare steroregular polymers of 4VP using Grignard and related reagents as initiators yielded only a random polymer and not the steroregular polymer they do with 2VP and this has been attributed to the greater distance between the vinyl bond and the nitrogen atom preventing formation of the required tightly packed complex.[8]

Polymerisation of 4VP by a cationic mechanism has been reported by Salamone et al, here initiation occures upon protonation in concentrated acid.[9]

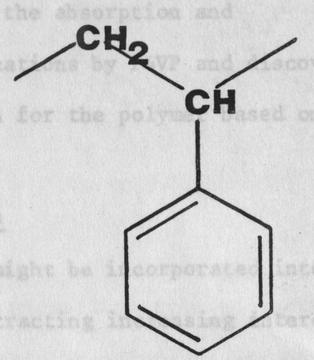
Free radical polymerisations have been the most widely used preparative routes to poly(4-Vinylpyridine) (P4VP), bulk,[10] emulsion,[12,13] suspension[14] and a variety of solution processes have been described. In the latter, alcohols have been the most common solvents though chloroform and DMF have been used.[15-18] There appears to be some difference in the solubilities of samples of the polymer produced in various ways.[19,20] Suspension polymerisation of 4VP works well under Nitrogen but as in many cases presence of oxygen causes failure of the reaction. Brief reviews of vinylpyridines as monomers have been published[21,22] together with a more recent and detailed work.[23]

I.3 The Polymer

The basic structure of the homopolymer, poly(4-Vinylpyridine) is much the same as that of polystyrene with pendant aromatic rings on the aliphatic backbone chains.



Poly(4-Vinylpyridine)



Polystyrene

Poly(4-Vinylpyridine) (P4VP) is a stable white solid, soluble in chloroform, low alcohols, DMF and aqueous acids (forming a Poly(4-Vinylpyridinium) polycation in the latter case). Solubility in acetone seems to decrease with increasing degree of polymerisation, this may also explain reported differences for solubility of P4VP in toluene. The polymer is insoluble in water ethers and generally in hydrocarbons.

From a comparison of the basic structure of P4VP with related low molecular weight analogues 4VP, 4-ethylpyridine and pyridine itself we can expect the polymer to show similar ligand type

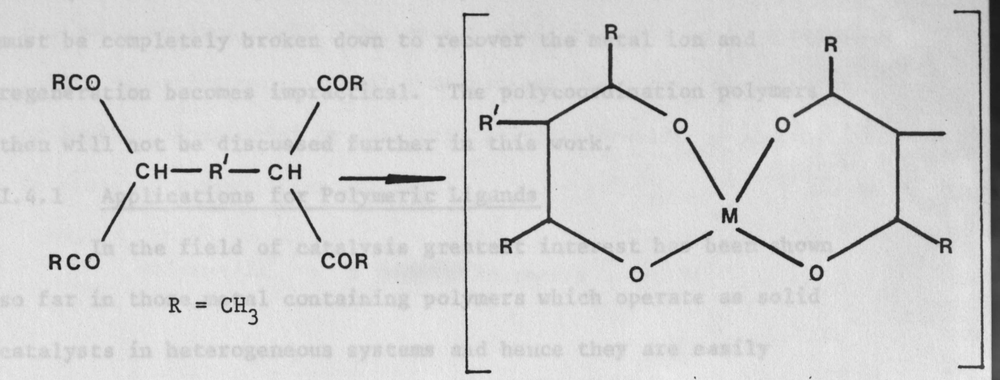
characteristics because of the electrons available in the SP^2 orbitals of the Nitrogen atoms. It is these basic properties which allow the polymer to act as a macromolecular ligand to Transition Metal ions and this forms the basis of the work in this project, which is to investigate the absorption and complexation of Transiton Metal (TM) cations by P4VP and discover if there might be a useful application for the polymer based on this property.

I.4 Metal Containing Organic Polymers

The possibility that metal ions might be incorporated into organic polymers is not new but is attracting increasing interest in two areas, the preparation of novel catalysts for use in industry and use of potential polymeric ligands for removal or separation of metal cations in solution.

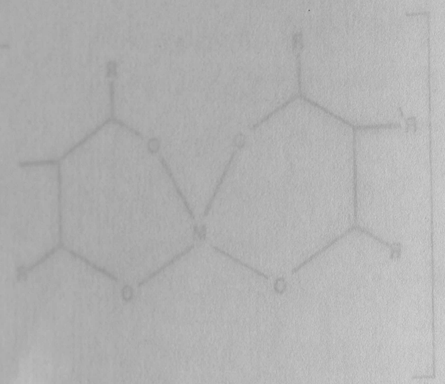
A number of patents dealing with such products as catalysts have been issued, usually however these reports deal with the preparation and effectiveness of the heterogeneous systems rather than detailed studies of the structures which are often non-stoichiometric.

There are two ways in which a metal ion can be introduced by complexation into a polymeric molecule, in the first the metal is involved in the main backbone chain of the polymer by reaction with a monomeric chelating agent, the reaction of divalent cations with some bis(β-diketones) is an example.[24]



These reactions may be likened to a condensation type polymerisation reaction and Kargin[25] has suggested that the polymeric products be known as polycoordination polymers as distinct from coordination polymers. The second type of metal containing polymer has the metal attached as a lateral group to a functional unit of a polymeric chain. Polymers considered in this project all fall into this group, but the list of macromolecular ligands which can be used to prepare such polymers is long and includes condensation polymers incorporating ligand containing groups (these are often based on Phenol-formaldahyde resins), vinyl polymers such as Polyvinylacrylates,[26] Polyvinyl amines,[27] Poly Schiff bases,[28] Polyvinylpyridines and a large number of chemically modified Polystyrenes.[29, 30]

This second type of polymer is certainly the more important because of one major advantage, that is the cation can usually be removed from the polymeric complex without destroying the macromolecular structure of the ligand which can be regenerated for



subsequent use. Polymers of the Polycoordination type clearly must be completely broken down to recover the metal ion and regeneration becomes impractical. The polycoordination polymers then will not be discussed further in this work.

I.4.1 Applications for Polymeric Ligands

In the field of catalysis greatest interest has been shown so far in those metal containing polymers which operate as solid catalysts in heterogeneous systems and hence they are easily isolated. In these cases regeneration is relatively simple. P4VP resins containing Copper (II) ions have been widely considered as potential catalysts in the oxidation of phenols and ascorbic acid. Kargin[25] has discussed polymeric heterogeneous catalysis and pointed out that besides their ease of isolation they also have the advantage that during the catalytic reaction there is a low but constant level of TM ions present in the liquid phase. Against this however is the likelihood of there being a diffusion controlled reaction at the polymer and perhaps some unexpected effects arising from possible non-uniform stoichiometry of the solid catalyst.

Heterogeneous catalysis is not the only area in which complexing and chelating polymers are finding application because the very reactions allowing preparation of the catalysts mean that the polymers will absorb TM ions. This is the basis of an expanding field of applied research: extraction of metal ions from solution in a chemical absorbtion process by polymers. The cation exchange resins immediately spring to mind. It is possible to carry out effective separation of cations using the simple exchangers provided there is careful choice of the system and of suitable solvents for elution,[29] such resins

however are generally quite unselective when applied directly to aqueous solutions of TM ions, merely absorbing cations from solution whilst releasing other, usually monovalent, ions such as Hydrogen or Sodium. Complexing or chelating polymers provide an alternative. In place of a simple ion exchange

$$\text{Polymer}/2A^{+} + B^{2+} \rightleftharpoons \text{Polymer}/B^{2+} + 2A^{+}$$

we have a reaction based on complexation of the polymer with the cation B^{2+}. In these cases cation exchange is no longer an essential part of the metal ion absorption reaction (e.g. Polyvinylamines, polyvinylpyridines, polyvinylpyrolidone) but chelating polymers which are also cation exchangers (chelating cation exchangers) do form an important group of such complexing macromolecular ligands (e.g. Polyacrylic acids, Iminodiacetic acid polymers etc.). It is the chelating ion exchange resins which first attracted attention to the ability of polymers to complex and absorb TM ions.

Griessbach[30] and Mellor[31] were among the first to suggest that complexing polymers may be able to selectively absorb metal ions, it appears that the modified polystyrenes prepared by Skogseid containing dipicrylamine units were the first successfully selective polymers.[32] Many complexing and chelating polymers have now been prepared and a number of reviews published.[33-35] A number of authors use the term chelating polymer or chelating ion exchange resin in a very general manner to cover all complexing polymers, this is perhaps understandable when macromolecular ligands are

involved. In this project a chelating polymer is considered to be a polymer in which more than one atom from each monomer unit forms a coordinate bond to the cation. The term complexing polymer (or complexing resin) will be a general expression to cover all polymers forming coordinate bonds. Early studies were made by Gregor[36] who examined phenol-formaldehyde condensation copolymers which incorporated various chelating agents (anthranilic acid and m-phenylenediglycine for example) and their ability to absorb metal ions. In studies carried out since the work by Gregor, selectivity in the absorption of metal ions has become an important aspect but although several requirements for a polymer to be a good selective complexing ligand are now known there can be little doubt that the production of such polymers for widespread use in science and industry is still some way in the future. The failings, although the polymer design may seem reasonable, are many and can include low cation capacity, expense of production and poor selectivity some or all of which can be related to the necessity of having several reaction steps in the polymer preparation. There have certainly been very few man-made complexing polymers which can truly be said to rival the selectivity shown by some biological polymers.

I.4.2 Factors Affecting Complexation by Polymers.

Several authors have described properties which are desirable in selective complexing polymers and outlined the general methods which have been used for their preparation.[37-39] Some have concerned themselves mainly with chelating ion exchange resins, these are resins which have a labile (acidic) proton which when removed gives a chelating moeity in the repeating unit of the polymer. For selective

resins the chelating group itself should be expected to show considerable selectivity, this has previously been a major problem with the majority of polymers relying on strongly complexing, but rather unselective, groups related to Ethylenediaminetetra-acetic acid (EDTA) or 8-Hydroxyquinoline. A related requirement with which all workers agree is that in introducing the chelating unit it is important that the spatial arrangement can remain the same during the polymer preparation as only then can it be expected that any selectivity will be retained. From this it follows that the chelating group should be fairly compact. Preparation of complexing polymeric ligands (CPL's) usually involves cross-linking the macromolecules in order to prevent dissolution or increase resistance to side reaction and degradation, such cross-linking will always inhibit mobility in the polymer chain and this loss of flexibility in conjunction with reaction as a two phase system nearly always means that the degree of selectivity or rate and capacity of cation absorption (or both) is less than might be expected. Indeed the performance of a polymer can be reduced by apparently minor changes in structure.[37,38]

Blasius, and Brozio[40] have listed various methods which are generally applicable for complexing polymers. They are:-

1. Use of enclosure compounds
2. Condensation polymerisations where one of the co-monomers is also complexing agent
3. Chemical modification of a condensation polymer to give complexing units

4. Polymerisation of vinyl monomers which are also ligands

5. Chemical modification of vinyl polymers to give polymers (resins) bearing complexing units

and 6. Chemical modification of linear polymers in solution followed by cross-linking to give stable resins.

These methods will be considered in turn:-

Method 1

Flett[41] has considered the compounds in group 1. These suffer the disadvantage of 'wearing out' rather quickly through loss of the trapped complexing molecules and for this reason can be ruled out for general applications. The remaining approaches have all been examined at various times.

Methods 2 and 3. Condensation Polymers

Condensation polymers have probably been used with most success to date in the studies of macromolecular ligands. The most widely studied systems have involved phenol-formaldehyde resins in various forms. Such resins were the basis of some of the very earliest work.[36]

Preparation of complexing polymers by route 2 where one of the monomer units is a chelating ligand can, under suitable conditions give products which have a high capacity for metal ions and which reach equilibrium quickly.[38] The complexing ligand required on the polymer may not be of a type which can be introduced as monomer during the condensation polymerisation either because of instability or lack of a suitable monomer. This difficulty can be overcome by incorporating the complexing unit at a later stage (method 3). An example of this is the preparation carried out by

Blasius,[42] here the complexing units are phenoxyacetic acid groups produced by reaction of phenolic groups of the basic resin with alkaline sodium chloroacetate solution. A considerable number of chelating condensation polymers have been examined[30-42] the results have perhaps not generally lead to commercial application as selective complexing agents though a number of patents have been issued. In a few isolated cases however the polymers have shown very real promise in separation and recovery of metals. Bayer[43] for instance has applied a copolymer of triaminophenol with glyoxal (chelating group glyoxal bis(2-hydroxyanil) units) to the recovery of metals from sea water. A related sulphur containing polymer selectively absorbed gold.[44]

Method 4 Polymerisation of Complexing Vinyl Monomers

Several authors have mentioned that preparation and polymerisation of polymers from chelating monomers is generally rather difficult and expensive, the latter being a major setback for potential industrial interest. This is certainly so for the true chelating monomer-polymer route and generally method 5 is employed here instead. Preparation of polymeric complexing ligands via method 4 is not necessarily expensive or difficult and this is where vinyl monomers such as vinylpyridines become of interest, as will be seen later. As mentioned such monomers are complexing ligands as are the related polymers; they are available as commercial products and can be used directly in polymer preparation. It is surprising then that work seems, until recently, to have been concentrated on chelating polymers almost to the exclusion of these much more simple complexing polymers, especially when it has been noted by a number of authors

that structure in the macromolecular ligand can often play a large part in the selectivity in absorption. Certainly there is much less doubt as to the structure of complexing polymers than for chelating polymers.[37,45]

Methods 5 and 6 Complexing Resins from Vinyl Polymers

Chemical modifications of vinyl resins widely used in preparation of cation and anion exchangers is also the second major method of preparation of chelating (exchange) resins. Most often a styrene divinylbenzene cross-linked polymer forms the backbone of the resin, and to this are attached the functional units often after a preliminary nitration step.[46] One problem these complexing resins have in common with those of method 3 is that the stepwise modification reactions each give well below 100% yield, and the final product does not generally consist only of the desired functional or chelating group but includes products from the side reactions. The resin product cannot be purified by removal of impurities from the side reactions as the low molecular weight analogues can for obvious reasons. The result is that the metal absorption capacity is often well below that which might be expected in an ideal case.[37]

Among those chelating groups which have been incorporated into resins by method 5 are oxine, salicylic acid and (2-Pyridylazo) resorcinol but probably the most widely used are those resins with iminodiacetic acid chelating groups as with condensation polymers.[47] Such groups might be expected to be quite strongly complexing but rather unselective and this seems to be the case. Hering among others has carried out a great deal of work with such resins but because the selectivity is not great separation processes become

rather complicated for general industrial uses.[47b] As for complexing resins produced from condensation polymers a few very selective vinyl polymers have been prepared. Vernon[48] describes Hydroxamic acid polymers which are selective for Vanadium (V), Iron and Molybdenum (VI) ions. Some problems have arisen with removal of the metal ions from the polymer in these cases however.

Solution preparation followed by cross-linking is a less commonly used route to complexing polymers. The starting polymer is usually polystyrene or polyethyleneimene. Blasius and Brozio have probably had greatest success with their reaction of 4-chloro-2, 6-pyridine dicarboxylic acid with the polyethyleneimine followed by cross-linking at the nitrogen by epichlorohydrin. The resin obtained was a general chelating agent but could apparently aeparate strontium from calcium.

Generally there are four desirable properties for complexing resins and these are pointed out by Blasius and Brozio

1. Mechanical and chemical stability especially with respect to acids and bases used for regeneration
2. Reasonable absorption capacity
3. Rapid equilibration with metal ions
4. High selectivity in absorption.

1. and 3. are often in conflict as gel type resins which cause no diffusion problems are often easily degraded chemically or mechanically and gels are quite often unsuitable for column packing in any case. Recent work[41] has shown that uniformity, with the polymer structure being as near perfect as possible is an important factor governing the absorption capacity of the resin. It seems that despite optimistic opinions [49] design of selective

complexing ligands has not been perfected; that such resins will be valuable materials in the quite near future is not in doubt.

I.5 Poly(Vinylpyridines) as Ligands

Several groups of workers have investigated the reactions of polyvinylpyridines (PVP's) with metal ions, usually those of the transition series but approaches have varied considerably. The work to date can best be described under two rather general headings, these are:-

a. Solution reactions of PVP's

and b. Two phase reactions of PVP's

a. Solution Reactions of Polyvinylpyridines

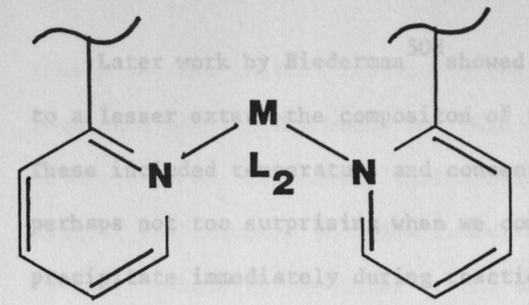
Biederman together with various co-workers has carried out most of the published work in this area and has considered the stoichiometry and structure of the products from reaction of linear PVP's with metal ions in dilute alcoholic solutions.[50] The complexes which are generally insoluble precipitate quickly during the reaction and those containing Transition Metal ions (T.M. ions) are often brightly coloured solids which are easily manageable when dry. Biederman found that the composition of these insoluble polymers could vary widely with changing reaction conditions. When dry ethanol was used as solvent and anhydrous metal chlorides reacted with the polymers the products contained no coordinated solvent molecules and empirical formulae of ML_2Cl_2, $M=Fe^{2+}, Co^{2+}$, Ni^{2+} and Zn^{2+}, CuL_3Cl_2 and FeL_2Cl_3 where L is a 4-vinylpyridine monomer unit of the polymer and NiL_4Cl_2, ML_3Cl_2, $M=Co^{2+}$ and Zn^{2+}, FeL_2Cl_3 and CuL_2Cl_2 where L is the corresponding monomer unit from poly(2-Vinylpyridine) (P2VP). When the reactions were carried out using the

hydrated T.M. chlorides however products having two associated molecules of water were obtained with empirical formulae of $ML_2Cl_2.2H_2O$, M=Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}. Biederman et al studied these complexes using the conventional techniques of infra-red spectroscopy, elemental analysis and magnetic susceptibility measurements on a Gouy balance. Cations of the first row transition series generally gave stoichiometric products such as the above with no evidence of uncoordinated pyridine units in the final products.

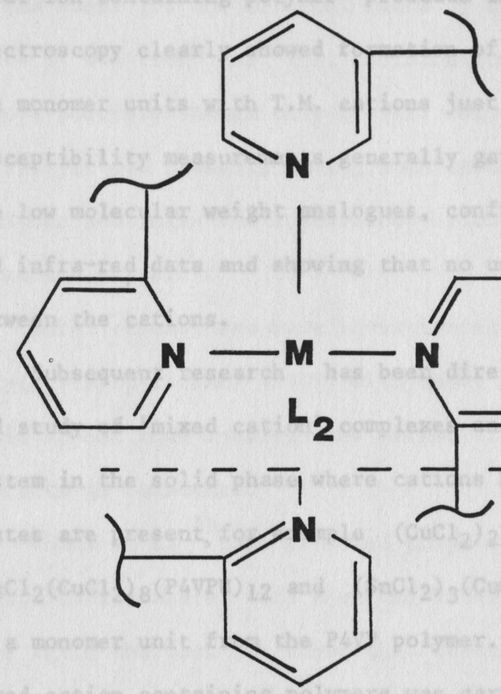
The occurrence of the series of compounds reported in the earlier paper by Biederman[50a] dealing with poly(4-vinylpyridine) (P4VP) shows then that a comparison can be made with related complexes involving low molecular weight analogues, pyridine for example. One quite major difference is that neither Biederman nor any other workers have reported products in which four monomer units from P4VP are associated with a cation, that is ML_4X_2 does not appear to exist. We have already seen that this formula can apply when Co^{2+}, Ni^{2+} and L= yridine, 4-vinylpyridine and 4-ethylpyridine. Smets in an earlier work provides an explanation which is satisfactory in part,[51] this is that flexibility of the backbone chain is insufficient and the distance between two adjacent pyridine monomer units on the same chain consequently too great to allow both to coordinate to the same cation. It should be added that the failure is probably due to incompatible alignment of orbitals as well. The cations then form bridging (cross-linking) groups between two separate P4VP chains, this explains the precipitation and general low solubility of the products. The presence of two polymer chains

so linked was supposed by Smets to cause considerable steric hinderance to approach of other macromolecules (bearing complexing monomer units) with the result that the vacant coordination sites are filled by water molecules. The formula established by Biederman et al for products from the reaction of P4VP with Copper (II) ions under anhydrous conditions suggests that Smets idea must be modified to some extent since under suitable conditions it seems that three chains might approach a cation or, perhaps more likely, that the hinderance is not great enough to prevent monomer units from separate parts of the same chain forming coordinate bonds with the cation. It is possible that when water is present that it competes effectively for the coordination sites but that in its absence three pyridine units coordinate. We might expect, from experience of the literature which indicates great flexibility in the stereochemical behaviour of the Cu (II) ion and from the Irving-Williams series which indicates such a system maximises stability at Cu (II), that this cation if any would coordinate more than two monomer units.

The rather different stoichiometric formulae obtained for the complexes of P2VP imply greater variation in ligand arrangement, Biederman has suggested (see diagram) as possibilities. Certainly the lower number of ligands complexed to Cu (II) ions in comparison with P4VP suggests a greater hinderance of the nitrogen in the 2 position next to the backbone chain of the polymer. The Ni^{2+} reaches the maximum coordination number with four monomer units reflecting the neat arrangement possible with P2VP where chains interact to a much lesser extent than with P4VP.

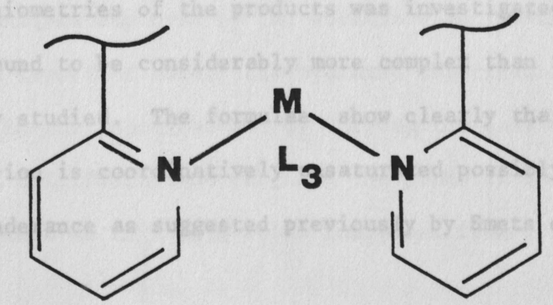


a $FeCl_2$
$CuCl_2$



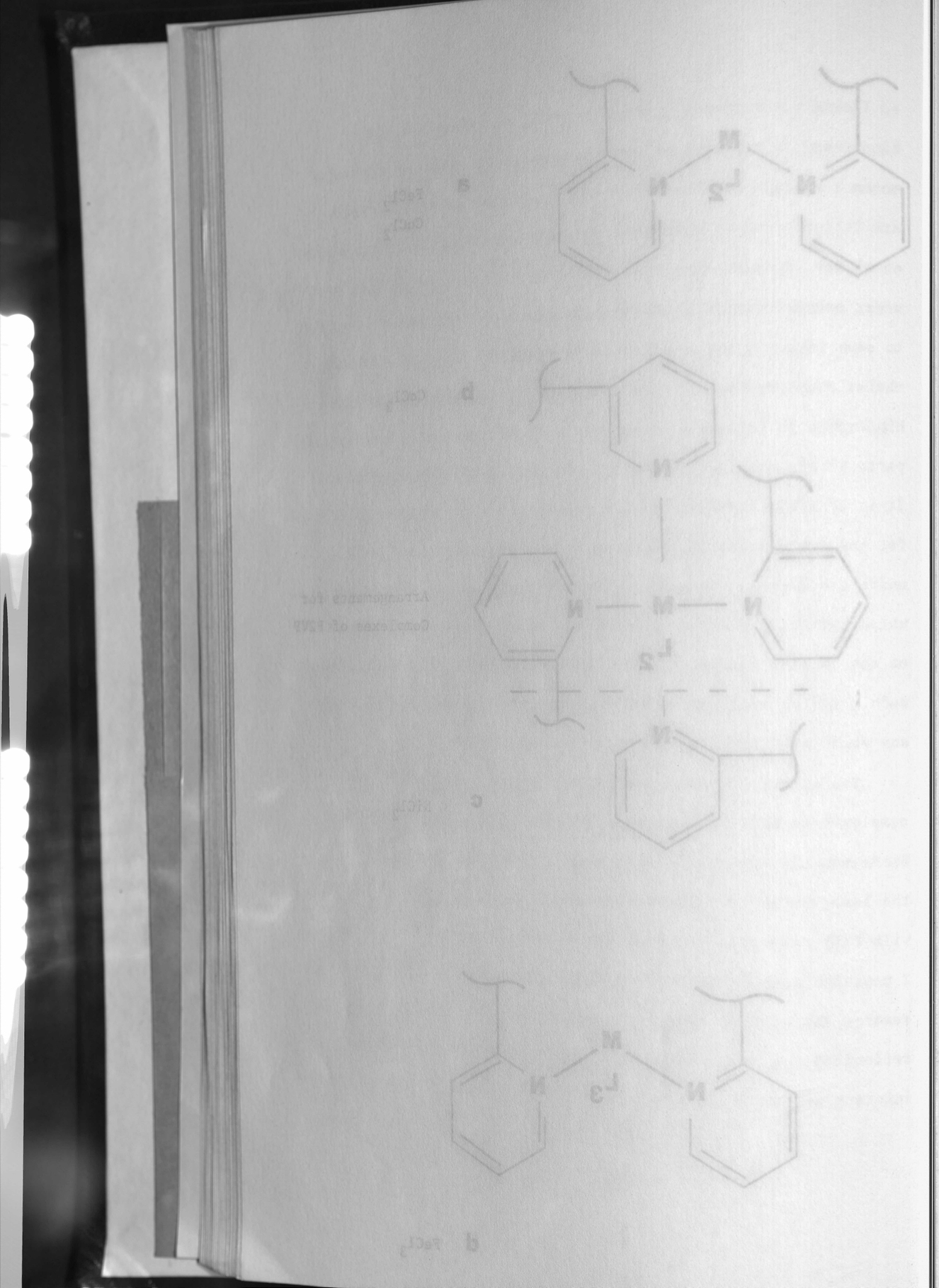
b $CoCl_2$

c $NiCl_2$



d $FeCl_3$

Arrangements for Complexes of P2VP



Later work by Biederman[50d] showed that other factors could affect to a lesser extent the compositon of the complexes formed by PVP's. These included temperature and concentration of reagents. This is perhaps not too surprising when we consider that the products precipitate immediately during reactions.

The information obtained by Biederman on the structure of the metal ion containing polymer products is considerable. Infra-red spectroscopy clearly showed formation of the coordinate bond of the monomer units with T.M. cations just as for pyridine. Magnetic susceptibility measurements generally gave values very much as for the low molecular weight analogues, confirming elemental analyses and infra-red data and showing that no unusual interaction occurs between the cations.

Subsequent research[52] has been directed towards the preparation and study of 'mixed cation' complexes and those which give a redox system in the solid phase where cations having complementary oxidation states are present, for example $(CuCl_2)_2(CuCl)_3(P4VPU)_3$, $FeCl_2(CuCl_2)_8(P4VPU)_{12}$ and $(SnCl_2)_3(CuCl_2)_3(P4VPU)_7$ where P4VPU is a monomer unit from the P4VP polymer. The preparation of these mixed cation containing polymers was carried out in much the same way as previously though the reactions were usually under 'dry' conditions. The products again precipitate quickly during reactions. The stoichiometries of the products was investigated by the workers and was found to be considerably more complex than for those previously studied. The formulae show clearly that in some cases the metal ion is coordinatively unsaturated possibly because of steric hinderance as suggested previously by Smets or perhaps more

likely because initial reaction gives a polymer which has metal ions forming cross-linking bonds and this results in greatly reduced flexibility of the polymer chains with the result that they cannot distort sufficiently to allow access of the monomer units to the cations. Whatever the cause of the unsaturation these new polymers may well be practical heterogeneous catalysts and this appears to be the basis for the interest shown by Biederman et al. In several cases it was found that full coordination of monomer units was not always possible though only Cr (II) ions from the first row T.M. series yielded products having such unreacted ligands. Elemental analysis and infra-red spectroscopy clearly revealed presence of unreacted units.

Other researchers have investigated the solution reactions of poly(4-vinylpyridine) (P4VP) with heavy metal ions and here too it would appear that interest has arisen from possible use of the products as catalysts.

Rhoda et al[53] have prepared polymers in which the macromolecular ligand is associated with Rhenium, Ruthenium and Palladium ions. Here again the work has shown that reaction conditions can greatly affect the composition of the resulting metal ion containing polymers, with differing numbers of monomer units coordinated to the central metal ion. Infra-red spectroscopy and elemental analysis were the major techniques employed by the workers with gravimetric analysis playing an important role. The hydrated chlorides of the heavy metals were used in the reactions and by varying the salt to polymer mole ratio (Mt Chl./P4VPu) and weighing the products Rhoda was able to determine that as this mole ratio increases from 0.16 to $\geq$1 the

mole ratio for the product rises to a maximum of 2/3, but whilst some uncoordinated monomer units are present in the product having mole ratio of 0.2 there are none in the product having a ratio of 0.4. These results suggested that there were several possible products in which all the P4VP units were fully coordinated (i.e. from at least 0.4 to 1) though this does not necessarily mean that all the metal ions need have the same number of monomer units as ligands.

Rhoda suggests that for the products having the maximum metal ion content (mole ratio = 2/3), which obviously cannot have exactly the same arrangement about each metal ion, constituent formula of

i. $(P4VPu)_2Mt + (P4VPu)Mt$

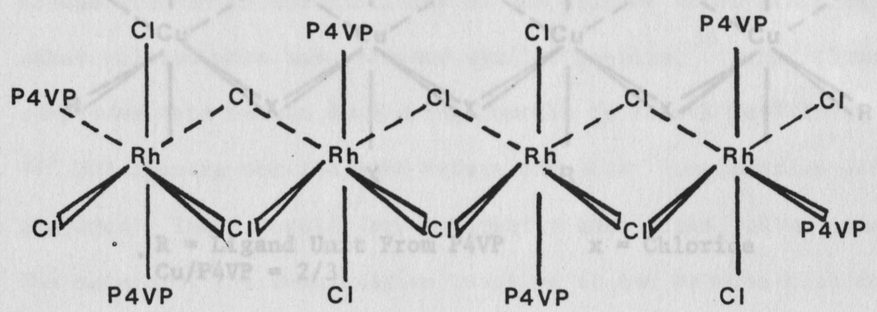
ii. $(P4VPu)_3Mt + 3(P4VPu)Mt$

iii. $(P4VPu)_3Mt + (P4VPu)_2Mt + 4(P4VPu)Mt$

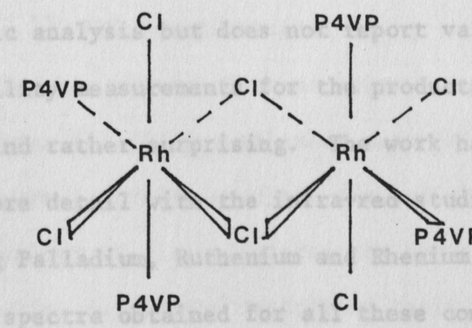
(where Mt = metal)

with various associated water where (P4VPu) is a monomer unit from the polymer chain. The authors suggest that although low molecular weight analogues exist for $(P4VPu)_3$ Mt and $(P4VPu)_2$ Mt there are none for the (P4VP)Mt unit. For reasons similar to those mentioned earlier concerning the decrease in flexibility of the polymeric ligands after initial cross-linking reactions by metal ions, Rhoda et al point out that the possibility of 1:1 stoichiometry occuring in the product can by no means be dismissed. This is a logical decision and similar situations often occur in polymeric systems, these will be discussed later. A similar argument can be applied for the product obtained previously by Biederman et al ($(CuCl_2)_2(P4VPu)_3$). In that case we might consider arrangements about the central cation of $Cu(P4VPu)_2Cl_2$ and $Cu(P4VPu)Cl_2$.

Real possibility of species such as $Mt(P4VPu)_3$ is discounted by Rhoda in his work however as preparations in which the Mt Chl/PVPu mole ratio was below 0.5 resulted in products containing uncoordinated monomer units as shown by infra-red spectroscopy. This would not be so if the $Mt(P4VP)_3$ arrangement was common. One product prepared had a mole ratio of 0.5 and was found to have no free ligand suggesting stoichiometries involving units such as $Mt(P4VPu)_2$ and Mt(P4VPu) with $Mt(P4VPu)_3$ discounted. The structures



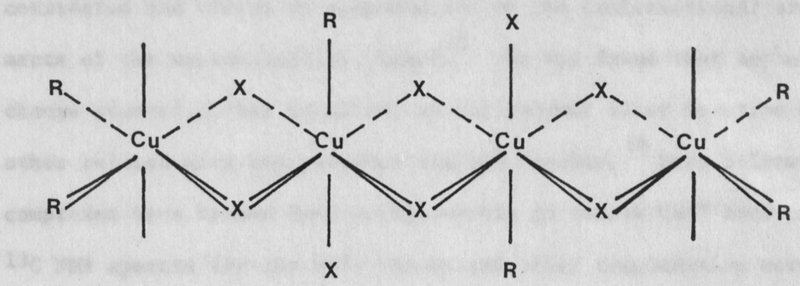
Rh/P4VP = 2/3



Rh/P4VP = 1/2

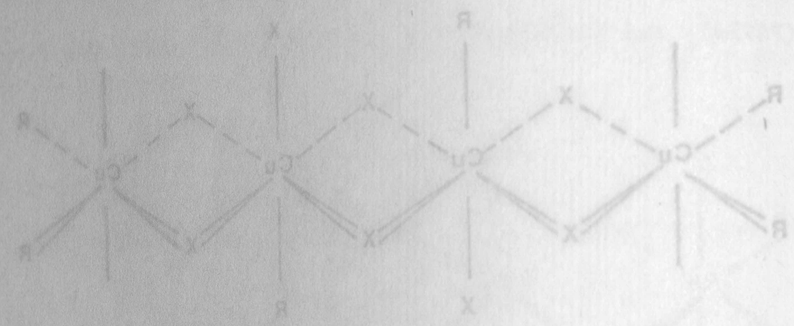
were suggested. Varying numbers of water molecules are supposed to be in the secondary coordination sphere. By comparison we

might consider a structure of



R = Ligand Unit From P4VP x = Chloride
Cu/P4VP = 2/3

for the product $(CuCl_2)_2(P4VP)_3$ obtained by Biederman et al. Rhoda relies heavily on the results of elemental and thermogravometric analysis but does not report values for magnetic susceptibility measurements for the products (to confirm them) this we find rather surprising. The work has been extended to deal in more detail with the infra-red studies of the polymers containing Palladium, Ruthenium and Rhenium cations.[54] The infra-red spectra obtained for all these complexes showed strong resemblance to those obtained by Biederman especially with respect to a shift of the highest energy fundamental vibration for the Pyridine ring (1600 to 1640 cm^{-1}) and, as previously, associated water molecules gave broad bands in the 2700-3500 cm^{-1} region and



contributed to bands which complicated spectra in the 1630-1640 cm^{-1} region in some cases. There will be a detailed discussion of infrared studies on such cation containing polymers in Chapter IV.

The remaining published work which describes preparation of metal complexes with PVP ligands generally does not involve study of the product structure itself. Kabanov et al for instance has considered the effect of complexation on the conformational arrangements of the macromolecular ligand.[55] It was found that appreciable change occured in the tacticity of the polymer after reaction and other related work has produced similar results,[56] here polymeric complexes were broken down using ammonia to remove Cu^{2+} ions and ^{13}C NMR spectra for the P4VP before and after complexation were compared. These results are not really unexpected, if we consider the nature of the complexation reaction it can be seen that the ligands must adjust to some extent to lower the overall energy of the complex and steric effects may contribute as each monomer unit is arranged about a cation. These aspects will be considered more carefully at a later stage when conformational studies made in this project using ^{13}C NMR are discussed.

A considerable amount of preparative work has been carried out involving copper (II)/P4VP complexes, again alcoholic solutions of the reagents are generally used but the actual structure of the products is seldom of direct interest to these workers the details usually appearing in patents describing their use as catalysts.[59] Applications of the polymeric products are described below in a separate section.

I.5.1 Two Phase Reactions of Poly(vinylpyridines) (PVP's)

Several other research groups have carried out studies of coordination reactions of PVP's with metal ions, again usually those of the T.M. series. These workers have approached the subject in a different manner from Biederman, Rhoda and others mentioned above. The investigations have involved a two phase reaction involving absorption by the solid polymers of T.M. ions from solutions usually in water or alcohol. Russian workers associated with Kopylova have probably contributed most to our knowledge in this area. The initial work in this series was published in 1970[57] and dealt with the stability of Copper (II) complexes formed by PVP's. The experiments provided evidence for the formation in the polymer of species having two or much more rarely three ligand units from the P4VP associated with each Copper (II) ion. The work was continued[58] to consider how the structure of the absorbing PVP resins affected formation of the metal polymer complexes. This involved study of results obtained from variation in type and degree of cross-linking of the PVP and of the solvent. A suggestion is made that the formation of the cation containing complexes in these two phase reaction systems may be represented by energy terms

$$E_{form} = E_c - (E_{des}+E_s+E_d)$$

where E_c is the energy of formation of coordinate bonds between the metal and ligand groups, E_{des} is the energy required to desolvate the ligand groups and E_s the related energy for the cations. E_d is loosely described as the energy consumed in defomation of the polymer network. The expression appears to be quite acceptable and it can be seen that the value E_d is expected to increase with increasing

degree of cross-linking and coordination of the polymer chains. These authors as others previously point out that there is little probability of formation of cyclic structures involving neighbouring pyridine units on the same P4VP chain being coordinated to the same metal cation. Chelate structures involving pyridine units from different points of the same chain (intra) and bonds involving related cross-linking reactions (inter as previously)are both possible though and will clearly contribute to the E_d term mentioned above.

The results of the work confirm that the complexing ability of the polymers decreases with increasing degree of cross-linking of the P4VP, that is with decreasing flexibility of the macromolecular network. Increasing ability of the polymers to absorb, i.e. complex the metal ion, usually Copper (II) in the work under review,was observed when the flexibility of the polymer network was increased by varying the cross-linking species. For resins having the same degree of cross-linking this flexibility increases as the distance between polymer chains and thus with increasing 'length' of the cross-linking molecule provided multiple bonds are absent. Kopylova et al have considered divinylpyridine and related species,[58] possibly the choice of cross-linking agents was not the best as they do themselves possess some ability to complex metal ions and this complicates the study. It is shown however by the Russian authors that their suggestions are qualitatively correct. The investigation reveals that absorption of Copper (II) by PVP resins is considerably poorer from aqueous solutions than from methanol, this of course is to be expected as alcohols are good solvents for the linear PVP's

and so can be expected to swell these cross-linked derivatives to a greater extent than water giving greater flexibility of the network and greater access for metal ions. The degree of protonation of the polymers is shown to have some effect on their absorption properties and a complex relationship between absorption, degree of protonation and solvent (water/methanol ratios) composition was described by Kopylova et al. It is clear that maximum absorption in water was found to occur when about 50% of the pyridine monomer units were protonated. This point is quite important and will be discussed further at a later stage (Chapter III). The conclusion of Kopylova et al that the unprotonated polymer (P4VP) has practically no coordinating ability in aqueous media however is not really borne out by the results of these workers or others in the field. Further, published work by the same authors [56] in which a study of the structure of the complexes formed by P4VP in absorption of various cations shows that the arrangement of the coordinating groups about the central metal ion may be far more complex in these two phase reaction systems than might at first be imagined from a comparison with products obtained by Biederman and Rhoda. Kopylova et al apply infra-red spectroscopy and electron spin resonance (e.s.r.) techniques to the study of the resulting complexes. The formation of a coordinate bond between the pyridine units of the polymer and the metal cations is shown to occur and a suggestion that in the special case where concentration of the monomer units is much greater than the metal ions being complexed that four pyridine ligands may coordinate to each Copper ion is made. It is considered however that steric hinderance prevents six monomer units coordinating to those cations which are usually found to be six coordinate and

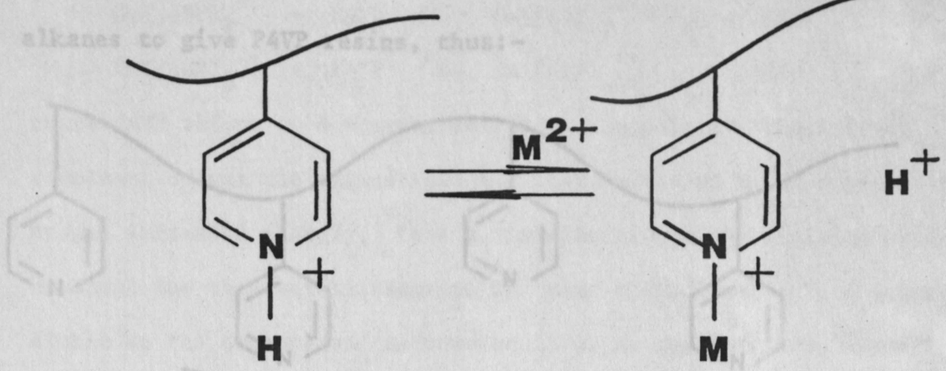
that solvent molecules coordinate in their place yielding species having mixed coordination at the cation. It is pointed out that an increase in the ratio of the concentration of the metal ion to that of the ligand groups in the polymer might lead to a reduction in the number of ligands from the P4VP coordinating to each cation. Using Cu^{2+} (which can be studied using electron spin resonance spectroscopy)direct increase in the ratio would lead to Copper (II) concentration levels which are too great to give useful information from e.s.r. studies. Kopylova overcame this problem by protonating a proportion of the monomer units whilst increasing the Copper (II) concentration in the solution, this limited the amount of the cation absorbed by reducing the number of ligands available for coordination whilst changing the ratio as required. E.S.R. confirmed the change of coordination around the metal ion and also revealed the complexity of the structures.

In considering absorption of metal ions other than Copper (II) from aqueous solution it was noted that whilst there is a considerable excess of ligand units from the polymer over cations then the polymer will continue to absorb a mixture of cations as if each were present alone, however, as the ratio of ligand to cation drops there will be competition for the pyridine units. This of course is to be expected and an order of absorption of Ag(I) > Cu(II) > Ni(II) > Cd(II) > Co(II) was determined. Some confusion arises over the actual capacities of the polymers to absorb various cations, with an apparent conflict between results published [57,58] and definition of the term α (optimum) when referring to the optimum degree of protonation of the P4VP resins. Some disagreement also appears as to whether permanent change of conformation occurs for the P4VP ligand chains during the complexation

reactions, this may arise from differing degrees of protonation in the polymeric ligands. The structural study of the metal ion containing products is continued in work published subsequently, here attention is focussed on application of infra-red spectroscopy (I.R).[58a] Generally observations of changes in the spectra of the polymers upon complexation were similar to those made previously by Biederman and Rhoda, the study is perhaps a little more extensive and values are given for position of bands assigned to metal - nitrogen coordinate bonds appearing in the region 200-400 cm^{-1}. Measured changes of position for the band at 1598 cm^{-1} upon complexation with various cations were used as a basis for obtaining an order for increasing metal - nitrogen (M-N) bond strength of

$$Zn^{2+} < Co^{2+} < Cd^{2+} < Ni^{2+} < Cu^{2+} < Ag^{+}$$

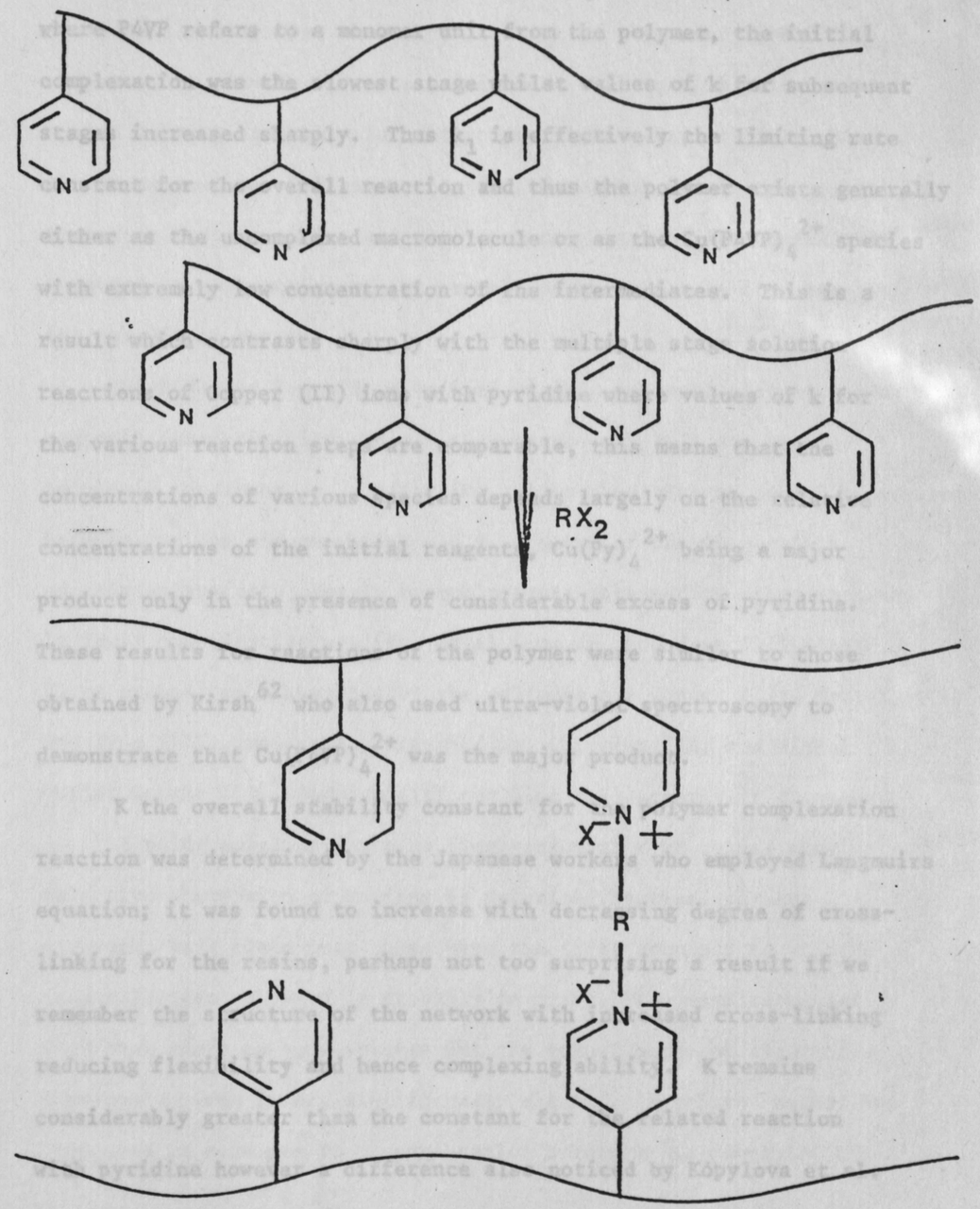
Spectra of complexes of earlier members of the series (Zn^{2+} - Ni^{2+}) clearly showed that not all available ligand units are coordinated to metal ions. The authors point out that the electronic configuration and preferred geometry of the complexed metal ion can be expected to play as important a part in the complexing reaction as allowed conformations of the polymeric ligand previously mentioned. Special attention is paid to the sorption of Copper (II) ions from aqueous solution by partially (α = 0.5) protonated P4VP resins by the Russian workers. Surprise is expressed in the work at the observation that fully protonated (α = 1) P4VP resins, could albeit to a rather small extent, act as cation exchanges, this should perhaps not be totally unexpected though certainly the relative strengths of the M - N and H - N bonds indicate that the equilibrium



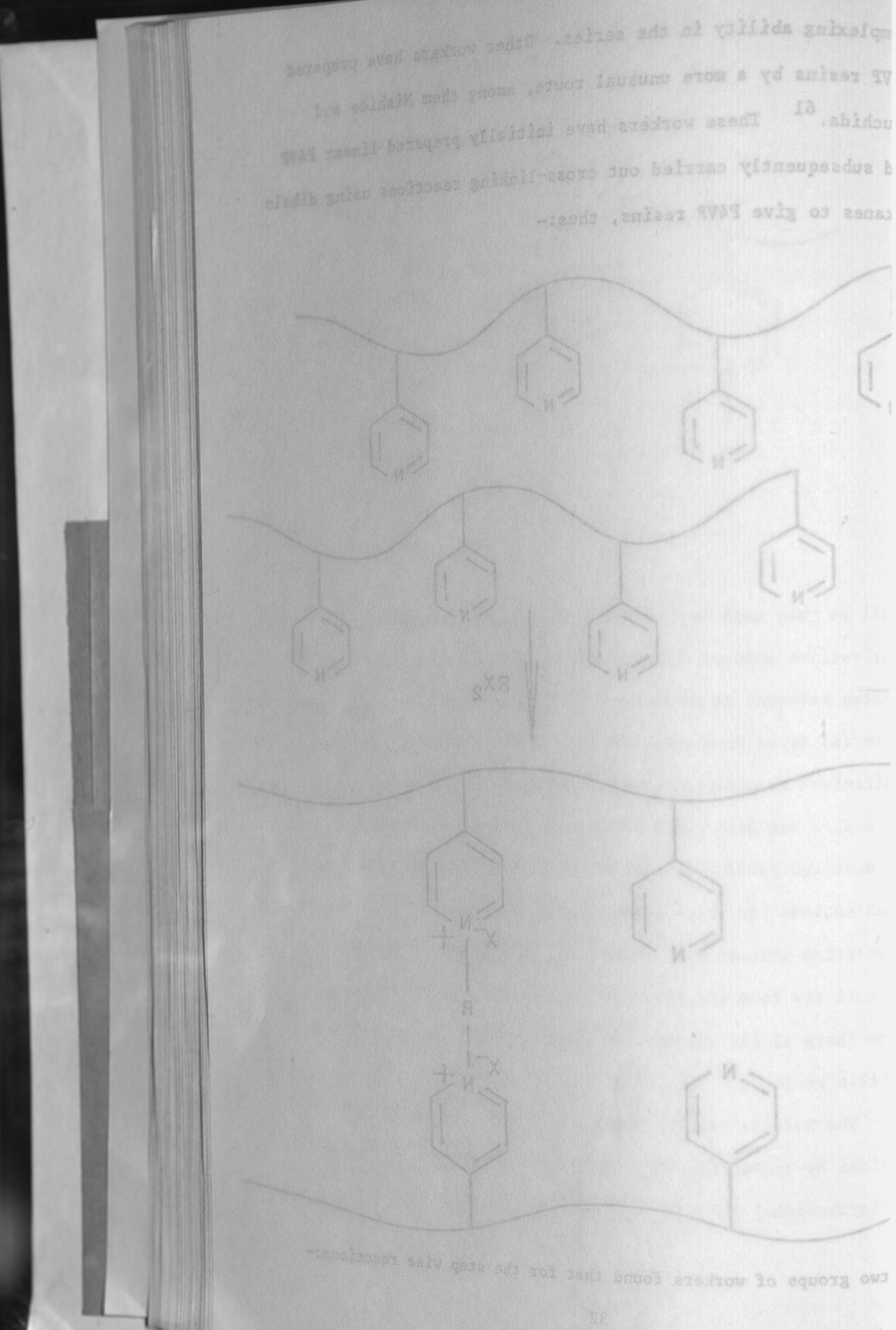
will be very much to the left. The poly(4-Vinylpyridinium) derivatives however are appreciably acidic suggesting some proton release, we could therefore expect some of the complexed form (a) to be produced. In fact Kopylova et al showed that sufficient absorption occurred to allow study of the products by e.s.r. and from these results they concluded that only one or at most two pyridine ligand units formed coordinate bonds with each cation. An anion dependance is shown to occur for the absorption process with Copper (II) ions being absorbed more effectively from solutions of the sulphate and chloride than from those of the nitrate.[60] This dependance will be examined in this project.

The Russian workers then have concentrated on absorption of cations by conventionally cross-linked PVP resins (i.e. using divinylbenzene) and have shown that P4VP has the greatest

complexing ability in the series. Other workers have prepared P4VP resins by a more unusual route, among them Nishide and Tsuchida.[61] These workers have initially prepared linear P4VP and subsequently carried out cross-linking reactions using dihalo alkanes to give P4VP resins, thus:-



The two groups of workers found that for the step wise reactions:-



$$Cu^{2+} + P4VP \xrightarrow{k_1} Cu(P4VP)^{2+}$$

$$Cu(P4VP)^{2+} + P4VP \xrightarrow{k_2} Cu(P4VP)_2^{2+}$$

$$Cu(P4VP)_2^{2+} + P4VP \xrightarrow{k_3} Cu(P4VP)_3^{2+}$$

$$Cu(P4VP)_3^{2+} + P4VP \xrightarrow{k_4} Cu(P4VP)_4^{2+}$$

where P4VP refers to a monomer unit from the polymer, the initial complexation was the slowest stage whilst values of k for subsequent stages increased sharply. Thus k_1 is effectively the limiting rate constant for the overall reaction and thus the polymer exists generally either as the uncomplexed macromolecule or as the $Cu(P4VP)_4^{2+}$ species with extremely low concentration of the intermediates. This is a result which contrasts sharply with the multiple stage solution reactions of Copper (II) ions with pyridine where values of k for the various reaction steps are comparable, this means that the concentrations of various species depends largely on the relative concentrations of the initial reagents, $Cu(Py)_4^{2+}$ being a major product only in the presence of considerable excess of pyridine. These results for reactions of the polymer were similar to those obtained by Kirsh[62] who also used ultra-violet spectroscopy to demonstrate that $Cu(P4VP)_4^{2+}$ was the major product.

K the overall stability constant for the polymer complexation reaction was determined by the Japanese workers who employed Langmuirs equation; it was found to increase with decreasing degree of cross-linking for the resins, perhaps not too surprising a result if we remember the structure of the network with increased cross-linking reducing flexibility and hence complexing ability. K remains considerably greater than the constant for the related reaction with pyridine however a difference also noticed by Kopylova et al. Nishide and Tsuchida suggest that a 'polymer effect' is responsible, that is the high concentration of the ligand in the polymer domain

of the two phase system leads to increased values for the formation constants.

One rather surprising result in the work was that values of K for the complexation of the linear polymer were found to be considerably less than those for reaction of the cross-linked polymers. A plausible suggestion is made that cross-linking gives a more compact structure for the polymer increasing still further the concentration of ligand units in the polymer domain, this more compact structure also means that upon complexation less energy is consumed in contraction of the overall network than is the case for the linear polymer.

Nishide and Tsuchida have used visible absorption spectroscopy, magnetic susceptibility and e.s.r. spectroscopy to study the polymeric complexes. μ effective values show that no unusual interaction between cations occurs whilst e.s.r. spectra of the Copper (II) containing products closely resemble those obtained by other workers. In their quantitative studies, metal ions are found to fall into three groups, well absorbed by the polymers are Copper (II), Mercury (II) and Iron (III), moderately absorbed are Chromium (II) and Nickel (II) whilst Cobalt (II), Cadmium (II) and Zinc (II) are poorly absorbed.

A quite novel approach to preparation of P4VP resins showing selective absorption of cations is described by these workers although their claim that these were the first attempts to prepare such selective polymers is probably in error. The results certainly show that there is some success but the actual order of absorption previously given is not significantly altered. A related method has been used in attempts to prepare cation selective polymers in this

project, the results will be compared in detail with those of Nishide and Tsuchida at a later stage (Chapter III).

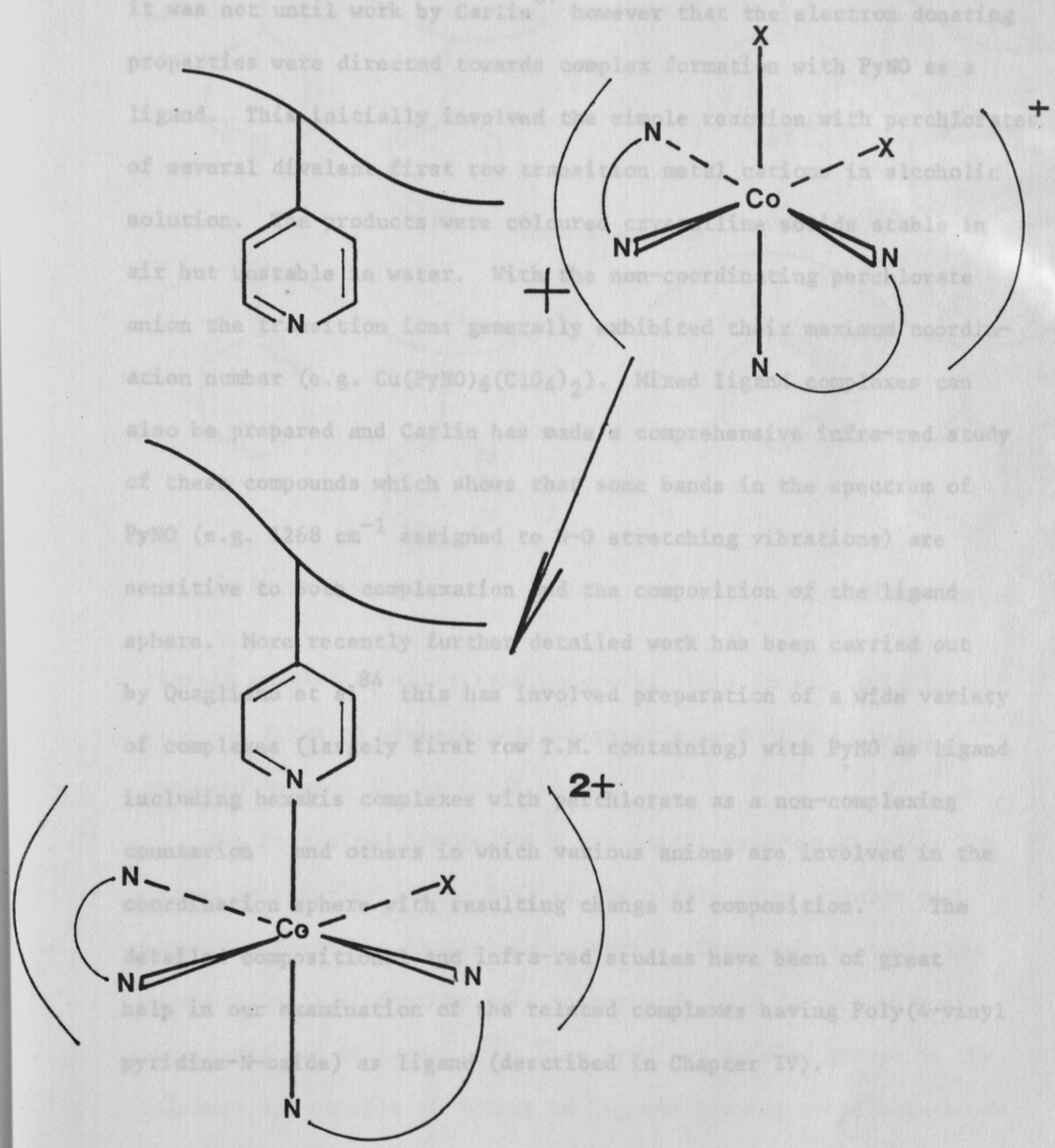
No other workers have studied two phase absorption - complexation reactions, a number of papers published however do provide information relevant to our studies. Generally other work has involved solution reactions in water or water - methanol mixtures made possible by quaternisation or the complexation reactions themselves. Kirsh et al for instance have shown that the partially quarternised linear P4VP reacts with Cu^{2+} to give $Cu(P4VPu)_4^{2+}$ in water in a single stage reaction rather than the multi-step reaction observed for pyridine and 4-ethylpyridine.[62] The Russian workers have used u.v.-visible and electron spin resonance spectroscopy together with viscometry in their solution studies; the e.s.r. spectra especially provide a great deal of information of interest to us in considering the results obtained in the present work. Kirsh discovered that with the quaternised polymers only 45 - 50% of the available pyridine ligand units are able to complex Cu^{2+} ions and this is perhaps unexpected if we remember that Biederman obtained products (albeit having differing arrangement about the cation) having no uncoordinated ligand groups. Detailed studies in solution will not be considered in the research to be described, though it seems quite possible that the quaternisation, with resulting positive charges on the polymeric ligand, contributes to the low degree of complexation, perhaps by electrostatic repulsion of the reacting cations. Kirsch, like other workers previously mentioned, draws the conclusion the the Cu (II) ions can form cross-links by reacting with ligand groups from different P4VP chains, it is surprising then that the products

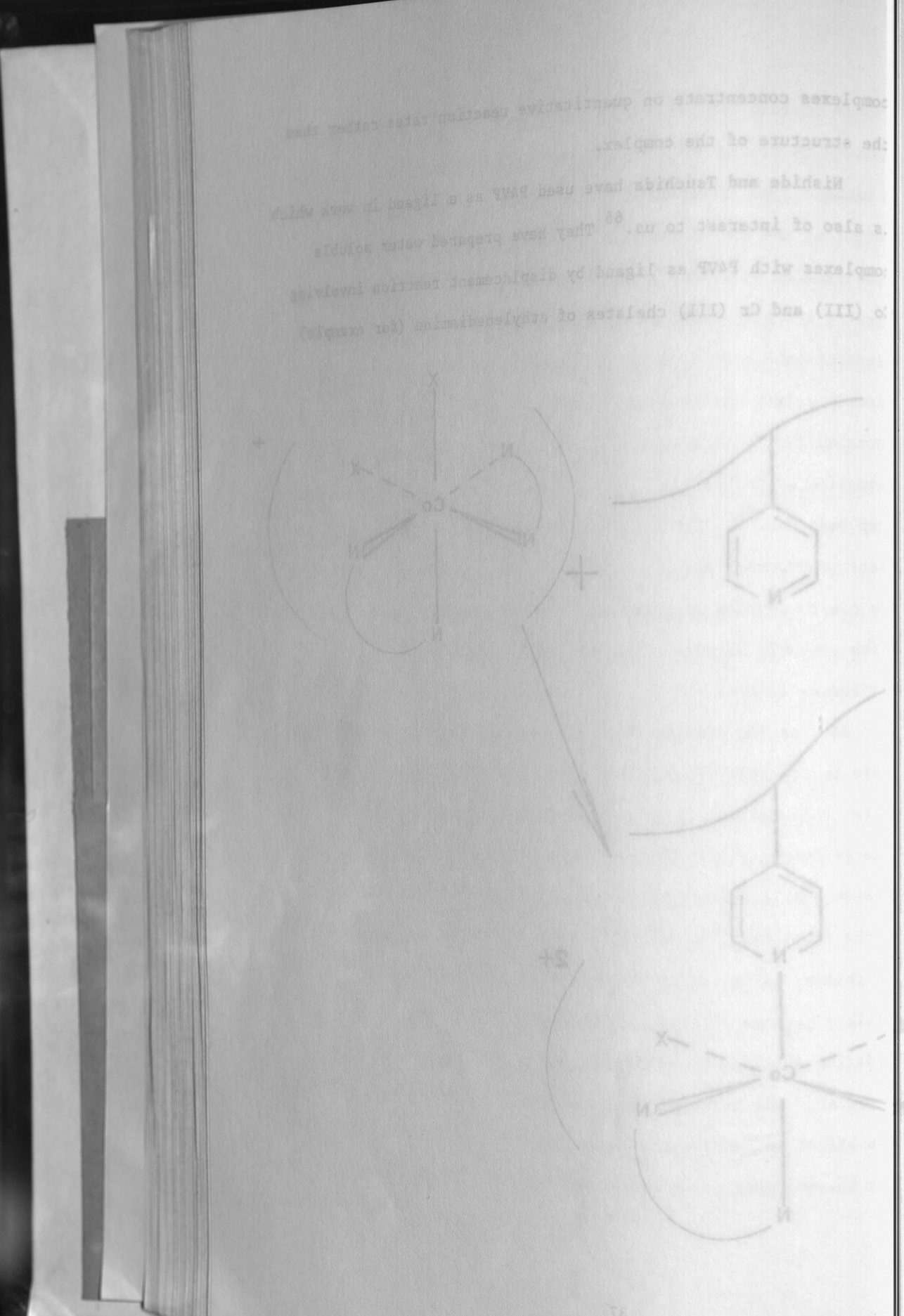
remain in solution. Kirsch suggests that the polymeric complex network is arranged with hydrophilic pyridinium units outside in a micelle type arrangement,[62] he does not explain why the molecular weight of the linear polymer only increases 2½ times during the complexation reaction however. If cross-links were common a much greater increase would be expected. It is possible that steric or electrostatic effects limit the approach of two polymer chains. Closely related research by Nishikawa and Tsuchida has also revealed the increased value of the formation constants and the formation of $Cu(P4VPu)_4^{2+}$ in a single step rather than a multiple step reaction.[63] The Japanese workers also use u.v.-visible spectrophotometry and e.s.r. to study the complexation with Cu^{2+}, the e.s.r. spectra provide much less information than those of Kirsh probably because of proton interaction with the complex in the former study.

Some of the complexation studies with Cu (II) ions have their basis in possible applications of the polymer products as catalysts. So far this has mainly involved oxidation of ascorbic acid or phenols. A large number of patents have been issued in this area [56] whilst Nishide and Tsuchida have published studies of the catalytic abilities of the complexes [64] in polymerisations of xylenol and suggest that the phenoxy anions occupy available coordination sites left vacant possibly because of steric hinderance. Kirsh [65] has examined the oxidation of ascorbic acid catalysed by the copper containing complexes. The conclusions are that the polymeric species are far more effective catalysts than low molecular weight analogues. Generally however workers concerned with the catalytic ability of the

complexes concentrate on quantitative reaction rates rather than the structure of the complex.

Nishide and Tsuchida have used P4VP as a ligand in work which is also of interest to us.[66] They have prepared water soluble complexes with P4VP as ligand by displacement reaction involving Co (III) and Cr (III) chelates of ethylenediamine (for example)



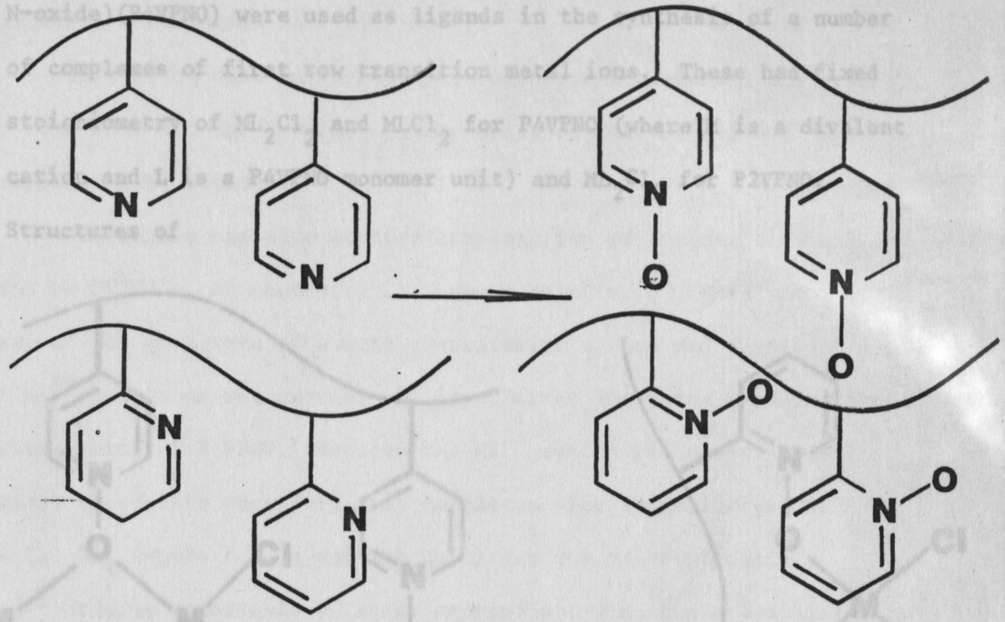


The resulting metal ion containing polymers have a quite similar structural resemblance to the complexes considered above save that here the cation cross-links are excluded by the nature of the reaction.[56]

I.6 Poly(Vinylpyridine-N-Oxides) (PVPNO's)

The bascicity of Pyridine-N-Oxide (PyNO) has long been known, it was not until work by Carlin[67] however that the electron donating properties were directed towards complex formation with PyNO as a ligand. This initially involved the simple reaction with perchlorates of several divalent first row transition metal cations in alcoholic solution. The products were coloured crystalline solids stable in air but unstable in water. With the non-coordinating perchlorate anion the transition ions generally exhibited their maximum coordination number (e.g. $Cu(PyNO)_6(ClO_4)_2$). Mixed ligand complexes can also be prepared and Carlin has made a comprehensive infra-red study of these compounds which shows that some bands in the spectrum of PyNO (e.g. 1268 cm^{-1} assigned to N-O stretching vibrations) are sensitive to both complexation and the composition of the ligand sphere. More recently further detailed work has been carried out by Quagliano et al[84] this has involved preparation of a wide variety of complexes (largely first row T.M. containing) with PyNO as ligand including hexakis complexes with perchlorate as a non-complexing counterion and others in which various anions are involved in the coordination sphere with resulting change of composition. The detailed compositional and infra-red studies have been of great help in our examination of the related complexes having Poly(4-vinyl pyridine-N-oxide) as ligand (described in Chapter IV).

Just as pyridine can be oxidized by the simple method of Ochai [68] to give PyNO so we would expect can many pyridine derivatives, this includes those polymers containing pyridine units such as P2VP and P4VP. The products would be expected to have general structures



Polyvinylpyridines

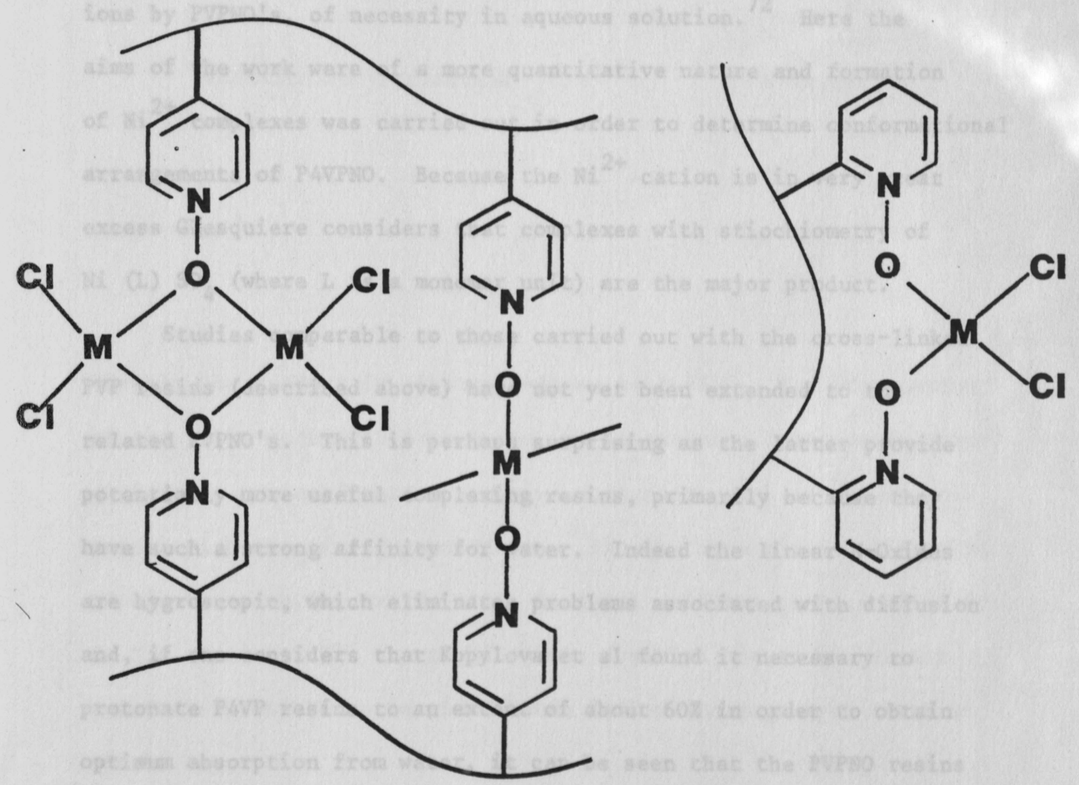
Polyvinylpyridine-N-Oxides

closely related to the parent polymers. This is so. Holt et al [69] were the first to prepare poly(vinylpyridine-N-Oxides) using a modified version of the Ochai method.

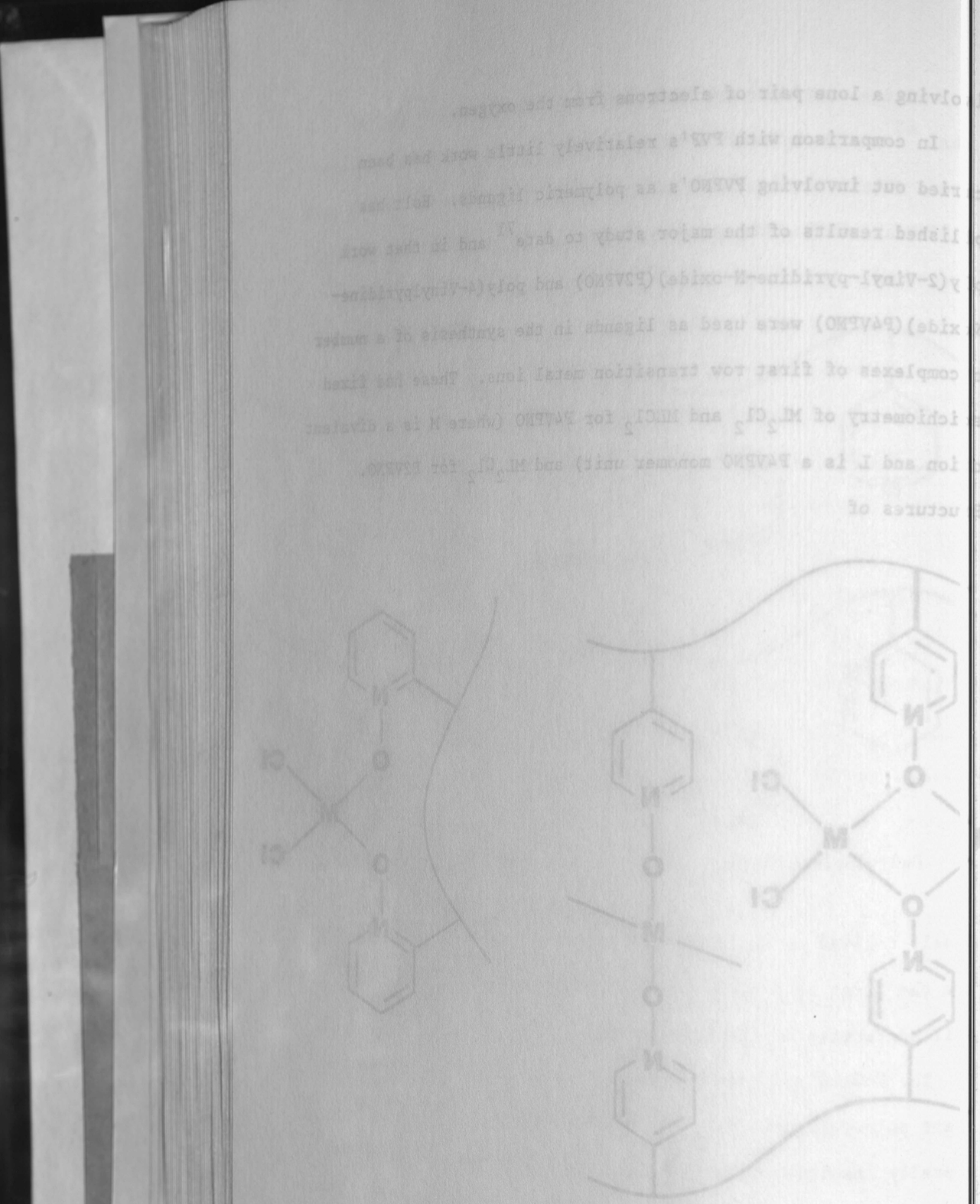
The N-Oxidized homopolymers are bright yellow and unlike the parent polyvinylpyridines (PVP's) are highly water soluble but generally insoluble in organic solvents. They are non toxic and were initially studied by Holt in research work dealing with treatments for Silicosis. [70] Like PyNO the N-Oxide groups in the polymers are capable of acting as ligands forming coordinate bonds

involving a lone pair of electrons from the oxygen.

In comparison with PVP's relatively little work has been carried out involving PVPNO's as polymeric ligands. Holt has published results of the major study to date[71] and in that work poly(2-Vinyl-pyridine-N-oxide)(P2VPNO) and poly(4-Vinylpyridine-N-oxide)(P4VPNO) were used as ligands in the synthesis of a number of complexes of first row transition metal ions. These had fixed stoichiometry of ML_2Cl_2 and $MLCl_2$ for P4VPNO (where M is a divalent cation and L is a P4VPNO monomer unit) and ML_2Cl_2 for P2VPNO. Structures of



were suggested by Holt. In both cases the metal ions form cross-



linking units between the polymer chains and this might be expected to lead to highly insoluble products. On the contrary the complexes were rather difficult to isolate from the aqueous solutions. This is surprising and the explanation may be similar to that put forward by Kirsch[62] in his consideration of the solubility of complexes of partially quaternised P4VP with Cu^{2+}.

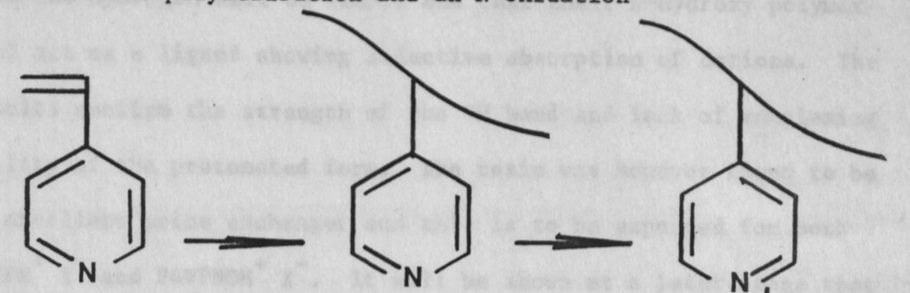
Holt et al used infra-red spectroscopy and elemental analysis to show that all the N-Oxide monomer units of the polymer had complexed T.M. cations.

Ghesquiere has also studied complexation of transition metal ions by PVPNO's, of necessity in aqueous solution.[72] Here the aims of the work were of a more quantitative nature and formation of Ni^{2+} complexes was carried out in order to determine conformational arrangements of P4VPNO. Because the Ni^{2+} cation is in very great excess Ghesquiere considers that complexes with stiochiometry of Ni (L) SO_4 (where L is a monomer unit) are the major product.

Studies comparable to those carried out with the cross-linked PVP resins (described above) have not yet been extended to the related PVPNO's. This is perhaps surprising as the latter provide potentially more useful complexing resins, primarily because they have such a strong affinity for water. Indeed the linear N-Oxides are hygroscopic, which eliminates problems associated with diffusion and, if one considers that Kopylova et al found it necessary to protonate P4VP resins to an extent of about 60% in order to obtain optimum absorption from water, it can be seen that the PVPNO resins may have greater absorption capacity here. Work described in this thesis deals in part with PVPNO's.

A final published work which has some relevance in this area

is that by Heller et al.[73] This involved preparation of a polymer described as an N-hydroxy derivative of P4VP. The resin was prepared by a single stage process involving reaction of monomer 4-vinyl-pyridine with ammonium persulphate in water. The reactions involved a free radical polymerisation and an N-Oxidation

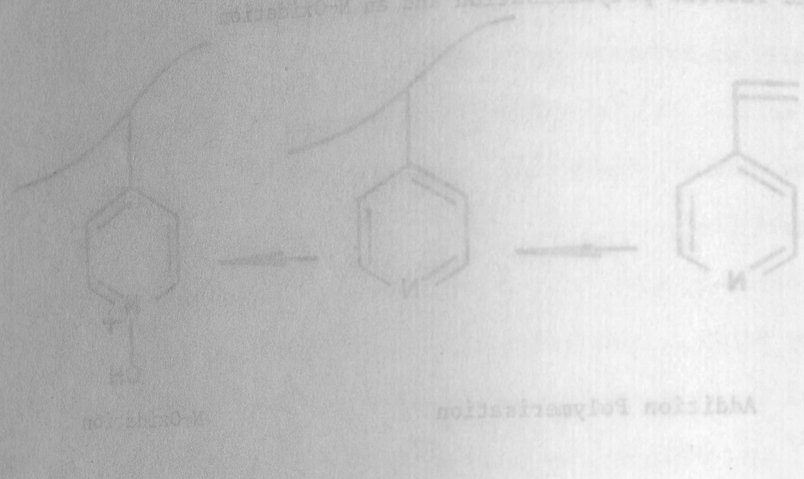


Addition Polymerisation N-Oxidation

Clearly the product is closely related to P4VPNO. The protonation of the resin occurs at some stage int he sequence (perhaps in error) yielding a product bearing positive charges on each of the monomer units, with associated counterions. Though there remains a lone pair of electrons on the oxygen atoms it seems unlikely that coordination to T.M. cations will occur whilst the positive charge is present but it is possible to imagine that a cation exchange type reaction, of the type

$$P4VPN^{+}OH + TM^{2+} \longrightarrow TM(P4VPNO)^{2+} + H^{+}$$ does,

by comparison with some of the chelating cation exchange polymers



previously considered. The O - H bond however can be expected to be relatively stable in this case though perhaps somewhat weaker than the N^+ - H bond mentioned earlier. It is this point which Heller et al overlooked and in their approach they initially assume that the hydrogen will be liable and that their N-Hydroxy polymer will act as a ligand showing selective absorption of cations. The results confirm the strength of the OH bond and lack of complexing ability of the protonated form. The resin was however found to be an excellent anion exchanger and this is to be expected for both $P4VPH^+ X^-$ and $P4VPNOH^+ X^-$. It will be shown at a later stage that the failure of these protonated forms is not total under suitable conditions. It is perhaps surprising that Heller did not extend the work to consider the 'neutral' N-oxidized P4VP, especially as attention is drawn in his paper to the ability of PyNO to act as ligand.

CHAPTER II

GENERAL EXPERIMENTAL AND INSTRUMENTAL TECHNIQUES

II.1 Introduction

The following is a brief description of general experimental methods and techniques used throughout the work together with details of various instruments and their application.

II.2 Preparation of Polymers

Here are given experimental procedures for preparation of P4VP, poly(4-vinylpyridine-N-oxide) (P4VPNO) and various poly (1.4 pyridylethylene) (ionenes) as these polymers are the basis of all reported work.

Purification of Monomer 4-Vinylpyridine

The monomer as supplied by Croda Synthetic Chemicals Ltd. (Four Ashes, Wolverhampton) was inhibited with 0.1% t-butyl Catechol and was yellow in colour. Each sample of the monomer was washed three times with five times its own volume of 10% aqueous sodium hydroxide in a separating funnel followed by washing with a large excess of water. Drying was carried out by standing the monomer over potassium hydroxide overnight followed by distillation (at 65° C) under reduced pressure of Nitrogen gas from fresh potassium hydroxide. The initial distillate (5 ml) was discarded and the remainder collected as a water white liquid with the final portion (10 ml) of liquid left in the distillation flask.

II.2.1 Preparation of Poly (4-Vinylpyridine)

Solution Polymerisation

To solution of 4-vinylpyridine (25g) in ethanol (75 ml) contained in a pyrex glass ampoule was added Azo-bisisobutyronitrile

(0.1g) as free radical initiator. The resulting solution was degassed by attaching the ampoule to a high vacuum line (10^{-6} Torr), freezing to liquid nitrogen temperature and evacuating, followed by thawing to room temperature. This freeze-thaw cycle was repeated twice prior to sealing the ampoule. The mixture was polymerised by heating to 60° C $\pm$ 1° C for twenty four hours in a water bath. The polymer was isolated by dilution of the ampoule contents to 500 ml followed by precipitation into 5 litres of diethyl ether. The precipitation was repeated twice with drying of the polymer at 50° C under vacuum to give 24.5g of a white low density fibrous product which could not easily be ground to a powder. The product was soluble in alcohols, chloroform, D.M.F. and aqueous acids but insoluble in acetone and hydrocarbons. Elemental analysis of the product gave C = 78.53%; H = 7.1%; N = 12.82%. The large volume of diethyl ether precipitant used necessitated recovery, this was effected by distillation of the ether from a mixture with aqueous ferrous ammonium sulphate after washing with water to remove alcohol. The azeotrope contains about 1% water this was removed by sodium drying prior to re-use.

Suspension Polymerisation of 4-Vinylpyridine

Suspension polymerisation in aqueous media is undoubtedly a much more convenient method of preparing large quantities of any polymer required in a dry solid form as final product, it avoids the need for a complicated precipitation stage during isolation and can under carefully controlled conditions provide reproducibly beads of the required size. Such a preparative

method has been of major importance in this project where most of the experiments carried out have used suspension products.

Procedure

Freshly distilled 4VP (300g) containing AIBN (2g) as free radical initiator was added slowly over twenty minutes with stirring and under a itrogen atmosphere to a heated solution of polyvinyl alcohol (16g; 'Poval' 220 e) in water (1800ml), which had veen thoroughly flushed with nitrogen gas to remove dissolved oxygen, contained in a split resin flask equipped with sealed stirrer, condenser and nitrogen bleed line. The flask and contents were maintained at 60° C for a further twenty four hours with stirring to give a white suspension of the solid polymer. After cooling this solid was filtered off on organdie cloth, washed with warm water for a prolonged period, allowed to stand at room temperature for five days and then dried by fluidizing in a glass column with a flow of dried air for twenty four hours. The polymer was finally dried at 60° C to give 287g of a white coarse particled (chip form 1.0mm x 0.5mm) extremely hard solid soluble in alcohols, chloroform, DMF and aqueous acid but insoluble in hydrocarbons, water and acetone, it could not be effectively ground to a powder form. Elemental analysis showed C = 79.4%; H = 6.4%; N = 13.4%.

The Cross-Linked Suspension Polymers

Cross-linked polymer beads were prepared in exactly the same way as were the linear products save that here small amounts of p-divinylbenzene as co-monomer were added to the 4VP prior to

polymerisation. The DVB monomer (BDH) was supplied as a 55-60% w/w mixture with ethylvinylbenzene and contained inhibitor, as previously for 4VP this was removed by washing with 10% aqueous potassium hydroxide followed by water and finally drying over magnesium sulphate. Separation of the two vinyl components in the mixture is not easily possible and following common practise in preparation of cross-linked resins the dried mixture was used without further treatment. This means that some care must be taken in calculating the actual quantities of DVB added and the number of cross-links in the final product, it should also be appreciated that some inert units from the ethylvinylbenzene will appear in the macromolecular chains and that the number of such units will be approximately equal to the number of DVB units. Effectively then the final product is a terpolymer of 4VP with DVB and ethylvinylbenzene.

Yields in suspension polymerisation to give cross-linked polymers were generally higher than for the linear product (~95% theoretical) but some polymer is unavoidably lost as emulsion during isolation as for the homopolymerisation. We have used 2%, 8%, 10% and 16% DVB (mole percent) to prepare cross-linked resins and one point which became clear is that control of bead size and shape is more easily possible for cross-linked products than it is for the homopolymer. It may be that deformation or adhesion of the suspension droplets at the reaction temperature occurs more readily for the homopolymerisation yielding the nonspherical 'chips'. Some indication that the latter may be so was shown when attempts to

dry the freshly isolated beads at 75° C in an oven were made, the cross-linked resins (∽8% DVB) dried easily and gave free flowing solids, the homopolymer however gave a mass of inseparable beads.

In all cases recovery of polymer lost as emulsion in the filtrate from the reaction medium was possible by the addition of a few drops of concentrated Hydrochloric acid, the polymer was deposited as gum-like solid.

Elemental analysis data was not sufficiently accurate to allow calculation of the exact degree of cross-linking and we have assumed that all monomer present polymerises and based the calculated degree of cross-linking on feed quantities. Elemental analysis does generally allow differentiation between resins with 2½%,8%, 10% and 16% DVB cross-linking.

Macro-reticular Resins

Previous published work has reported preparation of macro-reticular resins (often known as macro porous resins) from 4VP. Macro-reticular resins have greater surface area to weight ratios than do normal suspension beads of the same size, this is because 'pores' are introduced into the beads by some means, often by addition of a solvent into the system. Our attempts to prepare these voided suspension beads as reported with pyridine as a 'theta' solvent produced a fine bead linear polymer showing no evidence of macroporisity. We have subsequently found that other workers have found the reported procedure unsuitable for application to 4VP.

II.2.2 Preparation of Poly(4-Vinylpyridine-N-Oxide)(P4VPNO)

The linear polymer P4VPNO was employed only for studies described in Chapter IV but the procedure is described here to

allow continuity.

Procedure

Poly 4VP (10g) was dissolved in acetic acid (250 ml) and 50% w/v hydrogen peroxide (20 ml) was added, the mixture was stirred and heated to 75° C in a water bath for thirty six hours, further additions of the 50% hydrogen peroxide solution (5 ml) were made after twelve and twenty four hours. After cooling the mixture was rotary evaporated to remove as much solvent as possible. The resinous yellow mixture obtained was dissolved in aqueous potassium hydroxide (100 ml of 250g.$l.^{-1}$) and the resulting orange solution poured into excess (1500 ml) ethanol to deposit a yellow - orange gum. After decantation of the supernatant liquid the solid was dissolved in water (100 ml) and again precipitated into ethanol (2 l.), the process was repeated to yield the yellow-orange polymer again as an unmanageable gum, this was dried at 60° C under vacuum to give 10.31g of an orange - brown solid which could be ground to give a fine yellow powder which was rather hygroscopic and dissolved easily in water but was insoluble in organic solvents. Elemental analysis showed C = 70.5%; H = 5.9%; N = 11.8% confirming the formula of C_7H_7NO.

The Cross-Linked P4VPNO Derivatives

In contrast to the rather difficult isolation of the linear P4VPNO that of the cross-linked polymers was simple, the N-oxidation stage in this case involved a two phase reaction of the corresponding solid cross-linked P4VP with the peracetic acid mixture. The solid pale yellow products could be filtered,

washed and dried at 60° C to give a quantitative yield of yellow polymer beads which swell in water but not in organic solvents.

II.2.3. The Ionene Polymers

1. Poly(1,4 pyridylethylene) chloride (Ionene, chloride form)

i. Dry hydrogen chloride gas, generated by slow addition of concentrated hydrochloric acid to excess concentrated sulphuric acid, was bubbled through a stirred solution of 4VP (10g) in chloroform (250 ml) at room temperature. Profuse white solid quickly formed. The reaction was terminated after two hours and the solid filtered at the pump through a porosity three sintered glass crucible, washed with chloroform and ethanol and dried at 55° C under vacuum to give 13.4g (98%) of a white solid easily soluble in water but insoluble in organic solvents. It did not appear to be hydroscopic.

ii. To a solution of 4VP (10g) in methanol (350 ml) was added slowly with stirring concentrated hydrochloric acid (20 ml). A white precipitate quickly formed. The mixture was stirred for three hours at room temperature after which it was filtered at the pump through a porosity three sintered glass crucible, washed with ethanol and dried at 60° C to give 12.9g (90%) of the ionene product soluble as above.

2. Poly(1, 4 pyridylethylene) bisulphate

A solution of concentrated sulphuric acid (25 ml) in diethyl ether (200 ml) was cooled to -60° C and added slowly to a cooled (-68° C) solution of 4VP (10g) in diethyl ether (200 ml) with stirring, a white crystalline precipitate formed immediately and was isolated by filtration at the pump through a porosity two

sintered glass crucible, washed with diethyl ether and dried under vacuum at room temperature to give a quantitative yield (19.2g) of a white crystalline solid soluble in water and alcohols but insoluble in acetone, chloroform and hydrocarbons. A portion of this solid (5g) was dissolved in methanol (50 ml) and two drops of 4VP monomer were added, a white precipitate soom formed and the mixture was filtered (after two days) at the pump through a porosity three crucible, washed with dry ethanol and dried at 60° C under vacuum to give 4.92g of a white solid soluble in water but insoluble in organic solvents.

3. Poly(1,4 pyridylethylene) acetate

The corresponding acetate ionene was prepared by addition of acetic acid to a solution of 4VP in ethanol and also by addition of 4VP to acetic acid followed by precipitation into alcohol after standing at room temperature for two days.

4. Poly(1,4 pyridylethylene) perchlorate

The perchlorate ionene was still more easily prepared by addition of a solution of the chloride ionene (10g) in water (50 ml) to excess sodium perchlorate in water (100 ml). The perchlorate derivative precipitated immediately as a white solid, washing with water and methanol followed by careful drying at 45° C under vacuum gave a quantitative yield of a white powder.

II.2.4 Preparation of Poly (4-Vinylpyridinium chloride)

Poly(4-Vinylpyridine) (2g) was dissolved in methanol (25 ml) and a solution of hydrochloric acid (10 ml) in methanol (25 ml) was added slowly with constant stirring. The resulting solution was warmed to 50° C for six hours in a stoppered vessel followed

by rotary evaporation to dryness. The product was dissolved in methanol (50 ml) and precipitated into ten volumes of diethyl ether. This gave a white precipitate which was easily collected by filtration at the pump through a porosity two sintered glass crucible. The solid was dried under vacuum for sixty hours at room temperature to give 2.65g (96%) of a white very hygroscopic polymer which was soluble in water, low alcohols and DMF but insoluble in ethers, hydrocarbons, chloroform and acetone.

II.3. Preparation of Monomeric 4-Vinylpyridinium Salts

1. 4-Vinylpyridinium Bisulphate (4VPB)

4-Vinylpyridine monomer (4VP) (15 ml) purified as above was dissolved in diethyl ether (300 ml) and the resulting solutions cooled to -15° C to -20° C and added slowly (dropwise) to a solution of pure sulphuric acid (45 ml) in ether (900 ml), the latter solution having previously been cooled to -20° C. Moisture from the atmosphere was effectively excluded by surrounding equipment with a 'polythene' bag through which dry N_2 gas was passed. The mixture was rapidly stirred during the addition and the white solid which precipitates immediately was filtered at the pump and washed repeatedly with dry ether followed by extended drying under vacuum at room temperature. Reprecipitation of the solid product from ethanol into diethyl ether is probably possible but was not attempted in case of ionene polymerisation. The white solid isolated was easily soluble in water and low alcohols but insoluble in ether, chloroform and hydrocarbons. 14.0g of solid (96%) were obtained.

2. 4-Vinylpyridinium Triflouroacetate (4VPTFA)

A solution of 4VP (20 ml), purified as previously, in diethyl

ether (250 ml) was added with stirring to a solution of Trifluoroacetic acid (30 ml) in ether (250 ml) and the white crystalline precipitate which immediately forms was filtered off at the pump using a porosity two sintered glass crucible and reprecipitated from ethanol (200 ml) into diethyl ether. Drying under vacuum at room temperature gave 40.01g (97%) of a white crystalline (platelets) solid.

3. Preparation of 4-Vinylpyridinium Chloride

Pure monomer 4-Vinylpyridine (15 ml) was added slowly with stirring to pure hydrochloric acid (75 ml). The stirring was continued for thirty minutes and the stoppered solution allowed to stand at room temperature a further thirty minutes. The mixture was then rotary evaporated to dryness at room temperature, the product being a white solid (~90% yield) which was extremely hygroscopic.

All the 4-Vinylpyridinium salts were very soluble in water and low alcohols but insoluble in acetone, chloroform, diethyl ether or hydrocarbons.

II.4 Methods of Quantitative Analysis

II.4.1. Cation Determination

Wherever possible volumetric methods have been employed for determination of ions in solutions, for cation determination this has usually meant complexiometric titration with EDTA using a suitable indicator and following methods suggested in the two excellent reference texts of Vogel[78] and West.[77] Indicators used include Murexide (Cobalt (II), Nickel (II) and Copper (II))

Solochrome Black T (Zinc and Manganese (II)), Alizarin complexone (Cobalt (II), Copper (II) and Nickel (II)) and Variamine Blue B (Iron (III)), together with various recommended buffer solutions.

Problems were encountered in our attempts to use complexiometric titration methods for analysis of solutions of mixed cations, initially in solutions containing Cu (II), Co (II), and Ni (II). The recommended technique[77] involves determination of total metal ion content by titration with EDTA using Murexide indicator at pH 10 followed by titration of a sample having Cu (II) reduced to Cu (I) allowing determination of Co (II) and Ni (II) (sum). A second analysis involves oxidation of Co (II) to Co (III) allowing determination of the sum of the concentrations of Cu (II) and Ni (II). In this manner it was expected that determination of the components would be possible:-

Cu (II) + Co (II) + Ni (II) = x

Cu (II) + Ni (II) = y

Co (II) + Ni (II) = z

Cu (II) = x-z ; Co (II) = x-y Ni (II) = z+y-x

This proved not to be the case, the reduction stage of Cu (II) to Cu (I) appeared to be non-quantitative in some cases and resulted in erratic results, even when carried out under an N_2 gas atmosphere. Sodium thiosulphate, Ascorbic acid, sodium ascorbate and Hydroxylamine hydrochloride were used as reducing agents without success and it was therefore necessary to use Atomic Absorption Spectroscopy in analysis of mixtures of these cations and generally for mixtures this technique has been employed. In these cases results are generally reported as ppm concentrations.

Atomic Absorption Spectrophotometry

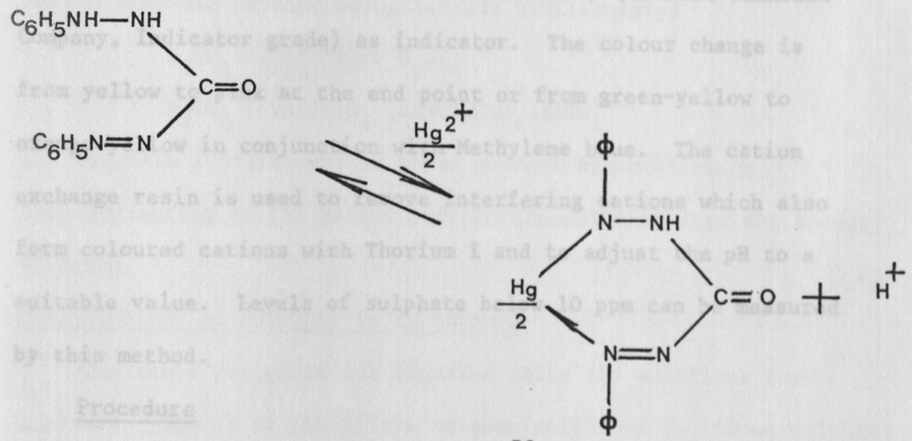
All mixtures were analysed using a Perkin-Elmer model Number 370 Atomic Absorption Spectrophotometer. Concentrations of cations below 10^{-3} M were also analysed using this technique as were those containing Vanadium (as VO^{2+}) for which a suitable volumetric technique does not exist. Mercury (II) was determined with the aid of a graphite furnace.

II.4.2 Anion Determination

Chloride

Chloride determination was carried out by titration of the chloride containing solution against standardised Mercuric nitrate solution using the complexiometric indicator Diphenylcarbazone. presence of excess mercuric ion causes a purple colouration of the clear solution only at the end point when the complex forms

$$Hg\ (II) + 2Cl^- \rightleftharpoons HgCl_2$$



The method is fully reported by Vogel [78] and was found here to be most satisfactory with great sensitivity and accuracy.

Sulphate

Attempts to use the gravimetric method reported by Vogel for determination of Sulphate ion and involving precipitation of Barium sulphate by reaction of the Sulphate containing solution with Barium chloride, were unsuccessful. At the levels in which we are interested (~.01 M) results were rather erratic possibly through lack of the required expertise rather than a failure of the method. We chose instead then to use and report here a method involving use of a cation exchanger to remove T.M. cation contamination.

Basis of Titration

The sulphate ion can be determined by a rapid titration against Barium perchlorate in 80% volume to volume Ethyl alcohol/water solution at pH 2.5 - 4.0 using Thorium (2(2-hydroxy-3:6-disulpho-1-naphtylazo) benzenearsonic acid) (Aldrich Chemical Company, Indicator grade) as indicator. The colour change is from yellow to pink at the end point or from green-yellow to orange-yellow in conjunction with Methylene blue. The cation exchange resin is used to remove interfering cations which also form coloured cations with Thorium I and to adjust the pH to a suitable value. Levels of sulphate below 10 ppm can be measured by this method.

Procedure

Polystyrene sulphonic acid cation exchange resin (SRC13 Zerolit 225 in this case) (10 ml) was regenerated using 4M Hydrochloric acid, carefully washed with water and 'wet' loaded into a pyrex glass column.

Standardisation of the Barium Perchlorate Solution (~ 5×10^{-3}M)

An accurately determined solution of Potassium sulphate

(about 100 mg.sulphate $ml.^{-1}$) was prepared from the 'analar' solid and a part (200 ml) of this solution was passed through the cation exchange resin ensuring that the resin remained under liquid at all times. An initial portion (40 ml) of the column effluent was discarded and the remainder collected. Ethanol (80 ml) was added to portions (20 ml) of this solution together with eight drops of 0.2% Thorium indicator solution and four of a 0.0125% methylene blue solution. Titrations against a previously prepared, approximately 5×10^{-3} M aqueous Barium perchlorate solution to a green-yellow to orange-yellow end point were carried out. The end point is sharp but easily missed because of the rather poor colour change.

The Thorium I indicator (more often used to determine Hf and Th) complexes excess Barium appearing in solution at the end point, the Barium sulphate product being largely undissociated

$$K_2SO_4 \underset{\text{Exchange}}{\overset{H^+ \text{ Cation}}{\rightleftharpoons}} H_2SO_4$$

$$H_2SO_4 + Ba(ClO_4)_2 \rightleftharpoons 2HClO_4 + BaSO_4$$

The sulphate solution was of known concentration allowing standardisation of the Barium perchlorate solution from the above equation.

Determination of Sulphate In An Unknown

The above procedure was repeated using the solutions for analysis. 200 ml of the dilute aqueous solutions (~150 mg.sulphate $ml.^{-1}$) were passed through the washed cation exchange column, the first portion discarded and portions (20 ml each) subsequently titrated against the now 'known' Barium perchlorate solution to the green-yellow to pink-yellow end point. Thus sulphate could be determined from

$$H_2SO_4 + Ba(ClO_4)_2 \longrightarrow BaSO_4 + 2HClO_4$$

Perchlorate

There are relatively few basically different methods available for determination of perchlorate ion and usually these involve various methods of reducing to chloride with determination of the latter either gravimetrically or titrimetrically. A more recent development by Aravamudan et al [80] indicates that a more direct titrimetric method of perchlorate analysis is possible. From a comparison with the behaviour of nitrate ion these authors considered that reduction of perchlorate might be possible using Iron (II) sulphate in strongly acidic media and that by determining the consumed Iron (II) by titrating of the resulting reaction mixture against standardised permanganate perchlorate could also be determined. Aravamudan et al proposed the reaction

$$ClO_4^- + 4H_2SO_4 + 8FeSO_4 \longrightarrow Cl^- + 4H_2O + 4Fe_2(SO_4)_3$$

for the analysis method. The conditions for reaction were found to be rather severe, 150 - 155°C for 10-15 minutes.

This method of perchlorate analysis was examined in some detail during the course of this work and although found to be an accurate if somewhat lengthy procedure for the determination. Some modification was found to be necessary, the temperature necessary for the quantitative reaction in the presence of T.M. cations was found to be $165^{\circ} \pm 2^{\circ}C$ over a period of fifteen minutes with use of suitable boiling chips and heating with an oil bath preferred. The modified procedure is described below.

Procedure

An accurately measured portion (20ml) of the unknown perchlorate

(0.01 - 0.04 M) and an accurately measured portion of at least sixteen times (preferably twenty) molar excess of a known Iron (II) Sulphate solution were placed in a pyrex conical flask (250ml capacity). Concentrated sulphuric acid (25ml) was carefully added together with a few boiling chips, the flask was heated quickly to 165°C by immersion in an oil bath at this temperature and allowed to remain a further fifteen minutes after the contents had reached temperature, water initially present was lost as vapour. The flask was then removed and quickly cooled and carefully diluted (to about 100ml), the white crystals of ferric sulphate which form during the reaction re-dissolve at this stage. The excess Iron (II) sulphate remaining unreacted was then titrated against a permanganate solution previously standardised with Potassium dichromate. Several precautions were necessary to ensure reliable results:-

i) All samples were reacted in triplicate to ensure accuracy, this allowed us to discard the odd spurious result which tended to occur.

ii) A known sample of the transition metal perchlorate was always reacted under the same conditions at the same time, as a reference.

iii) Samples of Iron (II) sulphate with acid but no perchlorate present were titrated against the permanganate, one with and one without the heating stage, the results showed that no reaction occured in the absence of perchlorate. Thus from the equation

$$M(ClO_4)_2 + 8H_2SO_4 + 16FeSO_4 \longrightarrow 8H_2O + 2Cl^- + 8Fe_2(SO_4)_3$$

the excess Iron (II) present could be related to perchlorate.

It is important to note an error in the reported recommended procedure of Aravamudan and Krishnan ([80] Page 521) in which 20ml. portions of 0.1 - 0.3 N ammonium perchlorate are used, this should read 0.01 - 0.03 N.

The method then was found to be accurate and was used in several cases for this project, it is however rather time consuming and in situations requiring analysis of several ions we have tended to discard it arranging instead to analyse for chloride and sulphate with perchlorate by difference. Generally accuracy of ± 0.5% was possible.

Nitrate

No direct volumetric method exists for determination of this ion and in all cases in this work it has been determined by a difference procedure.

II.5 Instrumental Techniques

Atomic Absorption:- see above

Magnetic Susceptibility Measurements

The Guoy method was used for all susceptibility measurements on finely powdered samples. The same procedure was used in all cases in order to obtain as reproducible results as possible. Generally the glass tube was tapped three times on a firm surface after addition of each microspatula load of powder with the average readings for two separate μ effective determinations being quoted.

Infra-Red Spectrophotometry

I.R. spectra were obtained for the various products using Perkin-Elmer model numbers 325 and 599B spectrophotometers in the range 4000 - 200cm^{-1}. The spectrum of P4VP was obtained for a

sample of the polymer deposited as a thin film from a chloroform solution evaporated to dryness on a Potassium bromide disc. The remaining monomers and polymers were studied as dispersions in polyethylene discs allowing observation of the far infra-red region. Initial study of some metal complexes showed that anion exchange could occur if Potassium bromide was used as the inert matrix, this became especially obvious for Copper (II) or Cobalt (II) containing samples, in the former blue samples turned green in the I.R. beam suggesting coordination of bromide ion to give $CuBr_4^{2-}$ and in the latter case pink samples turned blue suggesting again coordination of bromide with change from octahedral to tetrahedral coordination of ligands. KBr then was discarded as a medium for T.M. complex study.

U.V. - Visible Spectrophotometry

Beckman model number 5240 and Pye-Unicam SP8-100 spectrophotometers were used for examination of the Transition metal (T.M.) ion complexes in the visible region (400 - 800 n.m.), generally samples were presented as smeared filter papers for examination by transmittance with a filter paper in the reference beam. In some cases reflectance studies of the complexes diluted in Barium Sulphate pressed discs were examined using a reflectance technique with integrating sphere.

Nuclear Magnetic Resonance

A Perkin-Elmer model No. R12B 60 MHz nuclear magnetic resonance spectrometer was used for solution studies in deuterated chloroform and in Deuterium, with T.M.S or DSS as Oppm references.

Electron Spin Resonance Spectroscopy

A Japanese Electrical and Optical Co. e.s.r. spectrometer,

model No. JES Pe operating in the x band frequency range was used for studies in this project and spectra shown generally have width ± 1000 Gauss centered at 3300 or 3500 G. Samples were finely powdered before sealing in a small melting point tube and placing in the sample chamber tube for irradiation at room temperature. A sample of Calcium Carbonate doped with Mn (II) was used as a reference for spectra values of g = 1.981 for the fourth line with 86.9 G between third and fourth line were used.

CHAPTER III

TWO PHASE REACTIONS INVOLVING POLYMERS OF 4-VINYLPYRIDINE:- ABSORPTION OF TRANSITION METAL IONS FROM AQUEOUS SOLUTION BY THE POLYMERS.

III.1 Introduction

This section deals with results obtained from attempts to asses the ability of the P4VP and P4VPNO resins we have prepared, to complex T.M. cations and to examine the degree of selectivity in such reactions with particular consideration of the polymers as practical, selective chelating resins.

Several simple methods have previously been used by workers studying chelating and complexing resins. These methods can be considered under two headings, one we will refer to as static (or batch) and the other as dynamic (or column) absorption experiments. The static experimental method of assesment, where a known quantity of a standardised cation containing solution is exposed to a known mass of the polymer and the mixture allowed to stand, (with intermittant agitation), can allow determination of the thermodynamic preference for cation absorption/complexation reactions and of quantitative values for total ion absorption. It is clear however that such a 'static' method for absorption of cations in batch processes would not be the most effective method for large scale separations, for instance in industry and metal reclaimation from effluent. In such situations column type methods of solution treatment where the cation containing solution flows down a supported column of the polymer before discharge would be more applicable, such methods are already well established, in particular for the simple ion exchange resins commercially produced and results from previous work are often quoted in manufacturers literature.

Our major consideration was for treatment of aqueous effluent from the plating industry. This effluent we might expect to contain Nickel (II), Cobalt (II) and Copper (II) cations at a total concentration of perhaps 0.1M. It was decided initially to model, rather than use, bona fide industrial effluent. In this way control of various relevant factors is more easily effected.

Obviously examination of the structure of the T.M. cation polymer complexes was important and this aspect is dealt with fully in chapter IV. We have largely ignored the use of polymers to effect complexation in solvents other than water because in order to compete with other available treatments use of complexing/chelating resins must be cost effective and as most of the cation containing effluent can be expected to be in aqueous media, introduction of a second solvent is not advantageous.

The physical form of the polymers considered and the method of their presentation for reaction with the aqueous T.M. cations will obviously affect the reactions to a large extent, perhaps changing the order of preference for cations. We can imagine for instance complexing polymers which are gels in aqueous media where the initial cross-linking prevents total dissolution and others which are in various solid forms perhaps with varying particle size or shape, depending upon method of preparation. Obviously in two phase reactions such as are envisaged diffusion through the polymer can have some effect on the extent and rate of reaction, this diffusion will be fastest through gel-like polymers and will slow with increasing cross-linking and

particle size for particular polymers. Thus to speed the reactions we should consider using gels (P4VP and P4VPNO can both be prepared in gel form) or polymers having small particle size. Though effective in static reactions this can be self defeating if the polymer is intended as column packing for the dynamic chromatographic type reactions, the gels are difficult to retain whilst the very small particle size though providing greatly increased surface area and hence limiting diffusion control can severely limit the flow of liquid through columns, especially if upon complexation further contraction occurs leading to tighter packing. A compromise then is necessary in order to produce suitable column packings.

The most suitable form of P4VP for the intended experiments was in a spherical bead form, such beads can best be prepared by suspension polymerisation reactions. Preparation of polymers for commercial applications has resulted in products having chemical and physical properties which are very reproducible, examples are the commonly used ion-exchange resins.[81] With the relatively simple equipment available for this work full control of the final form of the prepared complexing ligands was not possible because of the large number of variables involved in the preparations. This has meant that study of the effects of changing some variables in the complexation reactions has not been possible as we should have liked. In particular, detailed study of the effect of particle size variation on the complexation reaction for polymers having the same chemical composition was not carried out. This aspect may become important in future work. Another factor we have been unable to study in great

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detail is effect of degree of cross-linking on the reaction with T.M. cations, this is for reasons related to the poor control of particle size. It is interesting to note that little, if any, previously published work has mentioned the effect of particle size variation on the complexation reaction rates of the polymers.

Methods of overcoming the detremental effects of particle size (avoiding diffusion control, hence making full use of available polymer, and poor flow rates through columns) are available, these include use of pelicular beads and production of the polymer in a macroreticular form. Pelicular beads where the polymer is deposited as a thin film on the surface of an inorganic unreactive base material (e.g. sand, glass spheres, silica, gel etc.) perhaps using vinyl silane coupling agents could allow careful control.[82] Macroreticular polymer beads are those which have 'open' vesicles thus increasing the effective surface area of the beads [83] produced in suspension polymerisation.

Presentation of Results

Data for figures shown in this Chapter are not generally presented in the main body of the text but appear in an appendix.

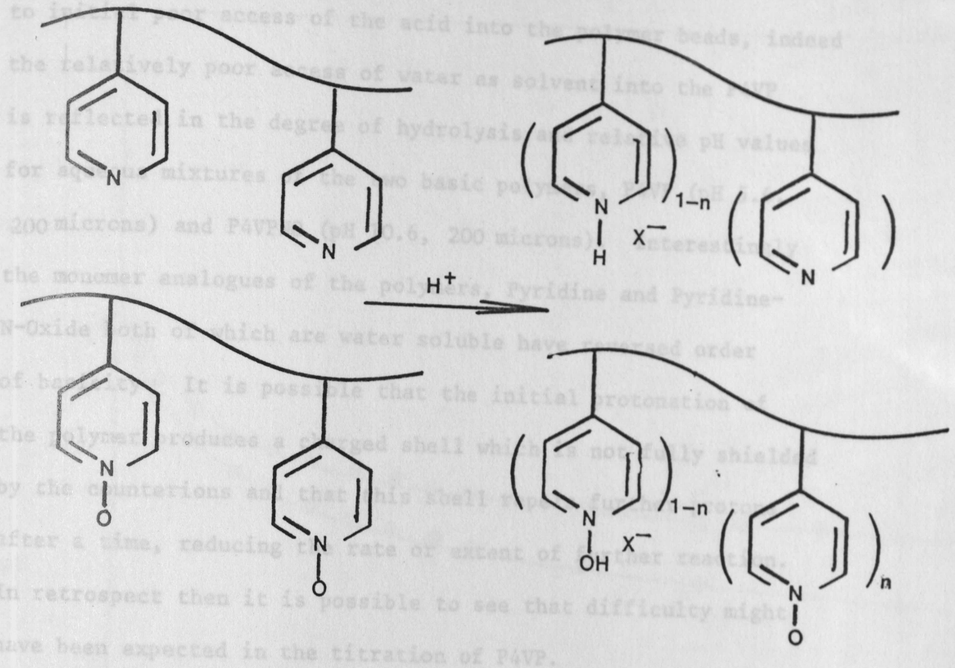
III.2 Results and Discussion

III.2.1 Poly 4VP and P4VPNO as organic bases

Titration curves for cross-linked samples of these polymers are shown in figures 1, 2 & 3 (Data Table 1).

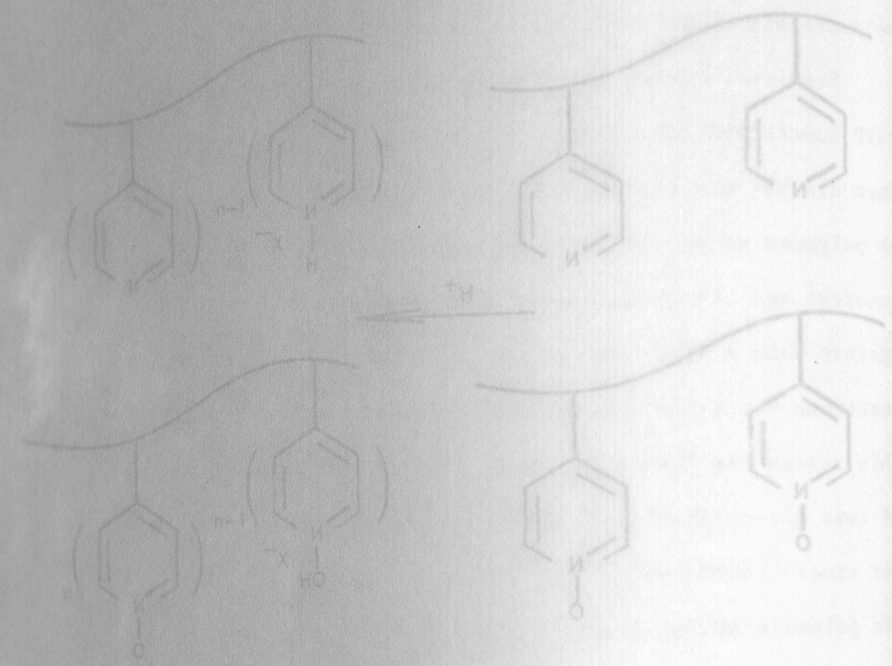
Previous workers had suggested that partially protonated P4VP functioned more effectively in complexation reactions than did the neutral (i.e. unreacted) polymer.[57,58] The ability of polymers to act as weak Lewis bases was then of considerable interest and the results above were obtained from titration against NaOH & HCl. We are primarily concerned with two phase reactions where the polymer is always present as solid, for this reason the titration curves for the linear polymer are of less direct practical importance than are those obtained for cross-linked species. We chose in these cases to study the polymers having 2 mole % DVB cross-linking and particle sizes of 50-70 microns (P4VP - optical microscope) and 50-70 microns (P4VPNO). These particle sizes varied according to conditions as shown later in Table 9.

As mentioned previously the protonation reactions (and other quaternization reactions) yield copolymers of the type



with increasing mole fraction of the ionic species as the reaction proceeds. When X = 1 the polymers are once again homopolymers (Polyvinylpyridinium Polymers). For linear P4VP this means that in titrations with acid the initial water insoluble polymer is gradually converted to a soluble product with solubilization occurring when about 20% of the monomer units in the chains are protonated. Both P4VPNO and $P4VPNOH^+$ are of course water soluble.

In initial attempts to titrate samples of the cross-linked polymers against 10^{-1}M acid Bromophenol Blue was used as indicator. This failed since the indicator appeared to be absorbed onto the surface of the polymer beads and functioned poorly.

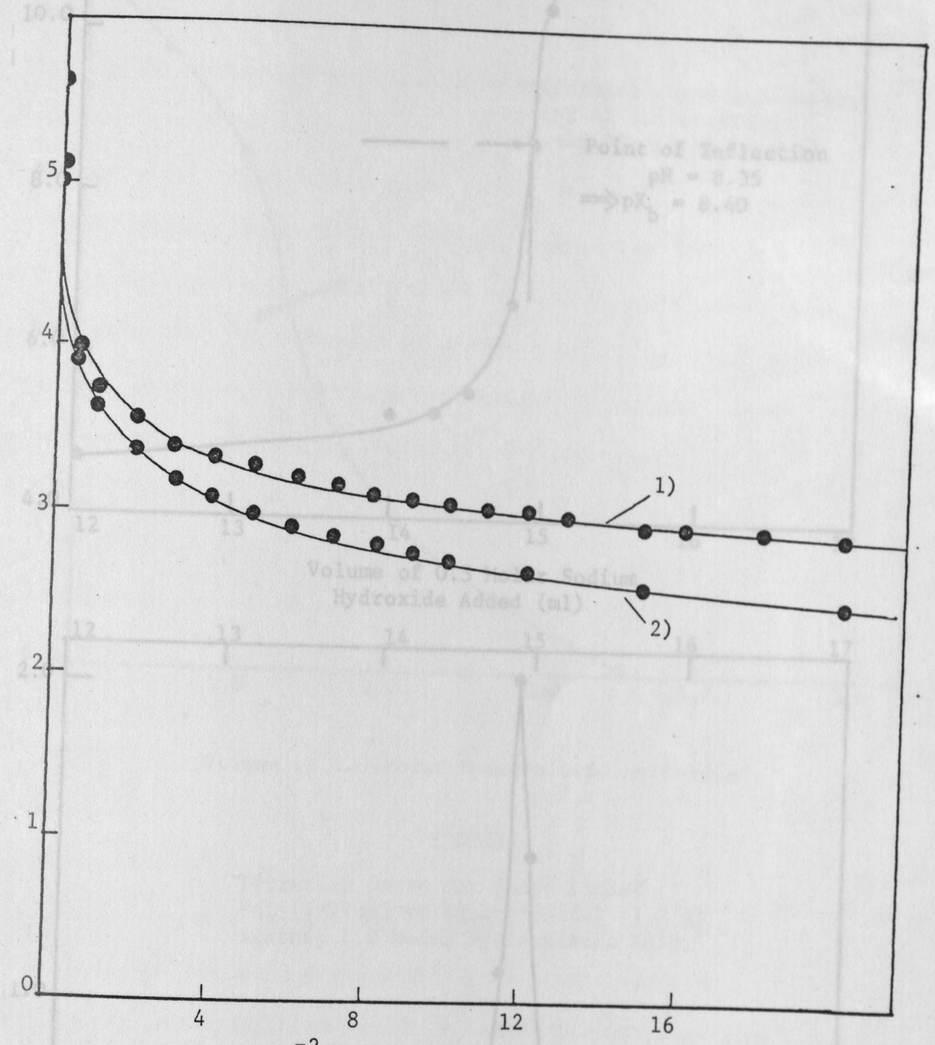


We can see from the titration curve (figure 1) obtained using a pH meter why this was so, there was no sufficiently sharp change of pH but rather a gradual decrease. This is probably due to initial poor access of the acid into the polymer beads, indeed the relatively poor access of water as solvent into the P4VP is reflected in the degree of hydrolysis and relative pH values for aqueous mixtures of the two basic polymers, P4VP (pH 5.6, 200 microns) and P4VPNO (pH 10.6, 200 microns). Interestingly the monomer analogues of the polymers, Pyridine and Pyridine-N-Oxide both of which are water soluble have reversed order of basicity. It is possible that the initial protonation of the polymer produces a charged shell which is not fully shielded by the counterions and that this shell repels further protons after a time, reducing the rate or extent of further reaction. In retrospect then it is possible to see that difficulty might have been expected in the titration of P4VP.

By preparing the conjugate acids of the polymers and titrating these against standard base a more useful curve could be obtained; this has allowed us to determine pK_b values for these macromolecular ligands. P4VPNO could be titrated directly against mineral acid. Figures 1-3 show the plots whilst pK_b values are compared with those prepared by other workers in Table 2. It seems quite probable that here for the protonated polymeric species access of the solvent and reacting ions therein is considerably easier than for the neutral P4VP and the acid/base reaction occurs more nearly as it might in solution.

Figure 1

Titration Curves for Poly(4-Vinylpyridine) against 10^{-2} Molar Hydrochloric Acid.



Volume of 10^{-2} Molar Hydrochloric Acid Added.

Polymer Sample:-

1) 200 mg of 2% cross linked (DVB) in 50ml initial concentration.

2) 200 mg of Linear 'chip' Polymer in 50ml initial Concentration.

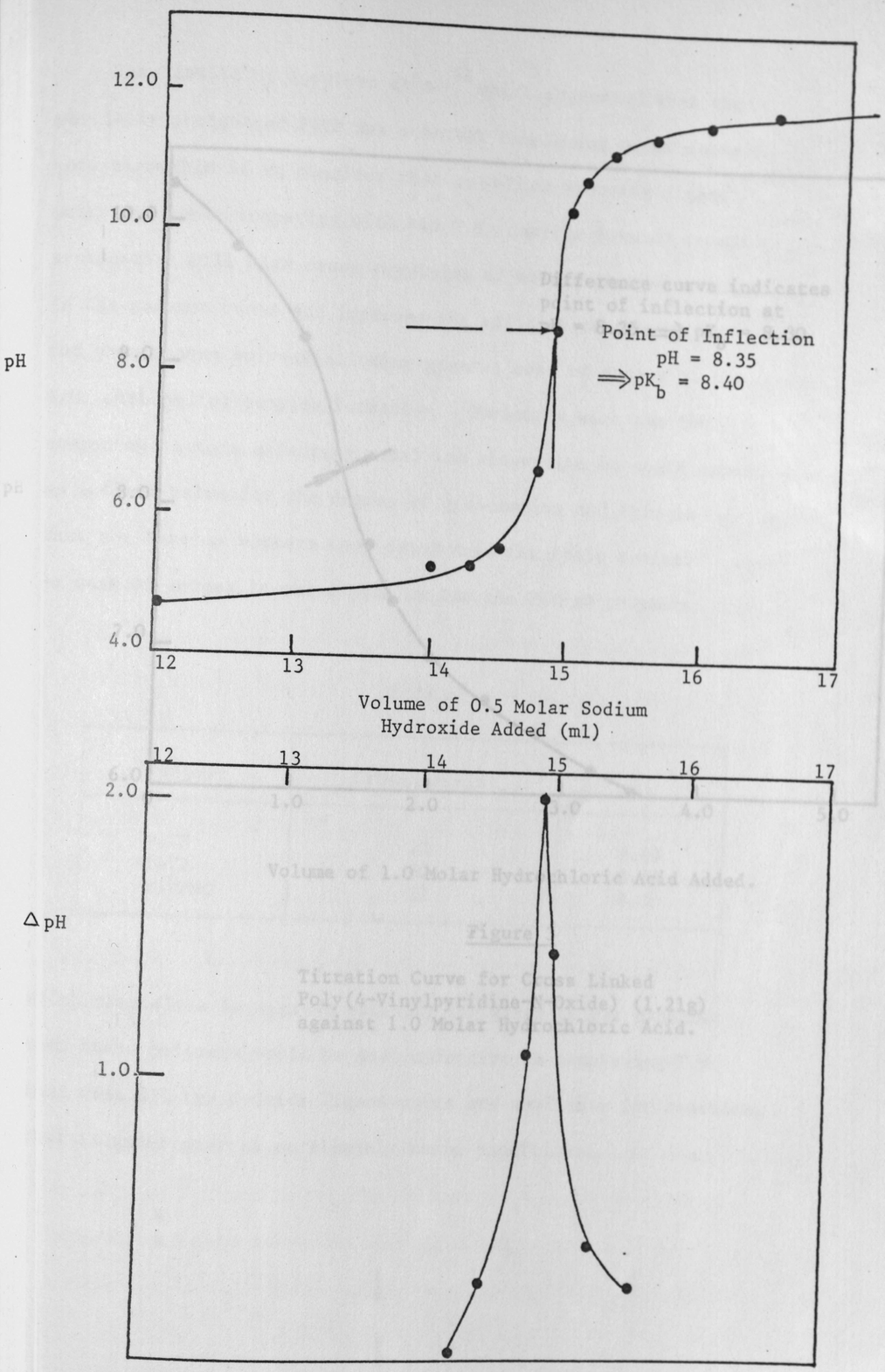
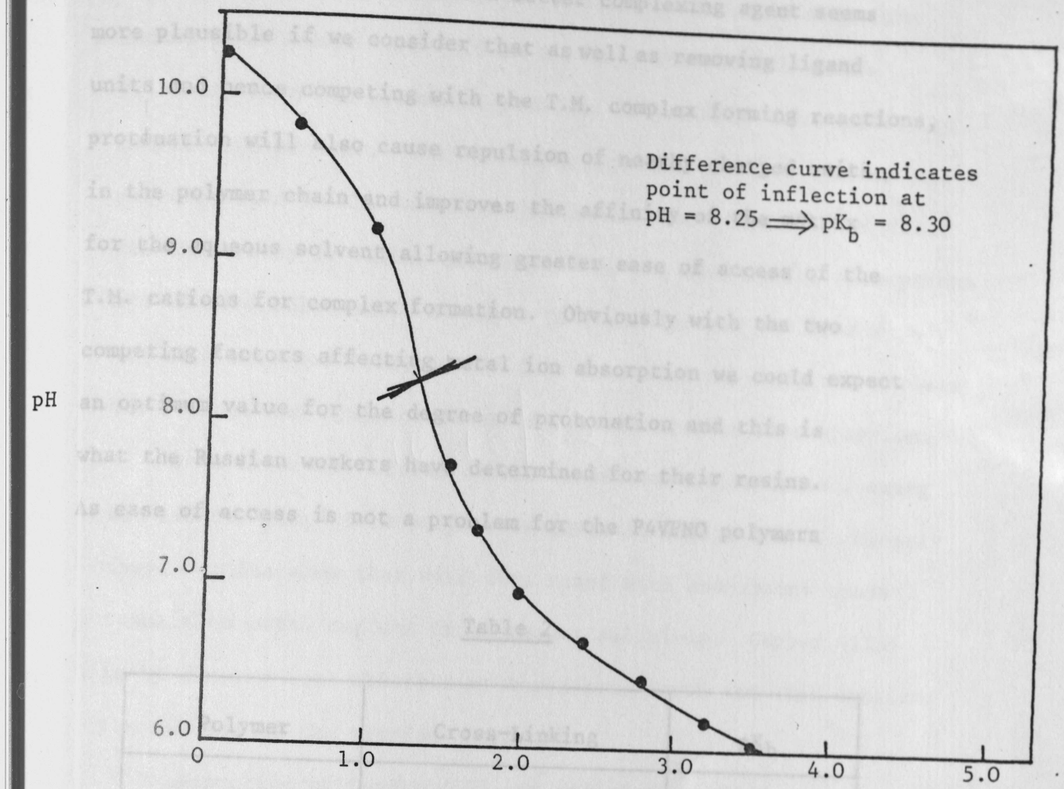


Figure 2

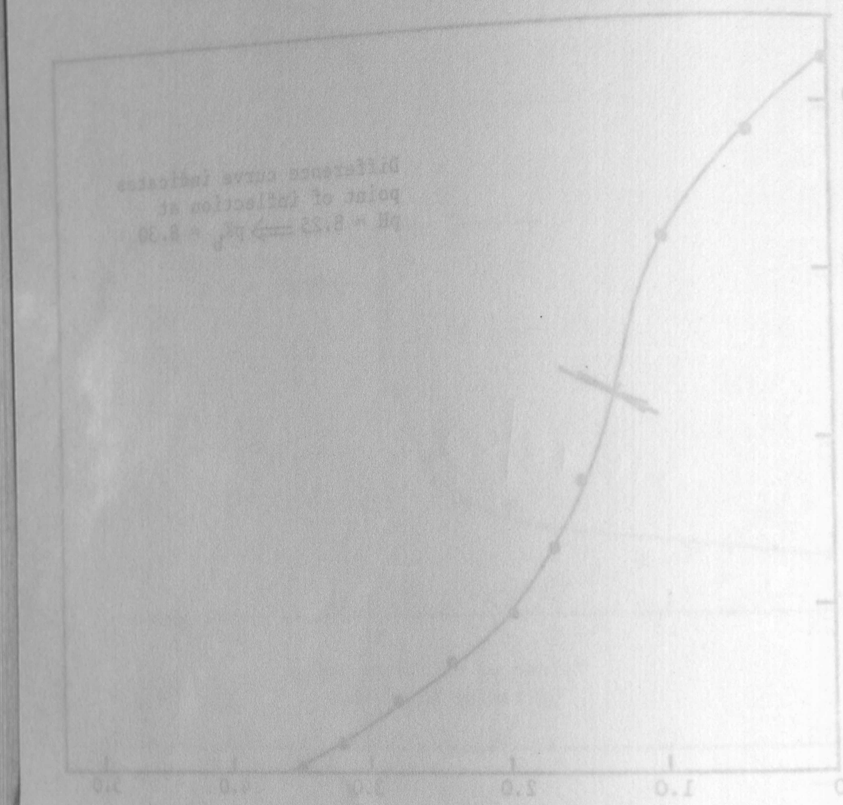
Titration of Poly(4-Vinyloyridinium chloride)
against 0.5 Molar Sodium Hydroxide.



Volume of 1.0 Molar Hydrochloric Acid Added.

Figure 3

Titration Curve for Cross Linked
Poly(4-Vinylpyridine-N-Oxide) (1.21g)
against 1.0 Molar Hydrochloric Acid.



The results of Kopylova et al[57] which suggested that the partially protonated P4VP was a better complexing agent seems more plausible if we consider that as well as removing ligand units and hence competing with the T.M. complex forming reactions, protonation will also cause repulsion of nearby charged units in the polymer chain and improves the affinity of the matrix for the aqueous solvent allowing greater ease of access of the T.M. cations for complex formation. Obviously with the two competing factors affecting metal ion absorption we could expect an optimum value for the degree of protonation and this is what the Russian workers have determined for their resins.

As ease of access is not a problem for the P4VPNO polymers

Table 2

Polymer	Cross-Linking	pK_b
P4VP	2%	8.40
P4VP	8%	8.65
P4VPNO	2%	8.30

which themselves have great affinity for water it was expected that these polymers would be most effective in complexing T.M. ions when all the N-Oxide ligand units are available for reaction, that is under neutral or slightly basic conditions.

III.2.2 The Static Complexation Reactions

Our initial linear polymer was produced in chip form rather than powder form (1.5 mm x 1 mm), the particles were extremely hard and presented problems in grinding which tended to compact the product. The differing physical forms of the various polymers used in the reactions has meant that comparison of their reaction rates is rather uninformative, the equilibrium absorptions are of more relevance. Attempts to reprecipitate the linear poly 4VP in a more suitable, powder form were unsuccessful, the product was fibrous and again could not be ground because of compaction.

Data from our initial static experimental comparisons using the linear 'chip' form polymer is given in Tables 3 & 4. Clearly these results show that P4VP does react with and absorb these transition metal cations from aqueous solutions. Copper (II) is by far the best absorbed of those considered and this confirms the results of the previous workers.

Absorption of Copper (II) and indeed the other cations is not identical from the different salt solutions and clearly some other factors must affect the complexation reaction. With Copper the chloride and the sulphate are absorbed more strongly than the perchlorate and nitrate. Nickel (II) and Cobalt (II) are rather poorly absorbed, there appears to be a change in order of preference for the salts here, the chlorides are most poorly absorbed followed by the nitrates and perchlorates. We have already mentioned the necessity for absorption of an equivalent amount of the anion by the polymer so that electrical neutrality is maintained during the complex forming reactions.

It appeared then that the counterion present could play an important part in the absorption reaction and that this 'anion effect' was sufficiently strong in some cases as to cause a change in the order of absorption for Cobalt (II) and Nickel (II) ions though Copper(II) would always be most strongly absorbed. This made a general statement as to whether Cobalt or Nickel is most strongly complexed by P4VP difficult though Tables 3 & 4 suggest that the former is slightly preferred.

The dependance of the P4VP/T.M. reaction upon the type of anion is considerably more complicated than for the cations and the data shows this clearly. There is a time factor involved in that absorption order sometimes changes during the reaction, Table 5 records this. That no particular counterion leads to consistantly greater absorption for all the cations was considered surprising. This suggests that further factors of which we were initially unaware affected the reactions.

On the basis of the results reported so far we could expect to be able to separate Copper (II) ions from mixtures of the cations in aqueous solution, this separation would be most effective with chloride present as counterion, Copper (II) chloride is absorbed strongly whilst Nickel (II) and Cobalt (II) chlorides react only slightly. Table 4 indicates other possibilities for use of P4VP in separation of these cation, Cobalt-Nickel mixtures might be separable for instance. Here chloride mixtures could not be used because of the limited reaction, neither could the nitrates nor the perchlorates as there the cations react to nearly equal extents. With sulphate counterion however we can see that the polymer can be expected to absorb ten times the amount of Co^{2+} as Ni^{2+} over a period of 24 hours.

It seemed then that selectivity could be controlled to some extent by adjusting reaction times and the counterion present together with polymer and T.M. ion concentration.

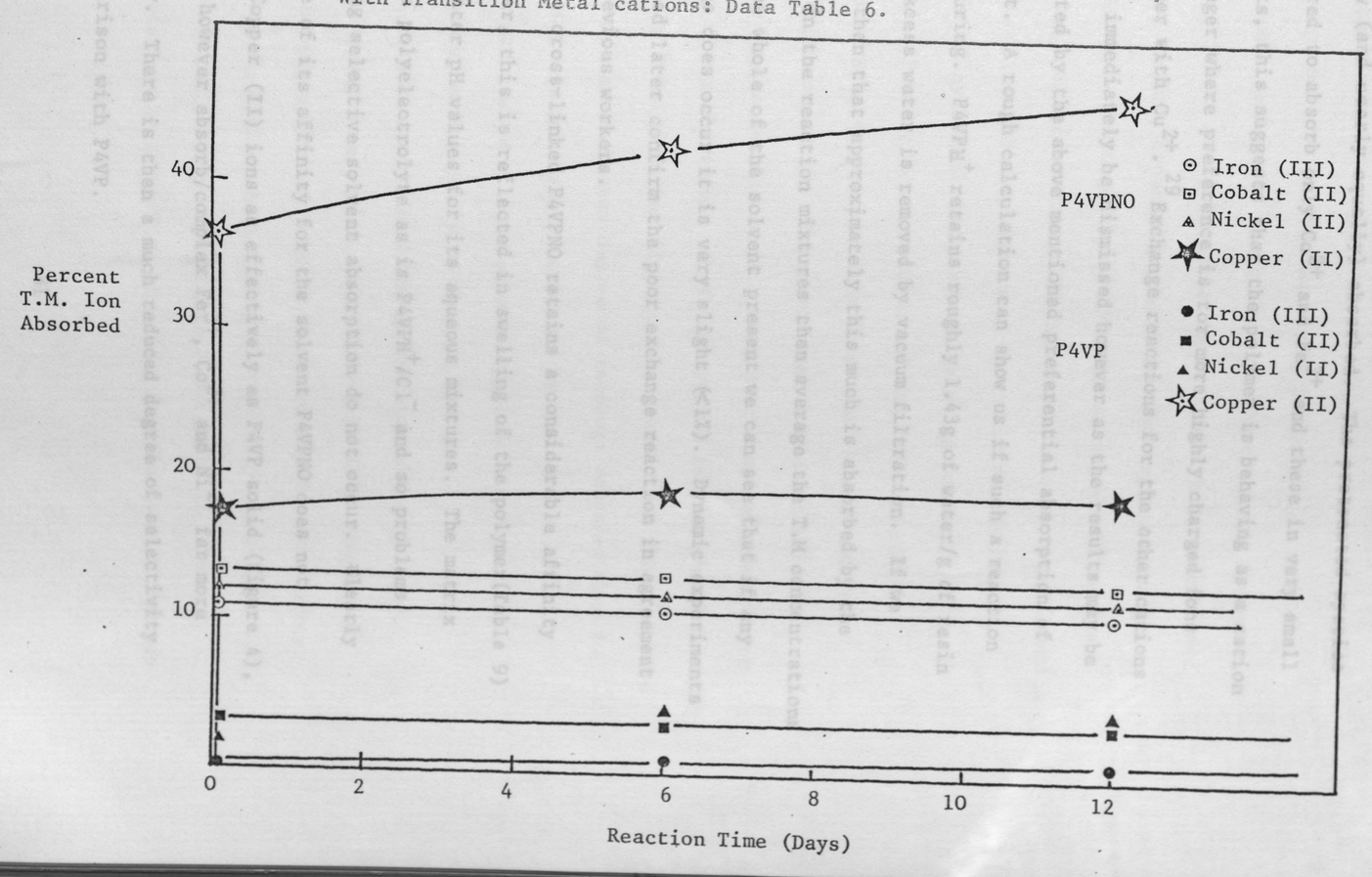
Two phase reactions of T.M. cations in aqueous solution with linear P4VPNO are not possible because of the high solubility of that polymer. Quantitative complexation/absorption reactions of the N-Oxide were then restricted to the cross-linked product.

III.2.2.1 Complex formation by (8% DVB) cross-linked Polymers

Further static experiments were carried out using the more regular particled 8 mole% DVB cross-linked P4VP and its derivatives $P4VPH^{+}Cl^{-}$, P4VPNO and $P4VPNOH^{+}Cl^{-}$. This allowed a direct comparison of the complex forming properties of the differently structured units in the chain. The base P4VP was used in production of all the derivatives. Samples of these four polymers were contacted with 0.1M solutions of Iron (III), Copper (II), Nickel (II) and Cobalt (II) solutions as chlorides. The results of the reactions are shown in figure 4 Table 6. Some problems arose with the protonated species $P4VPH^{+}$ where the concentration of the T.M. cations in solution actually appeared to rise in some cases. It seems likely that this is due to absorption of water by the hydrophilic polymer which then excludes M^{2+} cations, resulting in effective M^{2+} concentration increase. The process may be similar to that proposed in the protonation titration reaction where positive ions are thought to be repelled by the polyvinylpyridinium matrix because of ineffective shielding.

Figure 4

Reaction of Poly(4-Vinylpyridine and Poly(4-Vinylpyridine-N-Oxide) With Transition Metal cations: Data Table 6.



Once again the results show the very clear preference of the unreacted P4VP for Cu^{2+} over other ions. Even with the increased surface area for reaction Co^{2+} and Ni^{2+} seem to be poorly (and nearly equally) absorbed. The protonated species appeared to absorb only Cu^{2+} and Fe^{3+} and these in very small amounts, this suggests that the polymer is behaving as a cation exchanger where preference is for more highly charged ions together with Cu^{2+}. [29] Exchange reactions for the other cations cannot immediately be dismissed however as the results may be distorted by the above mentioned preferential absorption of solvent. A rough calculation can show us if such a reaction is occuring. $P4VPH^{+}$ retains roughly 1.43g of water/g of resin when excess water is removed by vacuum filtration. If we assume then that approximately this much is absorbed by the matrix in the reaction mixtures then average the T.M concentrations over the whole of the solvent present we can see that if any exchange does occur it is very slight (<1%). Dynamic experiments described later confirm the poor exchange reaction in agreement with previous workers.

The cross-linked P4VPNO retains a considerable affinity for water, this is reflected in swelling of the polymer(Table 9) and greater pH values for its aqueous mixtures. The matrix is not a polyelectrolyte as is $P4VPH^{+}/Cl^{-}$ and so problems involving selective solvent absorption do not occur. Clearly in spite of its affinity for the solvent P4VPNO does not absorb Copper (II) ions as effectively as P4VP solid (figure 4), it does however absorb/complex Fe^{3+}, Co^{2+} and Ni^{2+} far more strongly. There is then a much reduced degree of selectivity in comparison with P4VP.

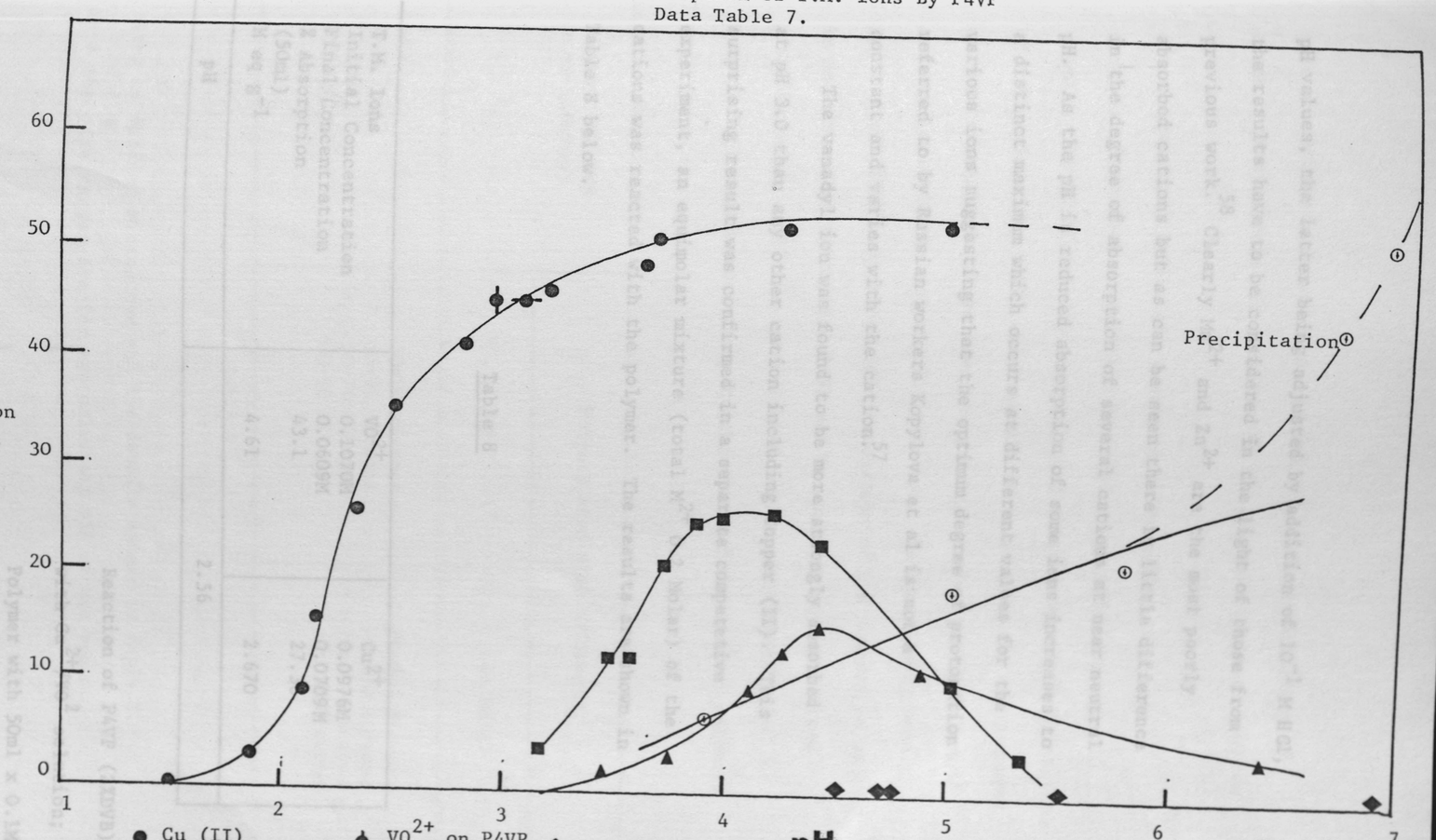
Several workers have considered the structure of complexes formed by reaction of T.M. cations with linear P4VPNO[71] none however have considered them as complexing resins which might find application in analytical or industrial chemistry. This is perhaps because an examination of the available data for the monomer analogues[67] suggests that the complexes formed by the N-Oxides would be rather less stable than those formed by other resins, especially the commercial cation exchange resins. One advantage that P4VPNO has over the P4VP resins is in its rate of reaction. We had expected rapid equilibration because of the affinity for water more akin to the imino-diacetic of hydroxamic acid based chelating polymers. Figure 4 allows direct comparison of the P4VP and P4VPNO reactions because here particle sizes are closely similar (150-200 microns dry). The protonated N-Oxide like $P4VPH^+$ is shown by the results to be a very poor complexing/absorbing polymer. From the values of pK_b determined earlier which showed the N-Oxide to be slightly less powerful as a nucleophile we had expected a greater degree of exchange reaction than for $P4VPH^+$, this is not really confirmed by the data.

The structures of the various complexes formed will be considered more closely in Chapter IV.

The static experimental series was expanded once more, this time using a very fine, cross-linked (2% DVB) suspension polymer having spherical beads. The reactions involved other first row T.M. cations besides those previously considered. The results are displayed in figure 5 and Table 7. These experiments involved the T.M. chlorides in reactions at various

Figure 5

pH Profile For Absorption of T.M. Ions By P4VP
Data Table 7.



1.08g P4VP 2% DVB Cross-linked with 50ml. of 0.1M Solutions.

pH values, the latter being adjusted by addition of 10^{-1} M HCl, the results have to be considered in the light of those from previous work.[58] Clearly Mn^{2+} and Zn^{2+} are the most poorly absorbed cations but as can be seen there is little difference in the degree of absorption of several cations at near neutral pH. As the pH is reduced absorption of some ions increases to a distinct maximum which occurs at different values for the various ions suggesting that the optimum degree of protonation referred to by Russian workers Kopylova et al is not a constant and varies with the cation.[57]

The vanadyl ion was found to be more strongly absorbed at pH 3.0 than any other cation including Copper (II). This surprising result was confirmed in a separate competetive experiment, an equimolar mixture (total M^{2+} 0.2 Molar) of the cations was reacted with the polymer. The results are shown in Table 8 below.

Table 8

T.M. Ions	VO^{2+}	Cu^{2+}
Initial Concentration	0.1070M	0.0976M
Final Concentration	0.0609M	0.0709M
% Absorption (50ml)	43.1	27.36
M eq g^{-1}	4.61	2.670
pH	2.56	

Reaction of P4VP (2%DVB) with Cu^{2+}/VO^{2} solution; 1g Polymer with 50ml x 0.1M

Care is necessary in reactions of the VO^{2+} ion precipitation of basic hydroxy species is possible if the pH value rises much above 4.

Copper (II) unlike the weakly absorbed cations did not show a well defined maximum but has a plateau region from pH 2.5 to pH 5. It had initially been expected that absorption/complexation of all cations (by P4VP) which remain in solution would be strongest at near neutral pH values when the greatest number of ligand units are available in the polymer for reaction. It has already been pointed out that only about 20% protonation of the monomer units is sufficient to solubilise P4VP and we can also expect limited protonation to swell the cross-linked polymer considerably in water. We have examined the particle sizes of the various polymers

Polymer (2% DVB Cross-Linking)	Polymer bead size (Microns)	
	Dry	In Water
P4VP	50-70 Microns	50-70 Microns
$P4VPH^+/Cl^-$	55-85 Microns	70-100 Microns
P4VPNO	50-70 Microns	70-100 Microns
$P4VPNOH^+/Cl^-$	60-90 Microns	70-100 Microns

Table 9

using an optical microscope and the details appear in Table 9. Here the size ranges are for approximately 95% of the beads.

From the results in Table 7 and figure 5 together with those reported earlier it is possible to give an explanation for the order of absorption and change in degree of complexation we have observed for the first row T.M. cations. Obviously in a two phase system initial complex formation will occur at the surface of the solid polymer beads with subsequent penetration of solvent and metal ions to lower levels. The polymer however has ligand units which are effectively locked in place and because of this inflexibility and consequent inability to adjust to give arrangements suitable to chelate T.M. ions reaction will generally be only slight. This is the case for Mn^{2+} and Zn^{2+} and Fe^{3+}, Co^{2+} and Ni^{2+}. That this failure to react (and absorb) is not due to an inability of these ions to form stable complexes is confirmed in the solution reactions of P4VP (see Chapter IV) which readily yield high cation content products. It appears however that Cu^{2+} and VO^{2+} are special cases and they can adjust to the distorted ligand arrangement of the monomer units provided by the solid polymer. This situation is not unusual for Copper (II) cations which are known for their ability to accommodate distorted ligand arrangements, indeed the Irving-Williams series is a summary of experience gained in this area of complex formation.

The situation for the N-Oxide polymer is somewhat different, this polymer has great affinity for water and is swollen in its mixtures (see Table 9). The macromolecular chains even when cross-linked are capable of adjusting to give arrangements suitable for complex formation with most T.M. cations.

This then explains the difference in selectivity between P4VP and P4VPNO, further, penetration of the latter is possible by all the cations which can then react throughout the matrix.

Protonation of the cross-linked P4VP causes swelling and consequently access to the lower levels of the polymer and remaining neutral ligands by reacting cations may improve dramatically as will resulting complex forming reactions. The swelling of the polymer matrix allows greater penetration by solvent and resulting increased freedom of the macro-chains means that conformations in which the ligands are more suitably arranged for complex formation (i.e. more regular arrangement of monomer unit ligands about cations) are possible. We should expect then reactions of P4VPNO and partially protonated P4VP to have some similarities in absorption of T.M. cations, this is so as can be seen from Tables 6 & 7, figures 4 & 5.

Though selectivity and overall absorption is relatively less the preference for Cu^{2+} remains, this may in part be a residual effect due to the ability of Cu^{2+} to exist in distorted complex arrangements. These effects would be similar to those encountered for the monomeric analogues, Copper (II) forms the stronger complexes with Py, 4VP and PyNO.

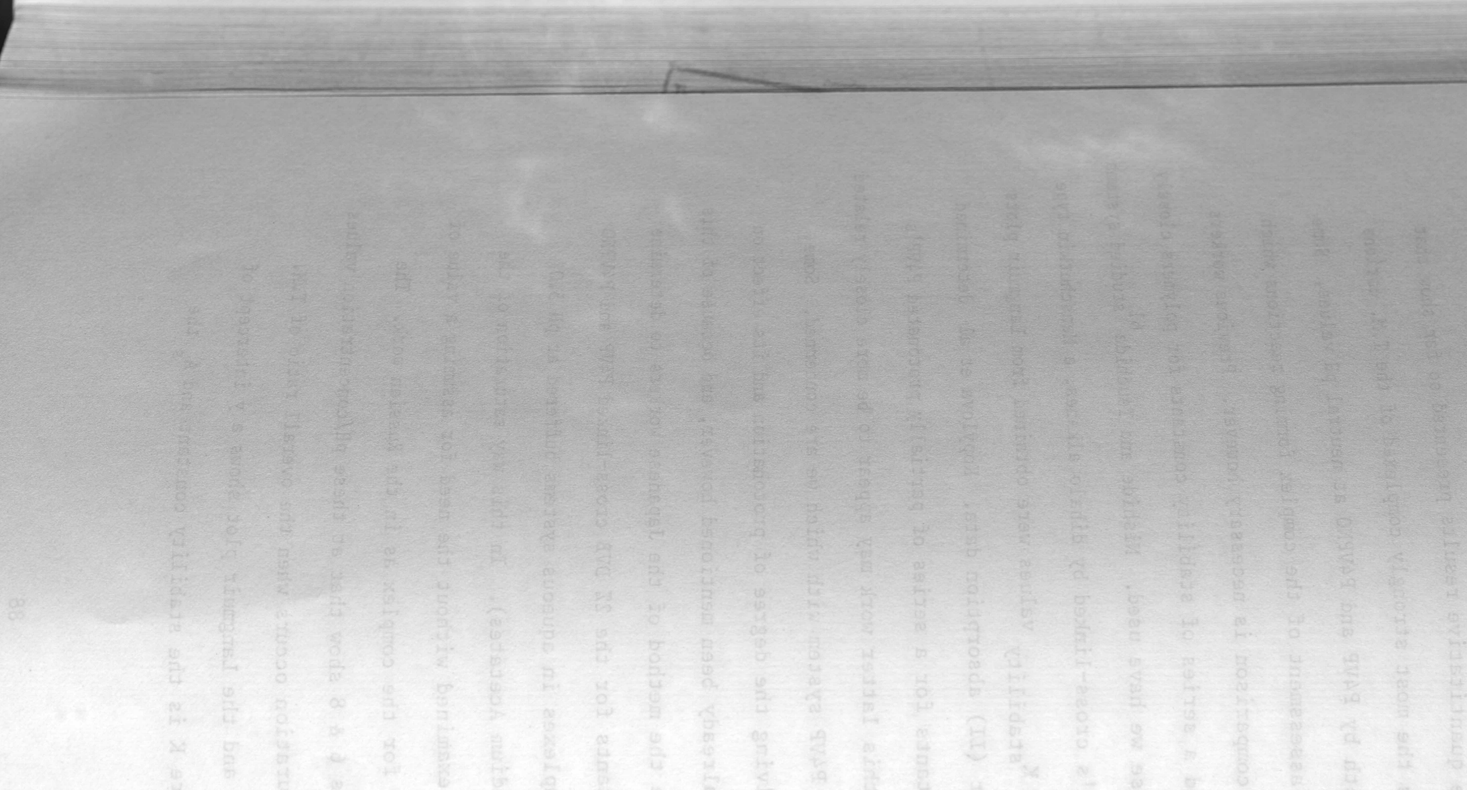
Previous workers have considered the effect of complex formation on conformations of the polymers,[55] this work will be discussed in Chapter IV.

III.2.2.2 Stability Constants of Copper (II)/P4VP and Copper (II)/ P4VPNO Complexes.

The quantitative results presented so far show that Copper (II) is the most strongly complexed of the T.M. cations considered, both by P4VP and P4VPNO at neutral pH values, Some more absolute assessment of the complex forming reactions which allows simple comparison is necessary however. Previous workers have determined a series of stability constants for polymers closely related to those we have used. Nishide and Tsuchida[61] studied systems involving P4VP's cross-linked by dihalo alkanes, a Menschutkin type reaction. The $K_{stability}$ values were obtained from Langmuir plots based on Copper (II) absorption data. Kopylova et al determined stability constants for a series of partially protonated P4VP's and initially this latter work may appear to be more closely related to the neutral P4VP system with which we are concerned. Some confusion involving the degree of protonation and its effect on structure has already been mentioned however, and because of this we chose to use the method of the Japanese workers to determine stability constants for the 2% DVB cross-linked P4VP and P4VPNO Copper (II) complexes in aqueous systems buffered at pH 5.0 (Acetic acid/Sodium Acetates). In this way saturation of the polymer can be examined without the need for assuming a value of Cu^{2+}:P4VP = 1/2 for the complex as in the Russian work. The plots in figures 6 & 8 show that at these pH/concentration values equilibrium saturation occurs when the overall ratio of T.M. to ligand = 0.4 and the Langmuir plot shows a y intercept of $\frac{1}{K.A_s} = 0.56$ where K is the stability constant and A_s the

Figure 6

Reaction of P4VP With Aqueous Copper (II) Solutions of Various Concentrations.



saturation ratio of 0.4. K then has a value of approximately $4.461.Mol.^{-3}$.

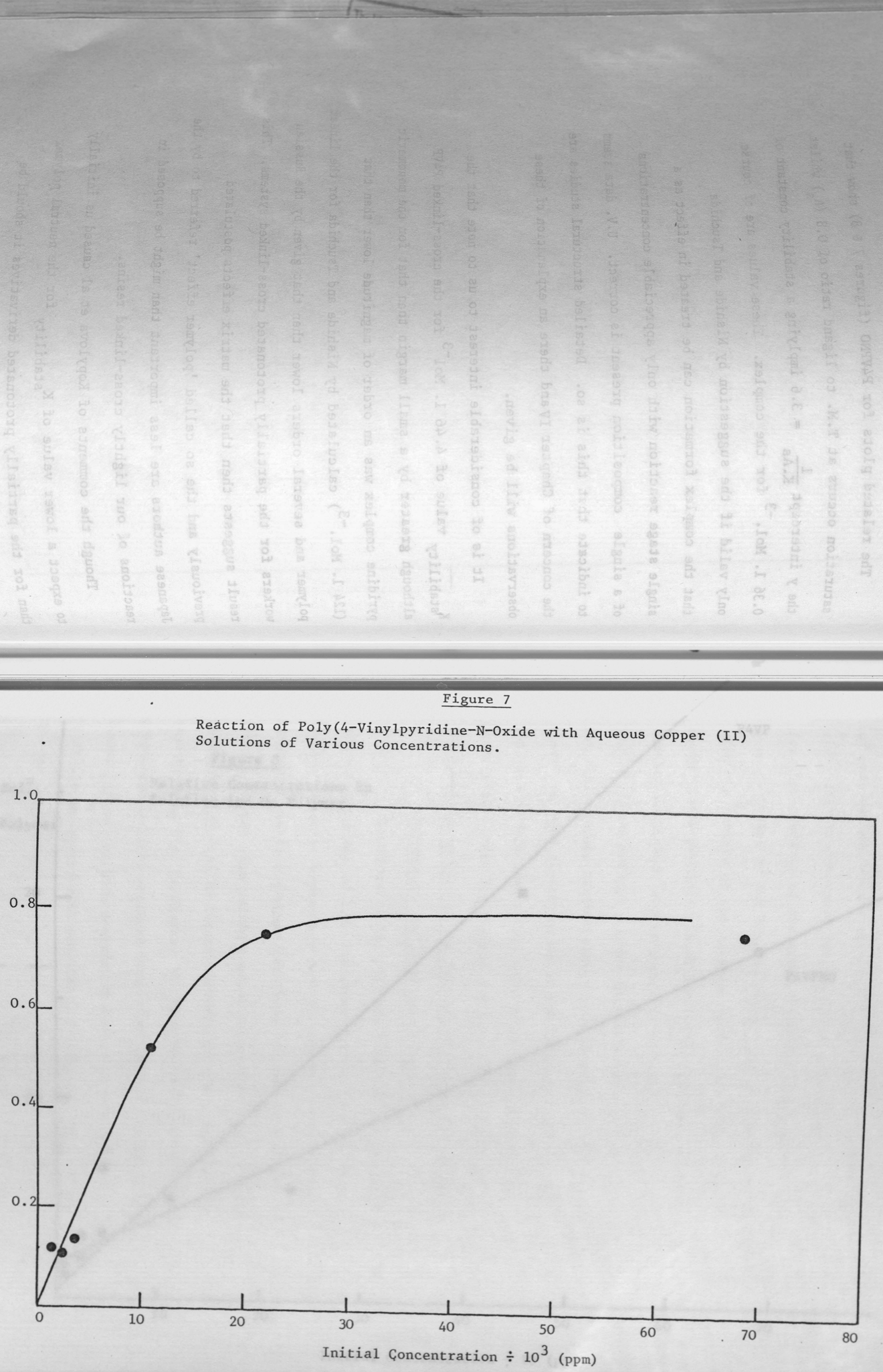
The related plots for P4VPNO (figures 7 & 8) show that saturation occurs at T.M. to ligand ratio of 0.8 (A_s) whilst the y intercept $\frac{1}{K.As}$ = 3.6 implying a stability constant of 0.36 1. $Mol.^{-3}$ for the complex. These values are of course only valid if the suggestion by Nishide and Tsuchida that the complex formation can be treated in effect as a single stage reaction with only appreciable concentrations of a single composition present is correct. U.V. data seems to indicate that this is so. Detailed structural studies are the concern of Chapter IV and there an explanation of these observations will be given.

It is of considerable interest to us to note that the $K_{stability}$ value of 4.46 1. Mol^{-3} for the cross-linked P4VP although greater by a small margin than that for the monomeric pyridine complex was an order of magnitude lower than that (124 1. $Mol.^{-3}$) calculated by Nishide and Tsuchida for the linear polymer and several orders lower than that given by the Russian workers for the partially protonated cross-linked systems. This result suggests then that the matrix effects postulated previously and the so called 'polymer effect' referred to by the Japanese authors are less important than might be supposed in reactions of our lightly cross-linked resins.

Though the comments of Kopylova et al caused us initially to expect a lower value of $K_{stability}$ for the neutral polymer than for the partially protonated derivatives it should be

Figure 7

Reaction of Poly(4-Vinylpyridine-N-Oxide with Aqueous Copper (II) Solutions of Various Concentrations.



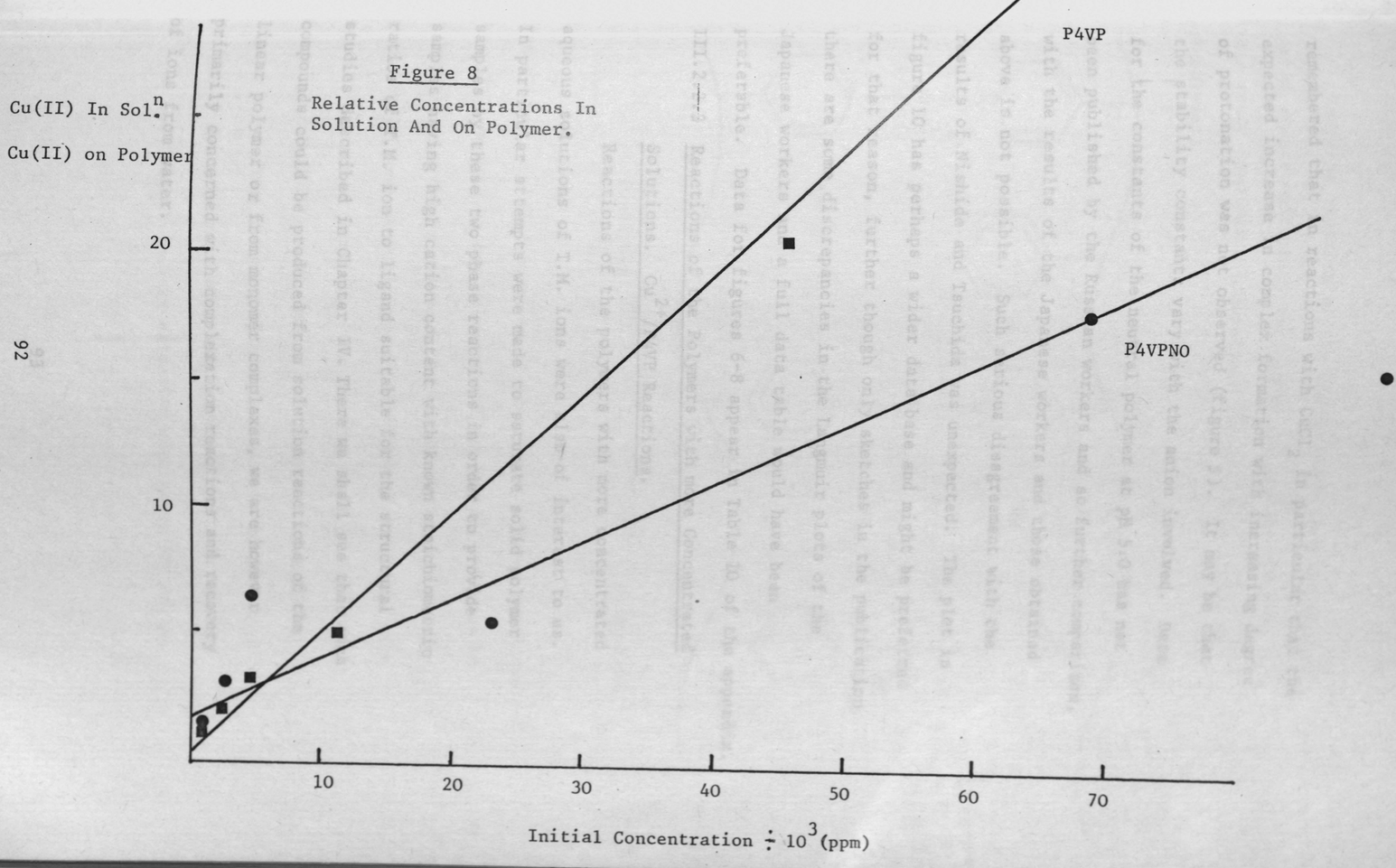
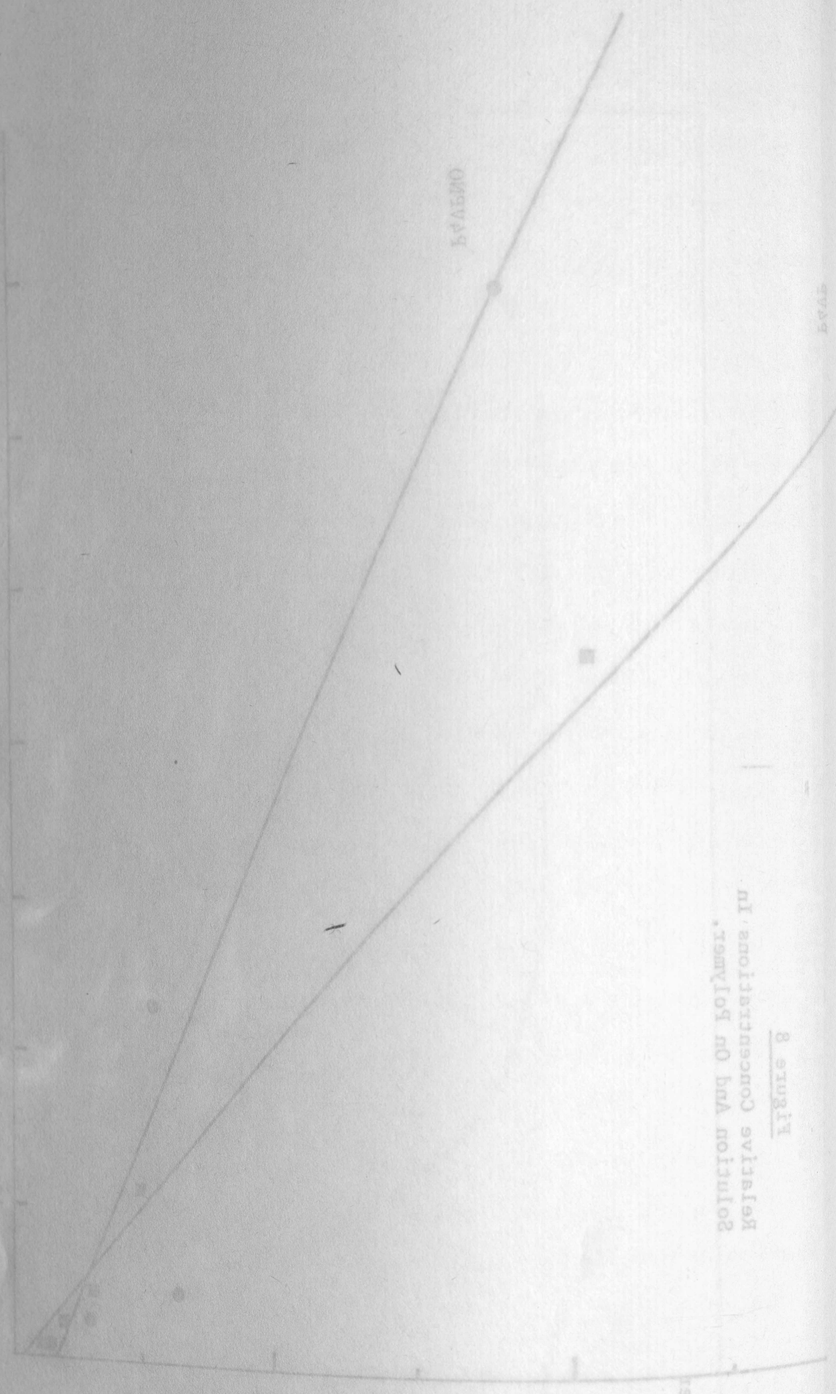


Figure 8

Relative Concentrations In Solution And On Polymer.

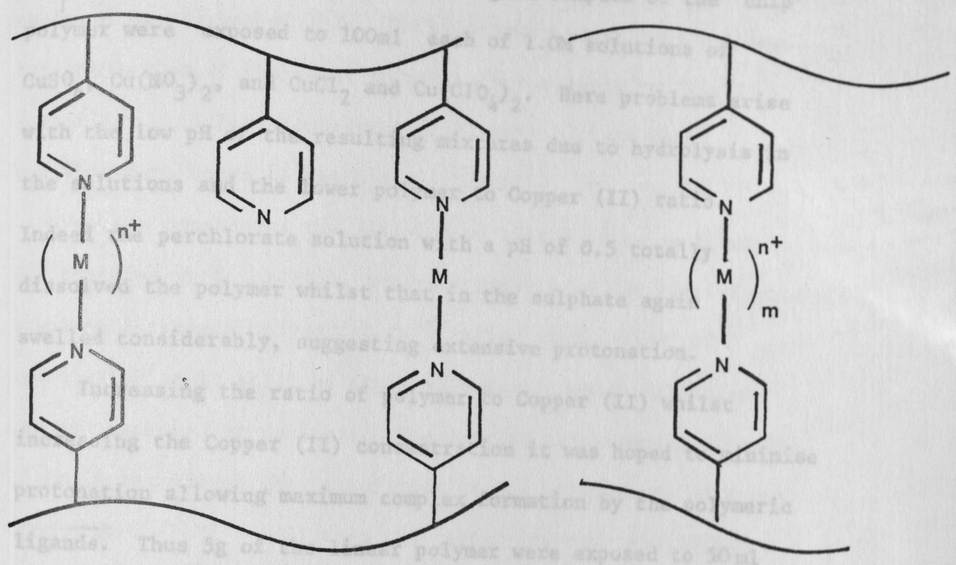


remembered that in reactions with $CuCl_2$ in particular that the expected increase in complex formation with increasing degree of protonation was not observed (figure 5). It may be that the stability constants vary with the anion involved. Data for the constants of the neutral polymer at pH 5.0 has not been published by the Russian workers and so further comparison, with the results of the Japanese workers and those obtained above is not possible. Such serious disagreement with the results of Nishide and Tsuchida was unexpected. The plot in figure 10 has perhaps a wider data base and might be preferred for that reason, further though only sketches in the publication there are some discrepancies in the Langmuir plots of the Japanese workers and a full data table would have been preferable. Data for figures 6-8 appear in Table 10 of the appendix.

III.2.2.3 Reactions of the Polymers with more Concentrated Solutions. Cu^{2+}/P4VP Reactions.

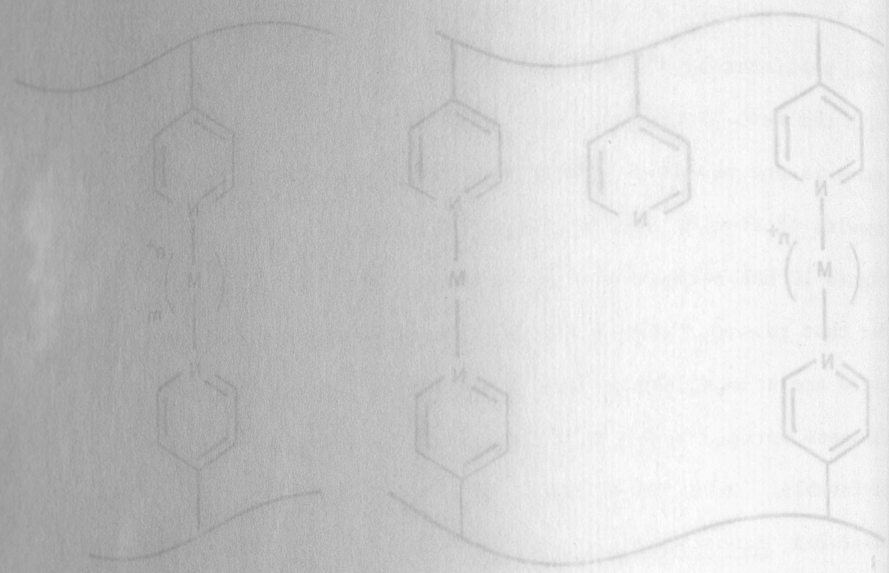
Reactions of the polymers with more concentrated aqueous solutions of T.M. ions were also of interest to us. In particular attempts were made to saturate solid polymer samples by these two phase reactions in order to provide samples having high cation content with known stoichiometric ratios of T.M. ion to ligand suitable for the structural studies described in Chapter IV. There we shall see that such compounds could be produced from solution reactions of the linear polymer or from monomer complexes, we are however primarily concerned with complexation reactions and recovery of ions from water.

Complete reaction of the ligand units from the polymer would ensure uniformity throughout the product and mean that the study involves a homopolymer rather than a series of copolymers



Copolymer Homopolymer

and allow careful comparison of structures. Copper was known to be well absorbed by the polymers and our initial attempts to saturate involved reaction of the linear coarse particled solid with highly concentrated Copper (II) Sulphate solution. The results appear in Table 11 and clearly imply an empirical formula of $Cu(P4VP)_{2.1}SO_4$ and as we can expect at most two ligand units from the macromolecular chains to complex each cation it is apparent that penetration and reaction of the Cu^{2+} in the polymer is very extensive with about 95% of the



theoretical max absorption taking place. Clearly absorption as expected is much greater from higher concentration solutions in this case. As a comparison similar reactions were carried out with several other Cu (II) salts. 2 gram samples of the 'chip' polymer were exposed to 100ml each of 1.0M solutions of $CuSO_4$, $Cu(NO_3)_2$, and $CuCl_2$ and $Cu(ClO_4)_2$. Here problems arise with the low pH of the resulting mixtures due to hydrolysis in the solutions and the lower polymer to Copper (II) ratio. Indeed the perchlorate solution with a pH of 0.5 totally dissolved the polymer whilst that in the sulphate again swelled considerably, suggesting extensive protonation.

Increasing the ratio of polymer to Copper (II) whilst increasing the Copper (II) concentration it was hoped to minimise protonation allowing maximum complex formation by the polymeric ligands. Thus 5g of the linear polymer were exposed to 50 ml of a 2.873M solution of $CuCl_2$. The results are shown in Table 11.

An empirical formula of $Cu(P4VP)_{2.7}\ Cl_2$ is implied. Saturation then does not give a regular stoichiometric formula under these conditions and it seems likely that considerable protonation occurs competing effectively with the complex forming reaction. The alternative explanation that there is a significant structural difference between the complexes formed from sulphate and chlorides seemed initially unlikely. More detailed investigations of these high cation content polymers are reported in Chapter IV.

Returning to concentrated solutions of copper sulphate, some idea of the time factor required for penetration throughout the polymer particles by Cu^{2+} ions was required. A number of

samples of the linear polymer were then reacted with a 0.5018M solution of the sulphate for differing periods of time and the solutions analysed. The data are presented in Table 12. Once again limiting saturation occurs at molar ratios of Copper absorbed to polymer of 1:2. The relatively short time required for completion of the reaction was rather surprising from comparison with less concentrated (0.1M) solutions which required many hours to reach equilibrium.

Having considered the dissolution of the linear polymer in its reaction with $Cu(ClO_4)_2$ a repeat experiment was carried out using an increased polymer to Cu^{2+} ratio. Some extent of protonation could still be expected though complex formation was now expected to dominate. The results are shown in Table 11. If it is remembered that saturation of the polymer was intended (probably Cu/P4VP = 1/2) then the rather low number of ligands complexed to Cu^{2+} was rather disappointing, again protonation was considered responsible.

Co^{2+}/P4VP Reactions

Having found that very extensive complex formation can occur throughout the solid polymer in reaction with Copper (II), attempts were made to produce high cation content polymer samples by similar two phase reactions with Cobalt (II) solutions. Approximately 1.0M solutions of $CoCl_2$, $CoSO_4$ and $Co(AcO)_2$ were reacted with the polymer. pH values of these solutions were considerably greater than those of corresponding Copper (II) solutions, being essentially neutral. The absorption of Cobalt(II) is detailed in Table 11. Absorption here is once again disappointing and is less than that generally observed for Copper,

this is much the same situation as is found in the reactions with the 0.1M solutions. The nearly total failure of $CoCl_2$ to react with the polymer in these concentrated solutions is puzzling, a small absorption had registered previously in 0.1M reactions and the pH of 6.0 for the reacting solution does not suggest high levels of competing protonation.

Further reactions at intermediate concentrations were carried out; samples of P4VP were exposed to 0.2M solutions of $CoCl_2$ and $Co(NO_3)_2$. The results appear in Table 11 and show that considerable absorption does occur and that the chloride and nitrate react to a nearly equal extent.

Clearly then it was possible to produce high Co (II) cation containing polymers by means of these two phase reactions though full saturation to give regular stoichiometry was not possible, we shall see later however that polymers of stoichiometry $Co(P4VP)_2Cl_2$ can be produced. These two phase reactions gave empirical formulae of $Co(AcO)_2(P4VP)_{3.46}$.

The generally observed lower level of absorption of Co^{2+} over Cu^{2+} is believed due to unsuitable conformation of the ligand chains and reduced ability of the Co^{2+} cation to adjust to distorted ligand arrangement.

Reactions of P4VPNO with Concentrated Solutions

Similar reactions to those described for P4VP were carried out on DVB cross-linked P4VPNO. Here full saturation of the polymer was expected to occur quite quickly because of the observed affinity of the polymer for water with resulting ease

of access for cations to the ligands and mobility of the polymer chains. Results are shown in Tables 11 & 13. Copper (II) is absorbed very well by the polymer to give products having an empirical formula of $Cu(P4VPNO)_{0.6 - 0.8}Cl_2$ and such results were quite unexpected, especially in the light of work carried out by Holt et al using the linear polymer as macromolecular ligand in solution reactions.[71] Explanation of such good Copper (II) absorption is difficult, the figures suggest that some of the N-Oxide units are coordinated to more than one Copper cation. One possible structural interpretation is given in Chapter IV section 3 where comparison is made with reaction products of the linear polymer.

Our attempts to saturate the cross-linked P4VPNO with Co^{2+} also yielded surprising results, here once again by comparison with reactions of the linear polymer we had expected a large proportion of the N-Oxide ligand groups to complex Co^{2+} ions. The results of the tests (Tables 11 & 13) contrast with this picture. Once again absorption from 0.2M solutions is greater than from these more concentrated (1.0M) and a possible explanation here is that reaction with concentrated solutions being faster, quickly saturates surface layers. The resulting dramatic increase in cross-linking due to complex formation may result in the polymer conformations being 'locked' into rigid arrangements having far less affinity for solvent and through which passage of further cations is restricted, possibly with diffusion control. The situation can be compared then with that in P4VP/Co^{2+} reactions or more realistically with reactions

of concentrated solutions of the linear P4VP & P4VPNO with concentrated solutions of T.M. cations, these result (Chapter IV, section 3) in failure of some ligands to coordinate because of fast precipitation of the product complex causing restricted access for cations.

III.2.3 The Dynamic Experiments

Though several previous studies involving static (batch) reactions of P4VP have been mentioned little previous work has been carried out using PVP's and their derivatives as chromatographic type column packings for studies of absorption of T.M. cations in a dynamic (flow) system of the kind which would be most suitable for application to large scale separation and recovery of the ions. Indeed it was the one previous such study which prompted the present investigation.

One of the initial aims of the dynamic experiments was to examine the suggestion of Haines that there were in fact two factors governing the reaction of cations with the polymeric ligands in the columns, one thermodynamic and the other kinetic. In that study it had been noted that the ratio of Cu^{2+} to Co^{2+} absorbed on the column decreased as the flow rate increased and it was suggested that the Co^{2+}/P4VP complex is initially formed fastest as a kinetic product when the flow rate of the solution prevents equilibrium but that Co^{2+} is displaced from the complex by Cu^{2+} ions at slower flow rates when there is time for equilibrium to occur with production of the thermodynamically preferred by Cu^{2+}/P4VP complex

i) $Co^{2+} + P4VP \longrightarrow Co(P4VP)_2^{2+}$

ii) $Co(P4VP)_2^{2+} + Cu^{2+} \longrightarrow Cu(P4VP)_2^{2+} + Co^{2+}$

Reaction of Copper/Cobalt Perchlorate Solutions

In the initial dynamic experiments a rather coarse (1.0 x 0.5m.m) particled linear P4VP was used (difficulties in preparation of fine particled linear P4VP either directly of by milling the coarser product have been mentioned in this Chapter and although not ideal because of the rather low specific surface area, the loosely packed column (12.5g, 1cm x 20cm) was acceptable for this study in which we were primarily concerned with relative rather than absolute absorption rates.

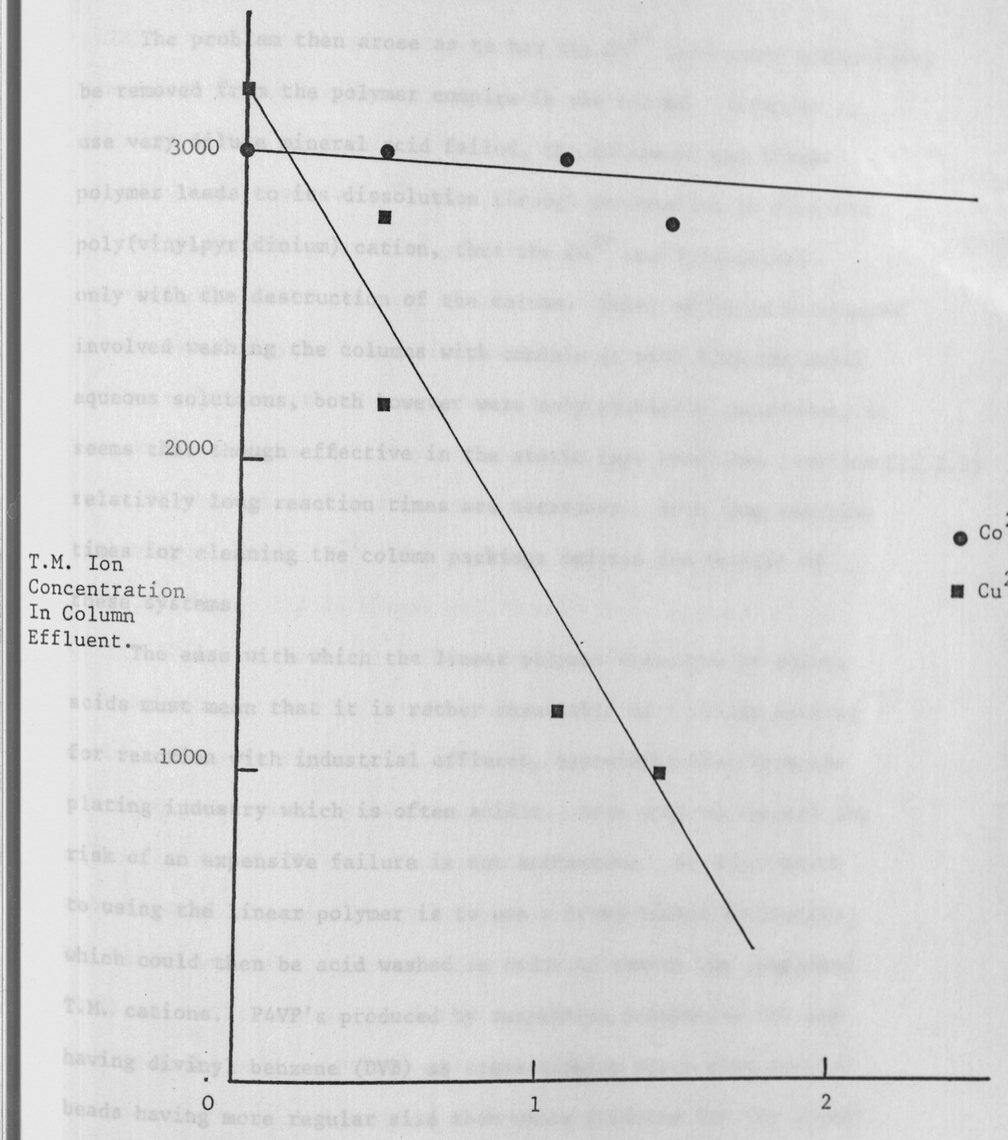
Using mixed solutions of Co^{2+} and Cu^{2+} perchlorates (total M^{2+} = 0.1M, Cu^{2+} = Co^{2+}) at various flow rates over the polymer gave the results summarized in figure 9. Clearly Cu^{2+} is preferentially absorbed at all flow rates whilst Co^{2+} is generally very poorly absorbed and shows no signs of improved complexation at higher flow rates. Absorption of Cu^{2+} improves considerably as the flow rate drops. The ratio of Cu^{2+} to Co^{2+} absorbed does indeed decrease with increasing flow rate, this however is entirely due to drop in Cu^{2+} complexation which we should expect at lower reaction times. It would appear then that there is very little 'kinetic effect' involving Co^{2+}.

Returning to the static experiments reported in the previous section Tables 3 & 4 show that even when there is no competing cation present Co^{2+} absorption by the polymer is slight even after 24 hours, thus only very small amounts of Co^{2+} absorption could be expected even with a powerful 'kinetic' factor.

The P4VP column at the end of the experiments had then effectively complexed only Cu^{2+}, Co^{2+} remaining in the effluent

Figure 9

Reaction of A P4VP Column
With A Solution of Mixed
Copper (II) And Cobalt (II)
Perchlorates.



solution, in agreement the proportion of Cu^{2+} in the effluent decreased with increasing reaction time (decreasing flow rate) and it seems possible that only the rather poor particle size prevented total separation of Cu^{2+} onto the polymer with Co^{2+} in solution.

The problem then arose as to how the Cu^{2+} ions could effectively be removed from the polymer complex in the column. Attempts to use very dilute mineral acid failed, the nature of the linear polymer leads to its dissolution through protonation to give the poly(vinylpyridinium) cation, thus the Cu^{2+} was solubilized only with the destruction of the column. Other attempts considered involved washing the columns with ammonia or with EDTA (Na salt) aqueous solutions, both however were only partially successful, it seems that though effective in the static type reactions (section III.2.2) relatively long reaction times are necessary. Such long reaction times for cleaning the column packings reduces the benefit of these systems.

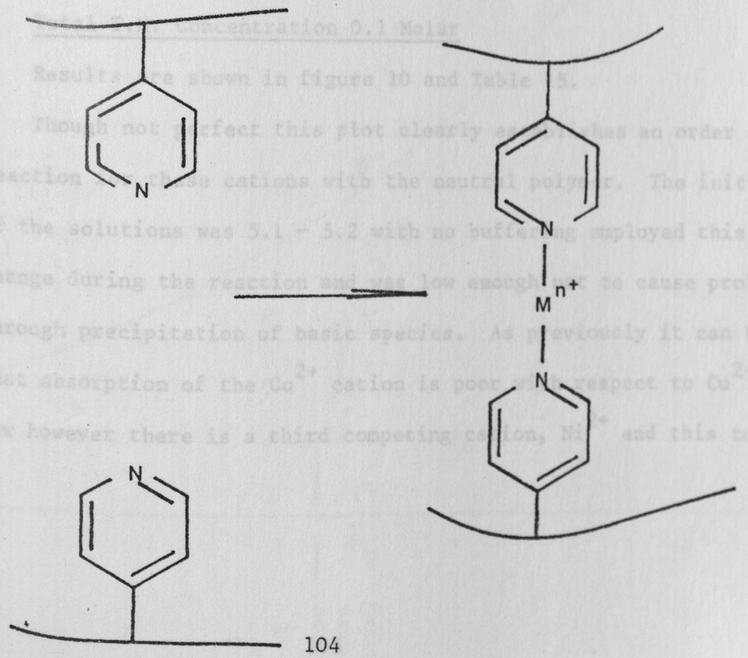
The ease with which the linear polymer dissolves in dilute acids must mean that it is rather unsuitable as a column packing for reaction with industrial effluent, especially that from the plating industry which is often acidic. Even with pH control the risk of an expensive failure is not attractive. An alternative to using the linear polymer is to use a cross-linked derivative which could then be acid washed in order to remove the complexed T.M. cations. P4VP's produced by suspension polymerisation and having divinyl benzene (DVB) as cross-linking agent gave smaller beads having more regular size than those produced for the linear

polymer, their preparation and reaction in the static complexation reactions have already been described (Chapters II and III). Those having lower degrees of DVB cross-linking (2 mole% and 8°mole%) were considered to have potentially more promise as chromatographic type column packings in line with a previously determined inverse relationship of absorption to cross-linking.[58] 8 mole% DVB cross-linking is frequently employed for commercially prepared exchange resins as providing the best compromise between resin stability and reactivity.[81]

Problems were immediately encountered when trying to use these finely beaded polymers in the narrow bore tube (1cm i.d) previously employed, limitations in the flow rates prevented study over the required range. Broader (1" i.d.) columns were prepared and these generally overcame the problems. Experimentation revealed that the columns could easily be regenerated by washing with mineral acid (10^{-1} - 2M) in excess followed by water, ammonia solution (0.5 - 2M) in excess and finally large amounts of pure water (30 column volumes). There was some difficulty when acid washing some columns because of the large volume increases which could occur upon protonation, this together with a softening of the beads could severly restrict the flow of liquid through the column. 2 mole% DVB cross-linked P4VP beads for instance gave columns which expanded by 45-50% based on initial column lengths. The effect was less pronounced for the 8% cross-linked polymer (25%) and still less so for 16% cross-linked polymers which in fact operated well as $P4VPH^{+}\ Cl^{-}$ anion exchange resin columns for some of the exchange studies described in this Chapter.

The swelling of the resins upon protonation can be ascribed to a combination of increased mass and solvation of the hydrophilic pyridinium units in the matrix together with some degree of repulsion between the adjacent positive charges though some degree of shielding by counterions is to be expected. Fewer problems were encountered with P4VPNO as column filling, here the swelling of the beads is much less on protonation (8%) and it seems likely that only mass and repulsion effects are contributing as both the N-Oxide and its protonated form are swollen by water as solvent.

Decrease of particle size during complex formation in the column could also cause changes in the rate of flow of solutions across the polymer in the course of an experiment in some cases. The reduction in bead size could be ascribed largely to further cross-linking of the polymer chains (and their contraction) by the cation during complex formation.



III.2.3.1. Dynamic Experiments with Cross-linked Polymer Packed Columns

Following our initial column experiment using the linear P4VP several other systems were considered. This involved various mixtures of cations which will be detailed. The columns used were of cross-linked polymer. Results of the experiments are shown in figures 10-22 whilst the full data tables are presented in an appendix. Each system will be briefly considered.

III.2.3.1.1. The Cobalt (II), Nickel (II), Copper (II) system

Our initial brief for examination and clarification of the $Co^{2+}/Ni^{2+}/Cu^{2+}$ (plating effluent) P4VP reaction system is reflected in this series of experiments. Previous work in the area has been mentioned and as well as examining the possibility of separating these ions using P4VP or related macromolecules it was intented to further clarify the suggestion by Haines that kinetic and thermodynamic factors were involved.

a) Column, 3 inch P4VP, 2 mole% DVB Cross-linked 50-70 micron beads

Reacting solution:- Equimolar in Cobalt, Nickel and Copper Chloride

Total T.M. Concentration 0.1 Molar

Results are shown in figure 10 and Table 15.

Though not perfect this plot clearly establishes an order of reaction for these cations with the neutral polymer. The initial pH of the solutions was 5.1 - 5.2 with no buffering employed this did not change during the reaction and was low enough not to cause problems through precipitation of basic species. As previously it can be seen that absorption of the Co^{2+} cation is poor with respect to Cu^{2+}, now however there is a third competing cation, Ni^{2+} and this too is

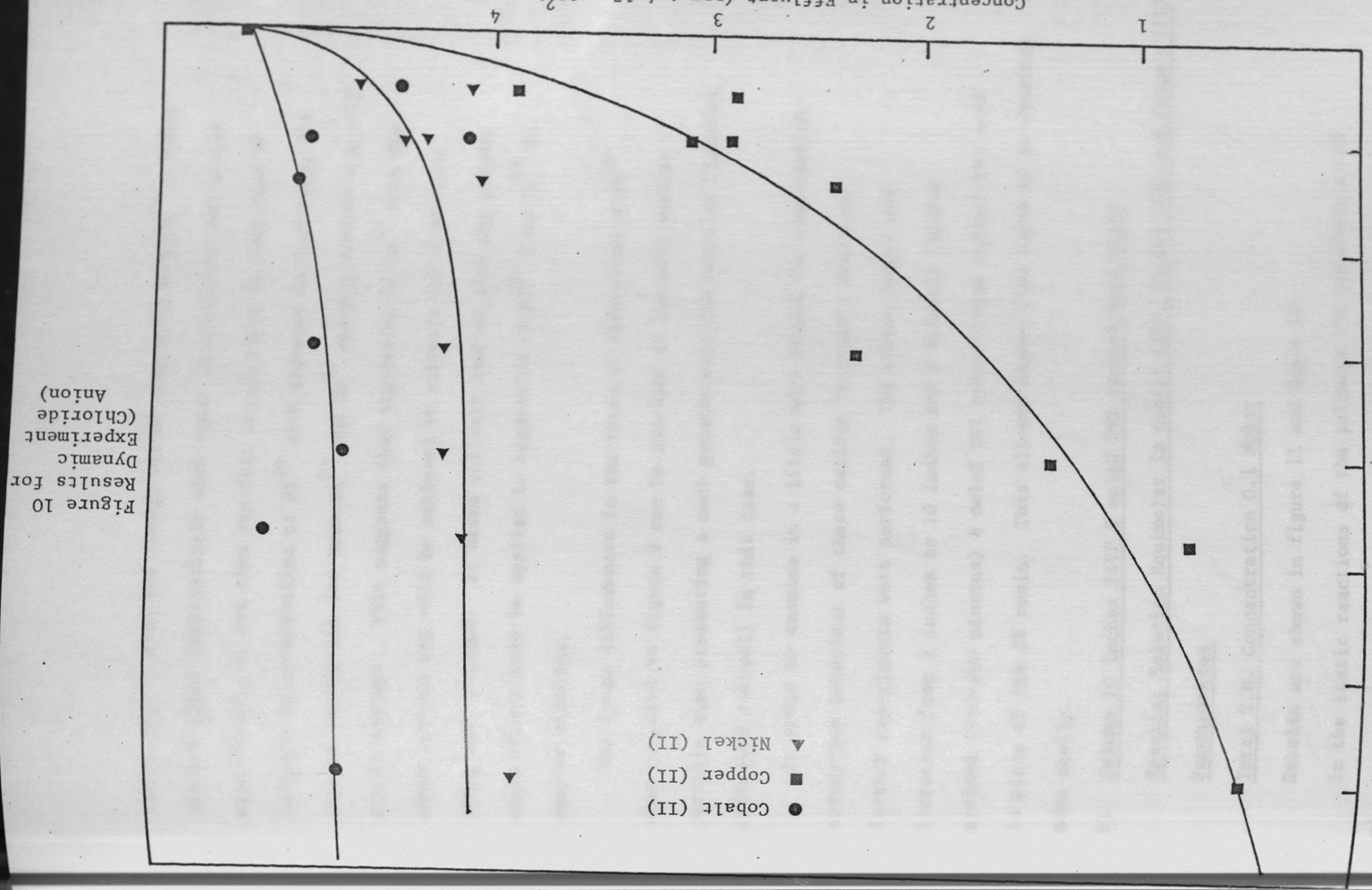


Figure 10
Results for
Dynamic
Experiment
(Chloride
Anion)

rather poorly absorbed though better complexed than Co^{2+}. These results agree qualitatively with those obtained from the static experiments, we can also see that though there is initially an increase in complexation of Ni^{2+} with decrease in flow rate, the rate of absorption for both Ni^{2+} and Co^{2+} quickly reaches a nearly static maximum. This suggests that separation of Cu^{2+} from the other cations may well be achieved at suitably low flow rates using such columns. It seems unlikely however that the polymer could effectively be applied to separation of Ni^{2+} from Co^{2+} in aqueous mixtures.

The large differences in the rates of absorption of Cu^{2+} when compared to figure 9 can be ascribed to the much smaller particle size presenting a much greater area for reaction (limiting diffusion control) in this case.

In order to examine in a little more detail the complexation/absorption behaviour of these cations in dynamic reactions further experiments were performed. The column length was increased from 3 inches to 10 inches and a slightly coarser grained (150-200 microns) 8 mole% DVB cross-linked polymer was used in place of the 2% resin. This allowed higher flow rates to be obtained more easily.

b) Column 10 inches P4VP 8 mole% DVB cross-linked beads

Reacting Solution Equimolar in Cobalt (II), Nickel (II) and Copper (II) Perchlorates

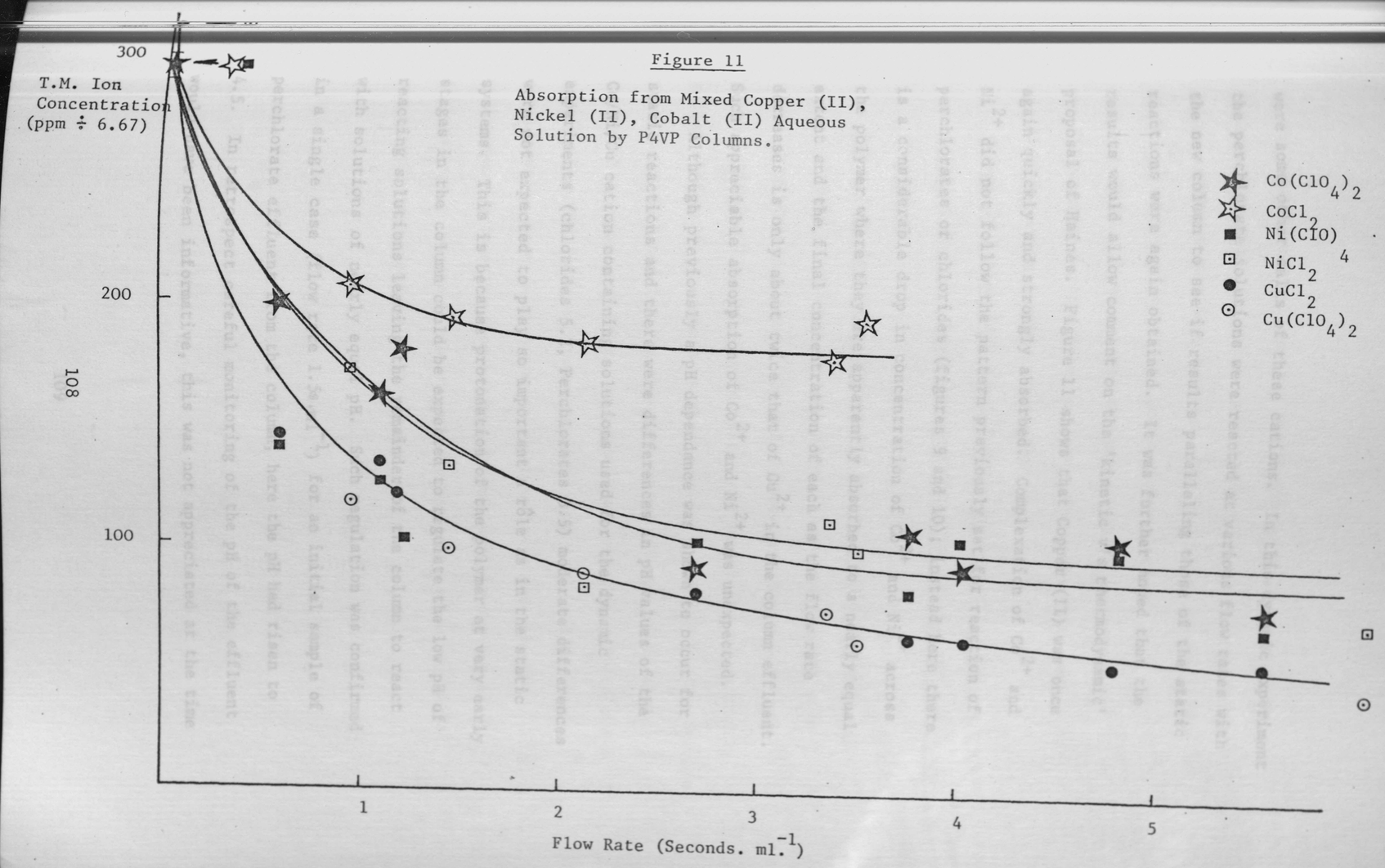
Total T.M. Concentration 0.1 Molar

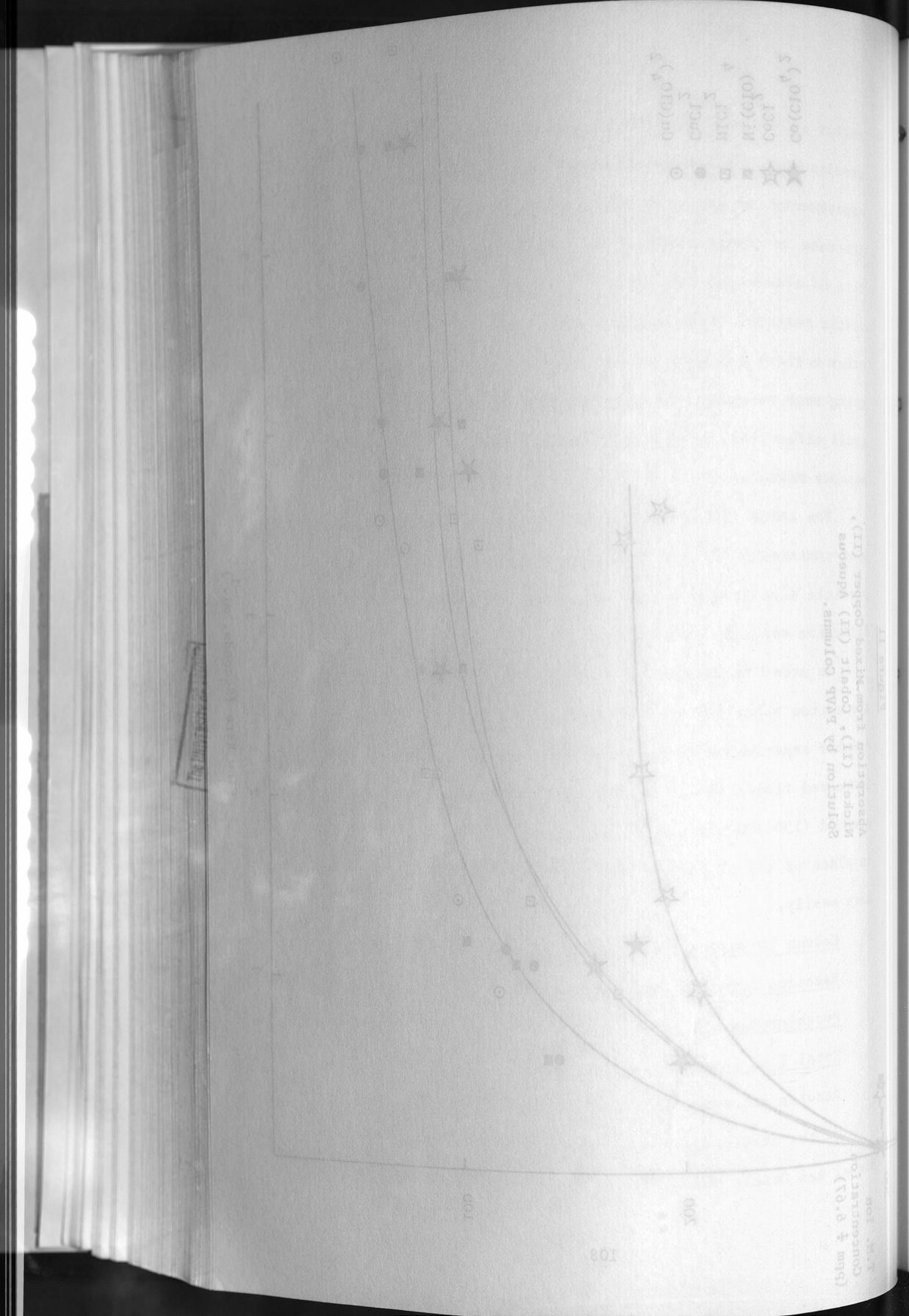
Results are shown in figure 11 and Table 16.

In the static reactions of the polymers the perchlorates of Nickel and Cobalt were shown to be considerably better absorbed than

Figure 11

Absorption from Mixed Copper (II), Nickel (II), Cobalt (II) Aqueous Solution by P4VP Columns.





were some other salts of these cations. In this dynamic experiment the perchlorate solutions were reacted at various flow rates with the new column to see if results paralleling those of the static reactions were again obtained. It was further hoped that the results would allow comment on the 'kinetic v's thermodynamic' proposal of Haines. Figure 11 shows that Copper (II) was once again quickly and strongly absorbed. Complexation of Co^{2+} and Ni^{2+} did not follow the pattern previously set for reaction of perchlorates or chlorides (figures 9 and 10); instead here there is a considerable drop in concentration of Co^{2+} and Ni^{2+} across the polymer where they are apparently absorbed to a nearly equal extent and the final concentration of each as the flow rate decreases is only about twice that of Cu^{2+} in the column effluent. Such appreciable absorption of Co^{2+} and Ni^{2+} was unexpected.

Although previously a pH dependance was shown to occur for static reactions and there were differences in pH values of the Co/Ni/Cu cation containing solutions used for the dynamic experiments (chlorides 5.2, Perchlorates 3.5) moderate differences were not expected to play so important a rôle as in the static systems. This is because protonation of the polymer at very early stages in the column could be expected to regulate the low pH of reacting solutions leaving the remainder of the column to react with solutions of nearly equal pH. Such regulation was confirmed in a single case (flow rate $1.5 s.ml^{-1}$) for an initial sample of perchlorate effluent from the column, here the pH had risen to 4.5. In retrospect careful monitoring of the pH of the effluent would have been informative, this was not appreciated at the time

of the experiments. Figures 9 and 10 did initially lead us to believe that there was quite appreciable anion or pH dependance in the column absorptions however. The similarity in absorption of Cu^{2+} from the chloride and perchlorate solutions indicated that a pH effect was the more probable explanation of the differences for the other cations. The conclusions were modified following further experimentation.

c) Column 10 inches P4VP 8 mole% DVB cross-linked (as for b above)

Reacting Solution Equimolar in Cobalt (II), Nickel (II) and Copper(II) Chlorides

Total T.M. ion Concentration 0.1 Molar. (Table 16 Figure 11)

A similar experiment to that above (b) was carried out with mixed chlorides in place of the perchlorates and the results are shown in figure 11. Once again these were surprising and initially rather difficult to explain as they clearly differ with the results previously obtained for the chloride system (figure 10) in that appreciable amounts of Nickel and Cobalt are absorbed, the column packing however differed from that previously used. After some consideration then an explanation which satisfys not only the differences in results from various dynamic experiments but also differences in degree of absorption for the same cation in static and dynamic reactions could be given:-

It seems that although Copper (II) ions are quite strongly absorbed at the surface and to a lesser extent throughout the body of the polymer, Cobalt (II) and Nickel (II) are absorbed initially only at a few surface sites with little penetration by these cations into the body of the polymer particles and this difference is reflected in the static reaction results (Tables 3 and 4). From the static reactions it is also clear that the penetration by the initially poorly absorbed species can be improved by a degree of protonation of the polymer network. In the dynamic system however the T.M. containing solution is effectively constantly exposed to a fresh polymer surface as it flows down the column and so at moderate pH values we can expect considerably more absorption of Co^{2+} and Ni^{2+} as the concentration of competing Cu^{2+} ions is reduced at an early stage in the column. This would explain the different absorption characteristics of the short and long columns with the mixed T.M. chloride solution. With the short column (3 inches) there is relatively little surface area and this is quickly saturated with cations, the solution meeting little unreacted polymer on its passage through the column. The preference for Cu^{2+} which cation competes effectively for the surface sites and which can also penetrate more effectively is then 'amplified' by such columns. When the column length was increased (10 inches, (3) above) the other factors mentioned mean that the polymer can absorb Co^{2+} and Ni^{2+} cations as well, the greater the surface area the greater the absorption of these latter ions, it must be remembered however that the total number of sites suitable for them is

considerably less than for Cu^{2+} and they are soon saturated. From the static reactions we saw that for fine (50-70 microns) 2 mole% DVB cross-linked P4VP beads only about 6×10^{-3}g of Ni^{2+} and Co^{2+} are absorbed by each gram of polymer and in a column system at the flow rates considered it is unlikely that this limit will be realised, the column operating as it does in a dynamic rather than an equilibrium system.

Absorption of Ni^{2+} only at or near the surface less strongly than Cu^{2+} explained basically then why that ion was complexed and removed to a similar extent (figure 11) from the chloride and perchlorate solutions and Cu^{2+} similarly forms the kinetic product, reacting quickly at the surface with some penetration and so once again absorption is similar from both chloride and perchlorate mixtures. The plots (figure 11) show these similarities clearly. Cobalt however is a special case, here there is a very distinct difference in absorption of the two salts, the chloride being absorbed to a much lesser degree than the perchlorate and this is rather difficult to explain. The static experiments had shown that Co^{2+} was poorly absorbed generally, with the large excess of polymer in those reactions it is difficult to ascribe the slight preference for the perchlorate to a pH variation. It was noted however that of the reaction products from two phase reactions of the polymer with Cobalt (II) solutions only the P4VP/$CoCl_2$ product was blue when fully dried, the related complexes remained red. This is indicative of weak binding of two ligands (water) and suggests that the chloride complex may prefer tetrahedral arrangement whilst complexes of other salts prefer an octahedral arrangement and this may be the basis of poor $CoCl_2$ absorption in the dynamic experiments; the tetrahedral structure being less compatible with the polymeric

ligand arrangement than is the octahedral complex. It seems likely that this is so rather than some inability of the tetrehedral Cobalt ion to actually incorporate ligand units from the polymer because preparation of $Co(P4VP)_2Cl_2$ by reaction of $CoCl_2$ with linear P4VP in alcohol solution or by polymerising $Co(4VP)Cl_2$ presents no problem, these products too are blue indicating tetrahedral structures.

The very poor absorption of Co (II)Cl_2 does perhaps indicate another possible application of P4VP in separation of $CoCl_2$ from other T.M. cations or salts. It might be possible to convert solutions to chloride by anion exchange followed by reaction with long P4VP columns at slow flow rates, Cobalt chloride would quickly pass through the column whilst other salts would be absorbed to an extent depending on surface area separation of ions as poorly absorbed as Ni^{2+} would require a large amount of polymer to effect such separation.

Returning to the initial column reaction of Co (II)/Cu (II) perchlorates with the larger particled linear P4VP (figure 9) the apparent failure of the column to absorb Cobalt (II) ions here is probably due to the rather low surface area, the few sites available quickly being occupied by Cu^{2+} and the swift development of blue (Cu^{2+}) colouration throughout the length of the column and the high concentrations in the effluent show even that cation is not as well absorbed as by the finer particled polymers. The situation can be compared to that for the short fine beaded polymer column (a) above).

III.2.3.1.2.Dynamic Experiments Involving other Cations

Following the success in examination of the Cobalt/Nickel/Copper ions system dynamic experiments were also carried out for

other systems of interest, in most cases comparison with Copper (II) reaction was a desired feature both to discover other strongly absorbed species which might cause problems in selective absorption of Cu^{2+} and discover other cations which can be selectively absorbed:

Whilst previously the method of study has involved monitoring the concentration of the cations in the effluent with variation of the flow rate, the method has been modified generally with a single flow rate and examination of cation concentration with variation in volume of solution passed through the column.

Reactions of mixtures containing Vanadyl, Copper (II) and Zinc (II) With P4VP

The static reactions had shown that Vanadyl ion was as strongly absorbed as Copper (II) ions under the correct conditions and Zinc ion was known to be an extremely poorly complexed species. The results of this dynamic experiment involving reaction of a mixed sulphates solution which was approximately equimolar in the cations with a total concentration of 0.1M are given in Table 17 and figure 12. Clearly Zinc cations are hardly absorbed at all and serve as a reference issuing from the column at the earliest possible stage as they do. The strongly absorbed species VO^{2+} and Cu^{2+} appear in the effluent much later with VO^{2+} slightly preceeding Cu^{2+}. This reversal is probably the result of the increase of pH over the earlier competetive static reaction of these ions, here buffering to pH 3.5 was employed.

Clearly then separation of Cu^{2+} and VO^{2+} from the remaining first row transition metal ions is possible using P4VP columns or

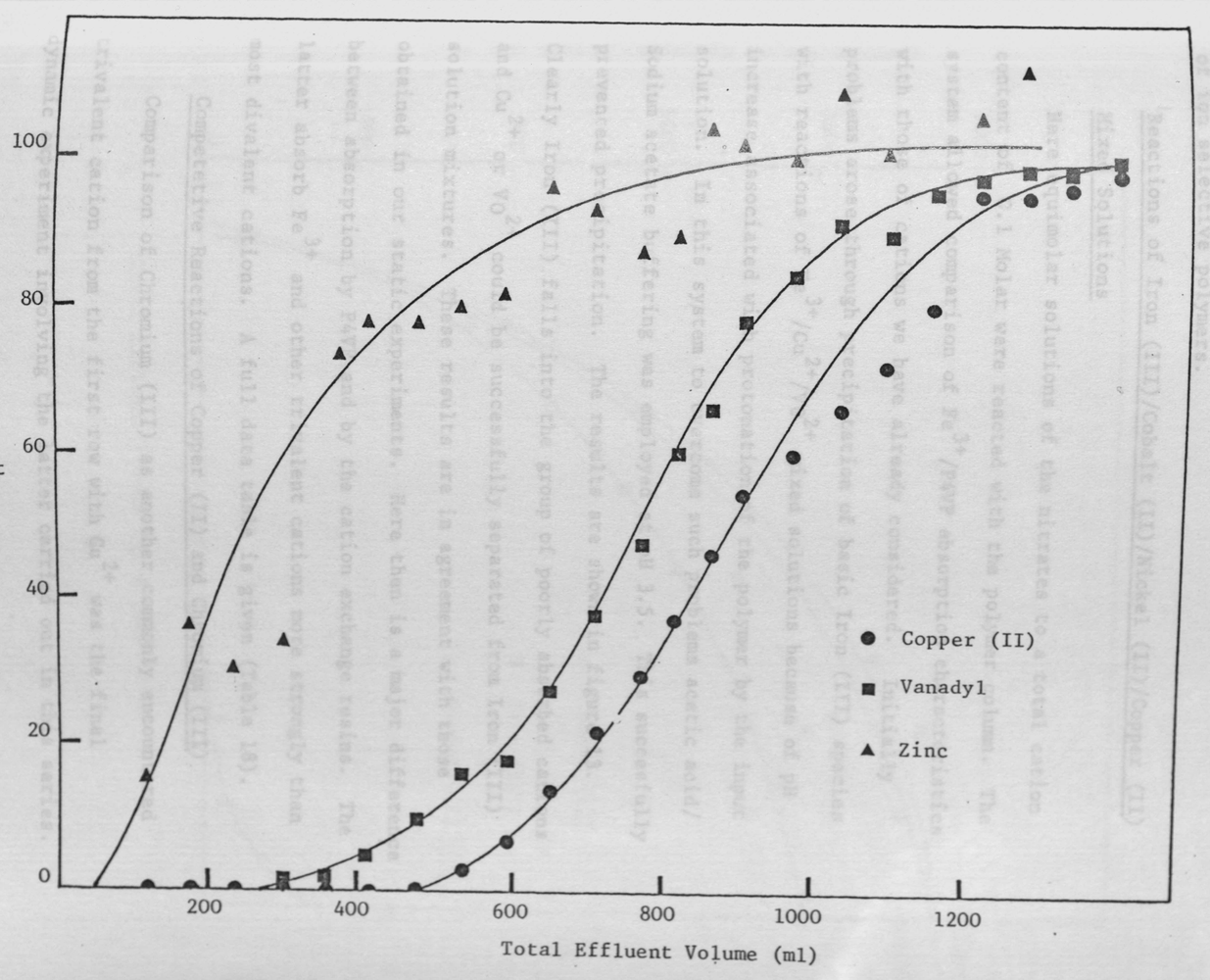


Figure 12

Dynamic Reaction of Mixed Sulphate Solutions with a Poly(4-Vinylpyridine) Column at pH 3.5

batch systems, separation of Cu^{2+} and VO^{2+} will obviously be far more difficult, once the mixture is absorbed on the column a selective eluent is required, this defeats the object of application of ion selective polymers.

Reactions of Iron (III)/Cobalt (II)/Nickel (II)/Copper (II) Mixed Solutions

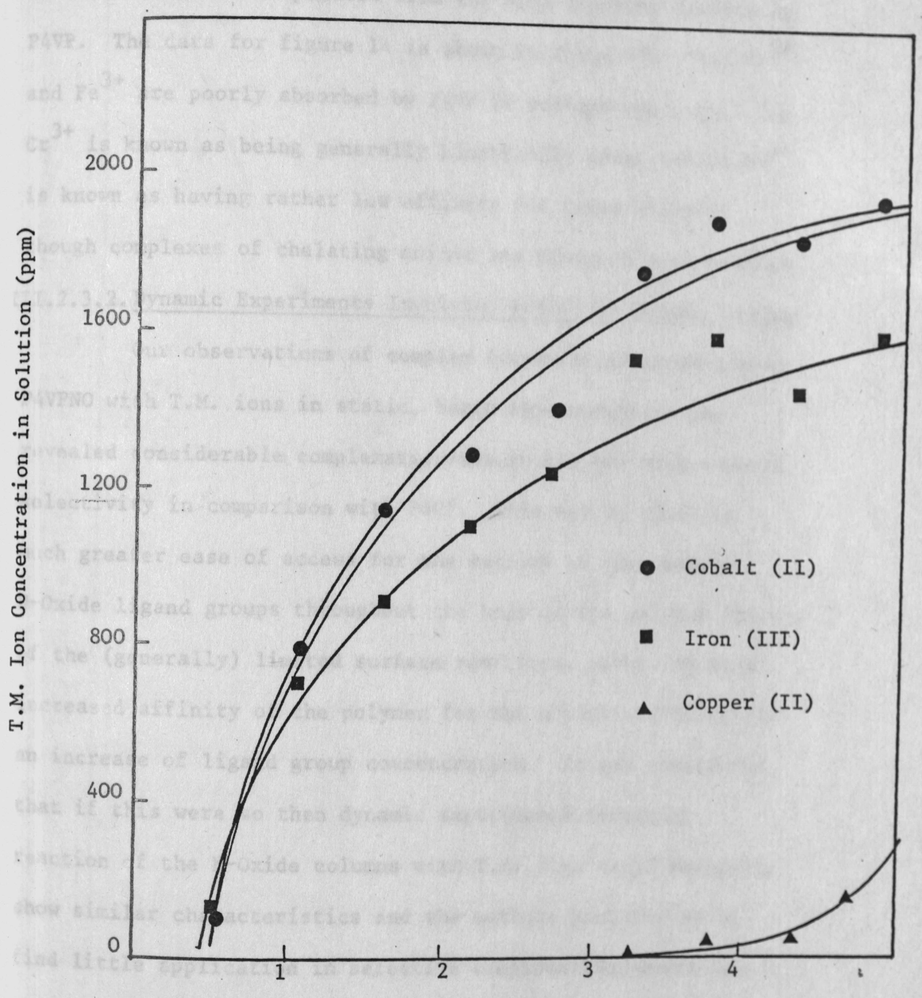
Here equimolar solutions of the nitrates to a total cation content of 0.1 Molar were reacted with the polymer column. The system allowed comparison of Fe^{3+}/P4VP absorption characteristics with those of cations we have already considered. Initially problems arose through precipitation of basic Iron (III) species with reactions of $Fe^{3+}/Cu^{2+}/VO^{2+}$ mixed solutions because of pH increase associated with protonation of the polymer by the input solution. In this system to overcome such problems acetic acid/ Sodium acetate buffering was employed at pH 3.5. This succesfully prevented precipitation. The results are shown in figure 13. Clearly Iron (III) falls into the group of poorly absorbed cations and Cu^{2+} or VO^{2+} could be successfully separated from Iron (III) solution mixtures. These results are in agreement with those obtained in our static experiments. Here then is a major difference between absorption by P4VP and by the cation exchange resins. The latter absorb Fe^{3+} and other trivalent cations more strongly than most divalent cations. A full data table is given (Table 18).

Competetive Reactions of Copper (II) and Chromium (III)

Comparison of Chromium (III) as another commonly encountered trivalent cation from the first row with Cu^{2+} was the final dynamic experiment involving the latter carried out in this series.

Figure 13

Reaction of Mixed Transition Metal Nitrate Solutions with a Poly(4-Vinylpyridine) Column.



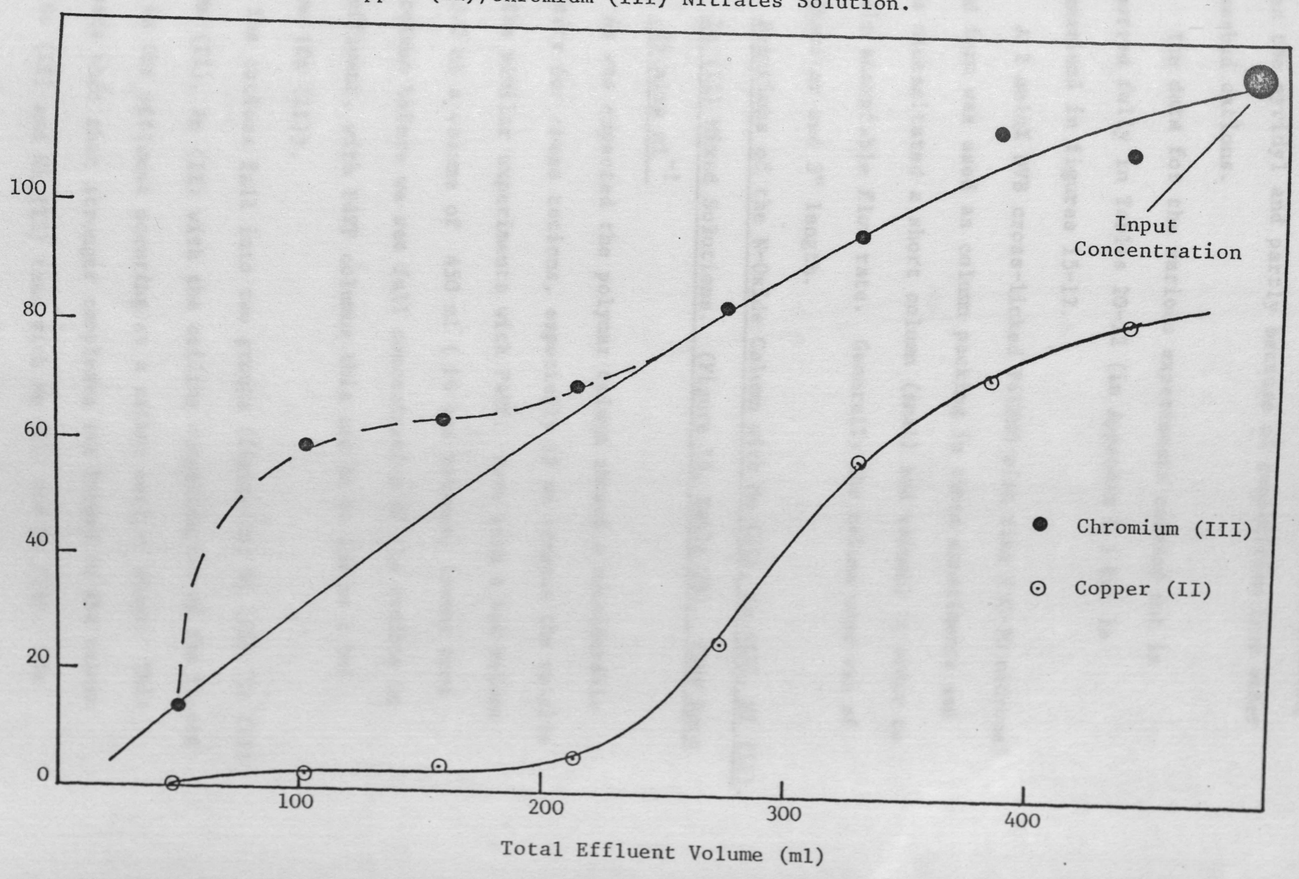
We had not assesed Cr^{3+} in our static absorption system and relied on the results of this experiment. The plot (figure 14) shows that Cr^{3+} does not compete effectively with Cu^{2+} for the ligand units and again falls into the 'poorly' absorbed class; it too then can be separated from the well absorbed cations by P4VP. The data for figure 14 is shown in Table 19. That Cr^{3+} and Fe^{3+} are poorly absorbed by P4VP is perhaps not surprising Cr^{3+} is known as being generally kinetically inert whilst Fe^{3+} is known as having rather low affinity for amine ligands though complexes of chelating amines are produced more readily.

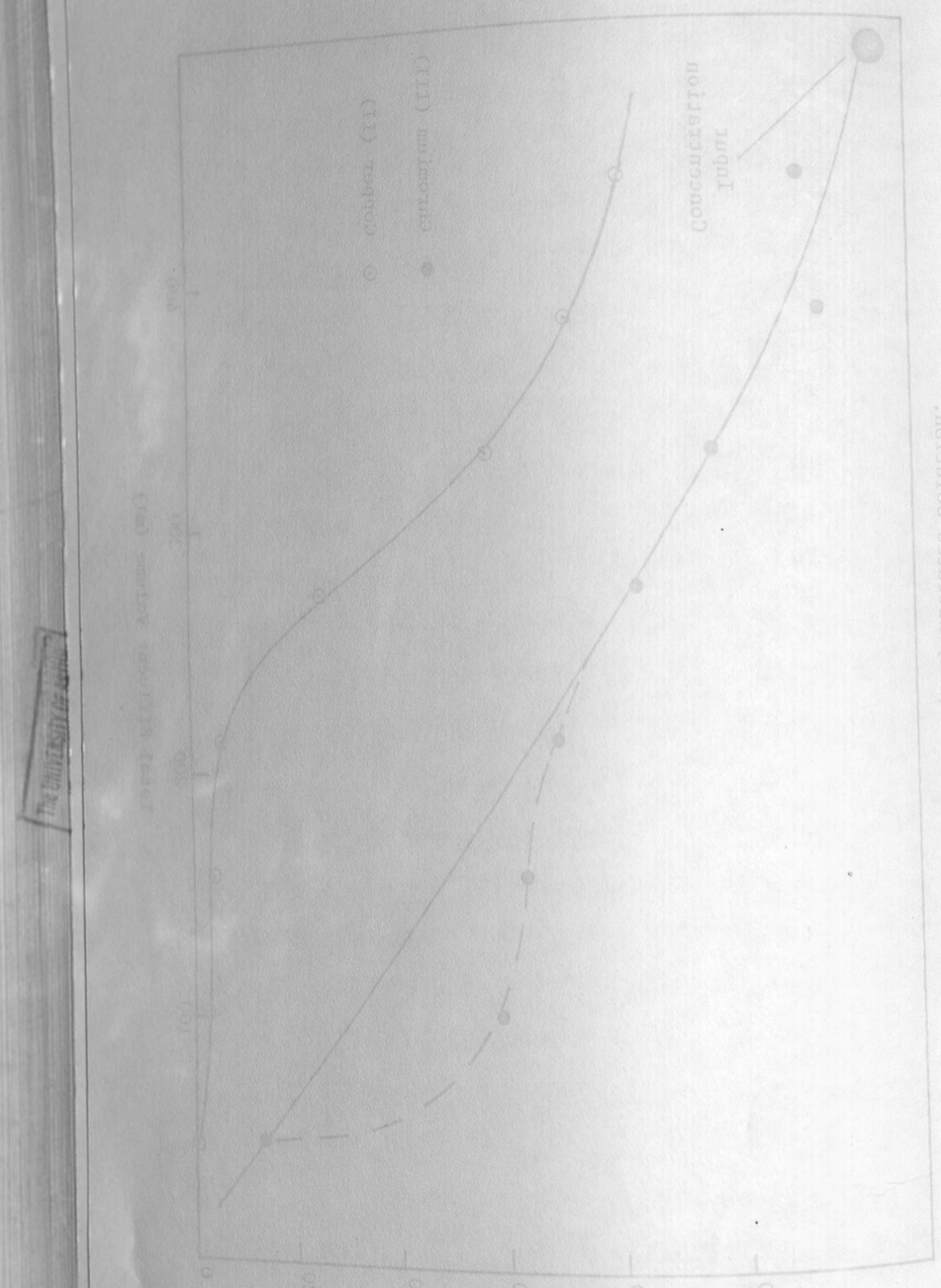
III.2.3.2. Dynamic Experiments Involving P4VPNO as Column Packing

Our observations of complex formation of cross-linked P4VPNO with T.M. ions in static, batch type reactions had revealed considerable complexation/absorption but much reduced selectivity in comparison with P4VP. This was ascribed to much greater ease of access for the cations to the pendant N-Oxide ligand groups throughout the body of the polymer instead of the (generally) limited surface reactions, resulting from increased affinity of the polymer for the solvent, effectively an increase of ligand group concentration. It was considered that if this were so then dynamic experiments involving reaction of the N-Oxide columns with T.M. ions would basically show similar characteristics and the methods probably would find little application in selective complexation/absorption reactions of cation separation. Obviously much improved complexation was expected of those cations only slightly absorbed

Figure 14

Reaction of a Poly(4-Vinylpyridine) Column with Mixed Copper (II)/Chromium (III) Nitrates Solution.





by P4VP with reduced absorption of Copper (II) ions, partly because N-Oxide groups are less powerfully electron donating than the pyridyl and partly because of competition from other absorbed cations.

The data for the various experiments carried out is reported fully in Tables 20-22 (in Appendix I) but is summarised in figures 15-17.

A 2 mole% DVB cross-linked P4VPNO with fine (50-70 microns) bead form was used as column packing in these experiments and this necessitated a short column (small bed volume) in order to obtain acceptable flow rate. Generally the column used was of 1" diameter and 3" length.

Reactions of the N-Oxide Column with Mn (II), Co (II), Ni (II), Zn (II) Mixed Solutions. (Figure 15, Table 20). Flow Rate .25 mins ml^{-1}

As was expected the polymer column showed a considerable affinity for these cations, especially if we compare the results for the similar experiments with P4VP. Here with a bed volume of 43.2 ml a volume of 450 ml (10 bed volumes) issues from the column before we see full concentration of the cations in the effluent, with P4VP columns this can be as low as 1 bed volume (Zn (II)).

The cations fall into two groups (figure 15) Ni (II), Co (II) and Mn (II), Zn (II) with the ceiling concentration of the latter ions in the effluent occuring at a rather earlier stage. This suggests then that stronger complexes are formed in the column with Co (II) and Ni (II) than with Mn (II) and Zn (II). The

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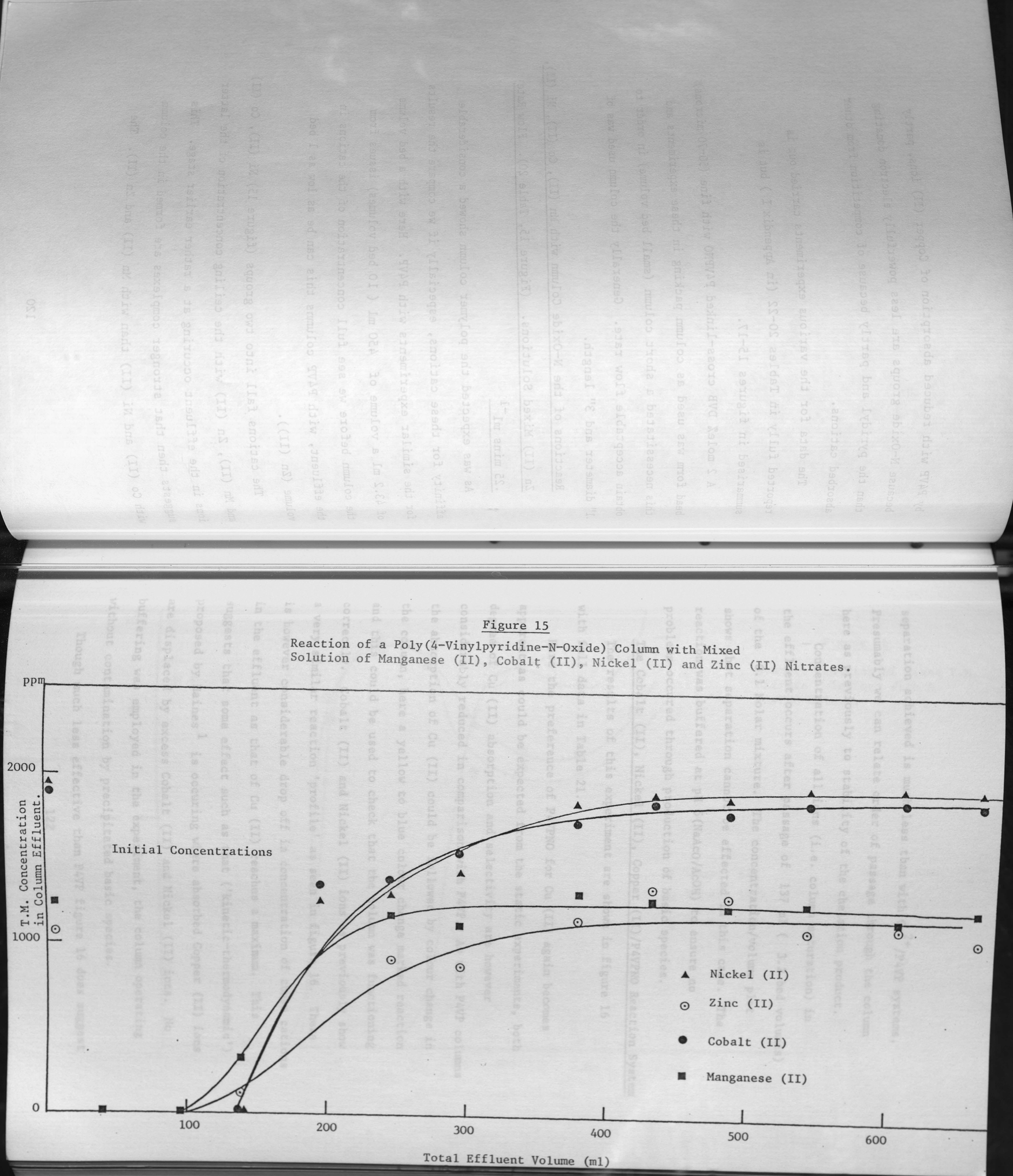
Figure 15

Reaction of a Poly(4-Vinylpyridine-N-Oxide) Column with Mixed Solution of Manganese (II), Cobalt (II), Nickel (II) and Zinc (II) Nitrates.



separation achieved is much less than with Cu^{2+}/P4VP systems. Presumably we can relate order of passage through the column here as previously to stability of the chelation product.

Concentration of all ions (i.e. column saturation) in the effluent occurs after passage of 137 ml (3.2 bed volumes) of the 0.1 Molar mixture. The concentration/volume plot shows that separation cannot be effected in this case. The reaction was buffered at pH 5(NaAcO/AcOH) to ensure no problems occured through production of basic species.

The Cobalt (II), Nickel (II), Copper (II)/P4VPNO Reaction System

The results of this experiment are shown in figure 16 with full data in Table 21.

Here the preference of P4VPNO for Cu (II) again becomes apparent as could be expected from the static experiments, both degree of Cu (II) absorption and selectivity are however considerably reduced in comparison with P4VP. As with P4VP columns the absorption of Cu (II) could be followed by colour change in the column, here a yellow to blue colour change marked reaction and this could be used to check that the column was functioning correctly. Cobalt (II) and Nickel (II) ions as previously show a very similar reaction 'profile' as seen in figure 16. There is however considerable drop off in concentration of these cations in the effluent as that of Cu (II) reaches a maximum. This suggests that some effect such as that ('kinetic-thermodynamic') proposed by Haines [1] is occuring where absorbed Copper (II) ions are displaced by excess Cobalt (II) and Nickel (II) ions. No buffering was employed in the experiment, the column operating without contamination by precipitated basic species.

Though much less effective than P4VP figure 16 does suggest

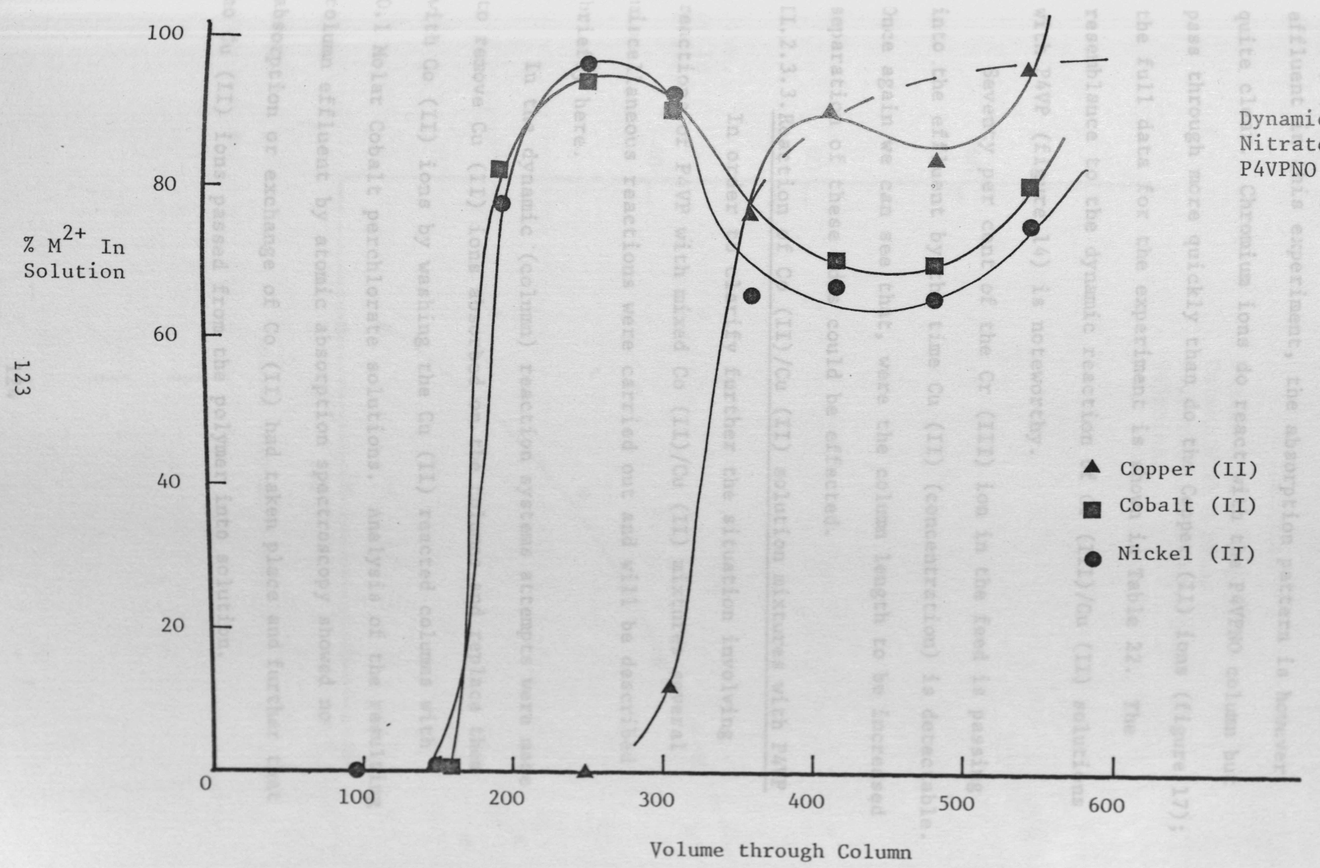


Figure 16

Dynamic Reaction of Mixed T.M. Nitrate Solutions With A P4VPNO Column.

that if much longer columns were employed Cu (II) might be effectively separated from other cations.

The Chromium (III), Copper (II)/P4VPNO Reaction System

Considerably fewer samples were analysed from the column effluent in this experiment, the absorption pattern is however quite clear. Chromium ions do react with the P4VPNO column but pass through more quickly than do the Copper (II) ions (figure 17); the full data for the experiment is shown in Table 22. The resemblance to the dynamic reaction of Cr (III)/Cu (II) solutions with P4VP (figure 14) is noteworthy.

Seventy per cent of the Cr (III) ion in the feed is passing into the effluent by the time Cu (II) (concentration) is detectable. Once again we can see that, were the column length to be increased separation of these ions could be effected.

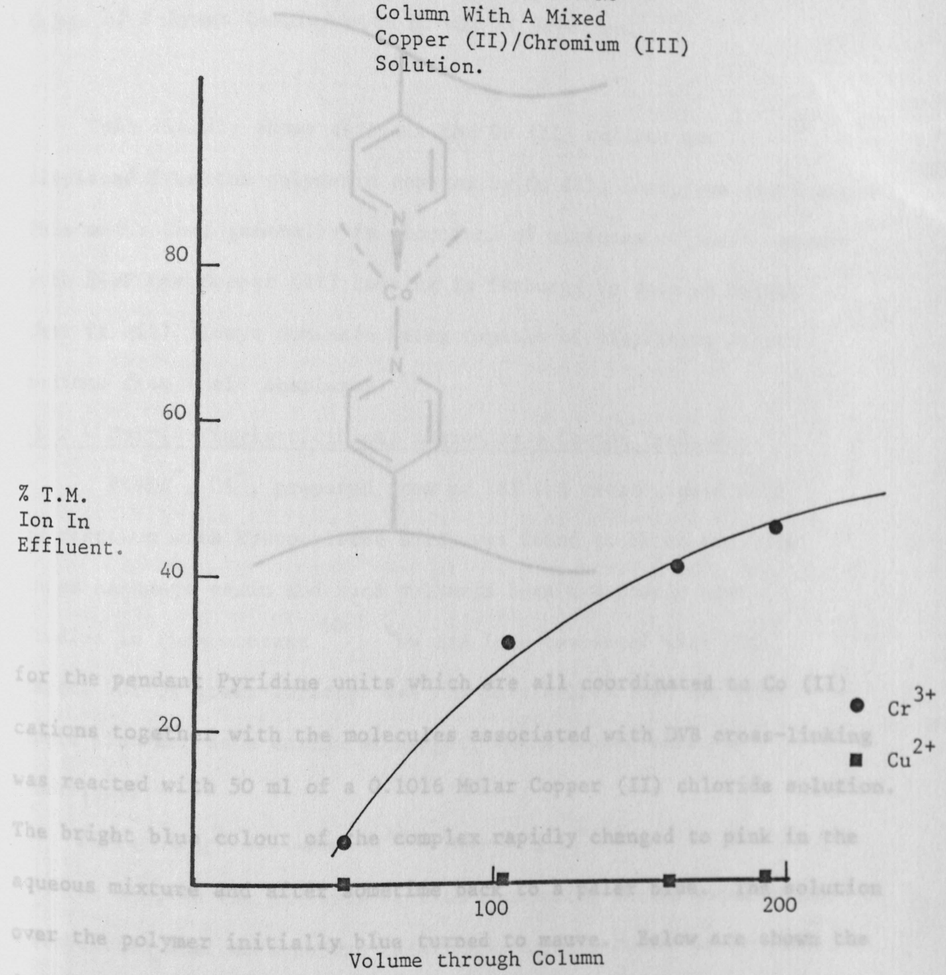
III.2.3.3. Reaction of Co (II)/Cu (II) solution mixtures with P4VP

In order to clarify further the situation involving reactions of P4VP with mixed Co (II)/Cu (II) mixtures several miscellaneous reactions were carried out and will be described briefly here.

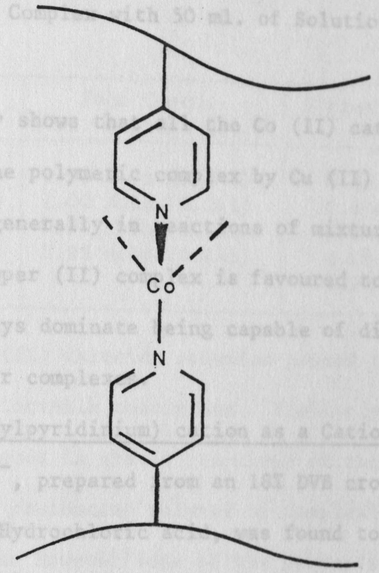
In the dynamic (column) reaction systems attempts were made to remove Cu (II) ions absorbed on the columns and replace them with Co (II) ions by washing the Cu (II) reacted columns with 0.1 Molar Cobalt perchlorate solutions. Analysis of the resulting column effluent by atomic absorption spectroscopy showed no absorption or exchange of Co (II) had taken place and further that no Cu (II) ions passed from the polymer into solution.

Figure 17

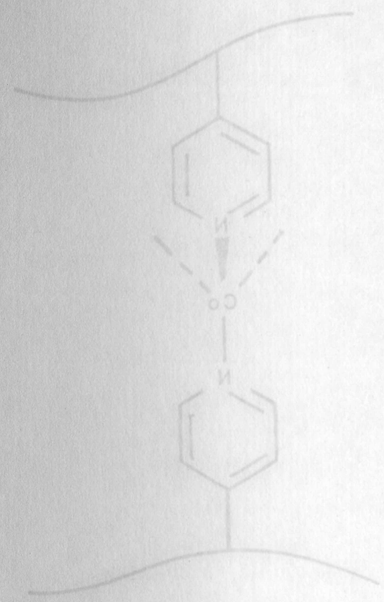
Reaction of A P4VPNO Column With A Mixed Copper (II)/Chromium (III) Solution.



The greater stability of the Cu (II) P4VP complex over that of the Cobalt complex was shown more dramatically in a static reaction. A 500 mg sample of the polymerised $Co(4VP)_2Cl_2$ which was cross-linked with DVB (fully described in Chapter IV). having a structure



for the pendant Pyridine units which are all coordinated to Co (II) cations together with the molecules associated with DVB cross-linking was reacted with 50 ml of a 0.1016 Molar Copper (II) chloride solution. The bright blue colour of the complex rapidly changed to pink in the aqueous mixture and after sometime back to a paler blue. The solution over the polymer initially blue turned to mauve. Below are shown the detailed results of various analyses.



	Cobalt (II) In Polymer (mole)	Cobalt (II) In Solution (mole)	Copper (II) In Polymer (mole)	Copper (II) In Solution (mole)
Initial	0.001190	0	0	0.00508
Final	0	0.001275	0.001145	0.003935

500 mg. of Polymer Complex with 50 ml. of Solution.

This clearly shows that all the Co (II) cations are displaced from the polymeric complex by Cu (II) ions from solution. This means that generally in reactions of mixtures of these cations with P4VP the Copper (II) complex is favoured to such an extent that it will always dominate being capable of displacing other cations from their complexes.

III.2.4 Poly(4-Vinylpyridinium) cation as a Cation Exchanger

$P4VPH^+$, Cl^-, prepared from an 18% DVB cross-linked P4VP by reaction with Hydrochloric acid, was found to be an excellent anion exchange resin and such polymers have previously been studied in this context [60]. We are less concerned with this aspect but of great interest was the possibility that the polymer could also act as a cation exchanger, which seemed entirely plausible.

$$P4VP\,H^+ + M^{2+} \rightleftharpoons M^{2+} - P4VP + H^+$$

We had, in the previous section concerning static experiments established that no apparent reaction occured between the Polymeric hydrochloride and 0.1 Molar T.M. ion solutions. It seemed that the situation may differ somewhat for reaction of more concentrated

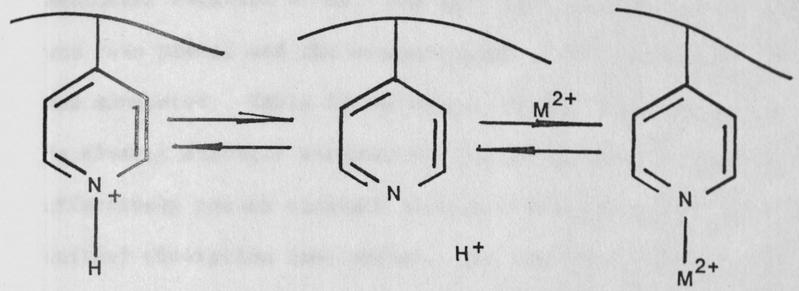
solutions of the cations with columns of the protonated polymer in dynamic, flow reactions. Using approximately 1.0 Molar solutions of Nickel chloride and of Cobalt chloride we found that whatever length of column was employed absorption was only slight or non-existant. With Copper (II) chloride however the situation differed, some considerable removal of Cu (II) from the solution occured.

Salt Solution	Feed Concn. (Vol. through Col.)	Effluent Concn.	Flow Rate
Cobalt Chloride	0.93 Molar(0.241)	0.93 Molar	1.2 secs ml^{-1}
Nickel Chloride	1.00 Molar(0.241)	0.996 Molar	1.725 secs ml^{-1}
Copper Chloride	0.99 Molar(0.241)	0.942 Molar	1.35 secs ml^{-1}
Ferric Chloride	0.98 Molar(0.241)	0.98 Molar	1.50 secs ml^{-1}
Column Volume		129 ml	

A Manganese (II) chloride solution passed through the column also showed no detectable absorption. Similarly absorption in general could not be assessed in static reactions of the concentrated solution with the protonated polymer by complexiometric titration. In this latter case however some of the products did have some slight colouration even after washing, suggesting some reaction. In some cases (VO^{2+}, Mn^{2+}, Cu^{2+}) quite clear e.s.r. spectra could be obtained for the solid products confirming that trace amounts of the P4VP - M^{2+} species are formed in the equilibrium reaction above. These spectra will be discussed in Chapter IV.

Russian authors Kopylova et al had suggested that reaction of the protonated form of the polymer with T.M. cations in exchange reactions should not occur because of the relative bond strengths of N^{+}-H and N-M^{2+}. [57-60] It was noted however that the pyridinium

polymers are appreciably acidic in character,



clearly if metal ions are present in condiserable excess over protons then we should expect at least trace formation of the metal complexes with the polymer, the degree of M^{2+} incorporation into the polymer generally increasing with M^{2+} excess concentration. Clearly those cations forming strongest complexes with the neutral polymer can be expected to be absorbed if any are. Thus we see Cu^{2+} absorbed in the above table whilst Ni^{2+} and Co^{2+} and Fe^{3+} react hardly at all. VO^{2+} could also be expected to react as well as Cu^{2+}.

Separation of Copper (II) and Mercury (II) on $P4VPH^{+},NO_3^{-}$ Columns

It was stated earlier that we are not primarily concerned with P4VP derivatives in their reactions as anion exchangers,

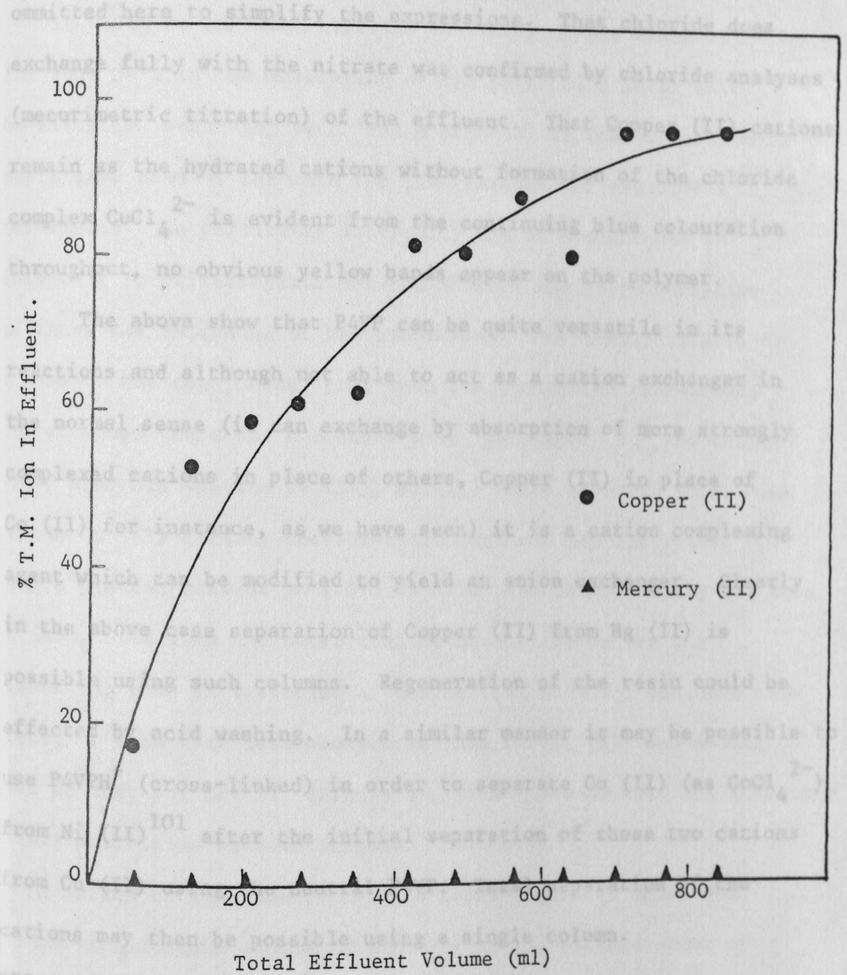
there is however the single case examined of reaction of a $P4VPH^+$, NO_3^- column with mixed neutral solutions of Cu^{2+} and Hg^{2+} chlorides. Here the column was prepared by reaction of P4VP (18% DVB cross-linked) with nitric acid, the poly(4-vinylpyridinium nitrate) was washed and wet loaded into the column, mixed equimolar solution of Cu^{2+} and Hg^{2+} chlorides (total M^{2+} 0.1 Molar) was then passed and the concentration of the cations in the effluent was monitored. Table 23 and figure 18 show the results. Mercury (II) is clearly strongly absorbed by the column whilst Copper (II) effectively passes straight through with presumably some slight initial absorption (see above). The reactions occurring are generally applicable to anion exchangers and it is not suggested that $P4VPH^+$, NO_3^- is significantly different in these. In this particular case exchange of anion occurs giving the chloride form of the polymer $P4VPH^+$, Cl^- though at what stage remains uncertain. It is known that in solutions high in nitrate anion direct formation of the nitrate complex can occur.

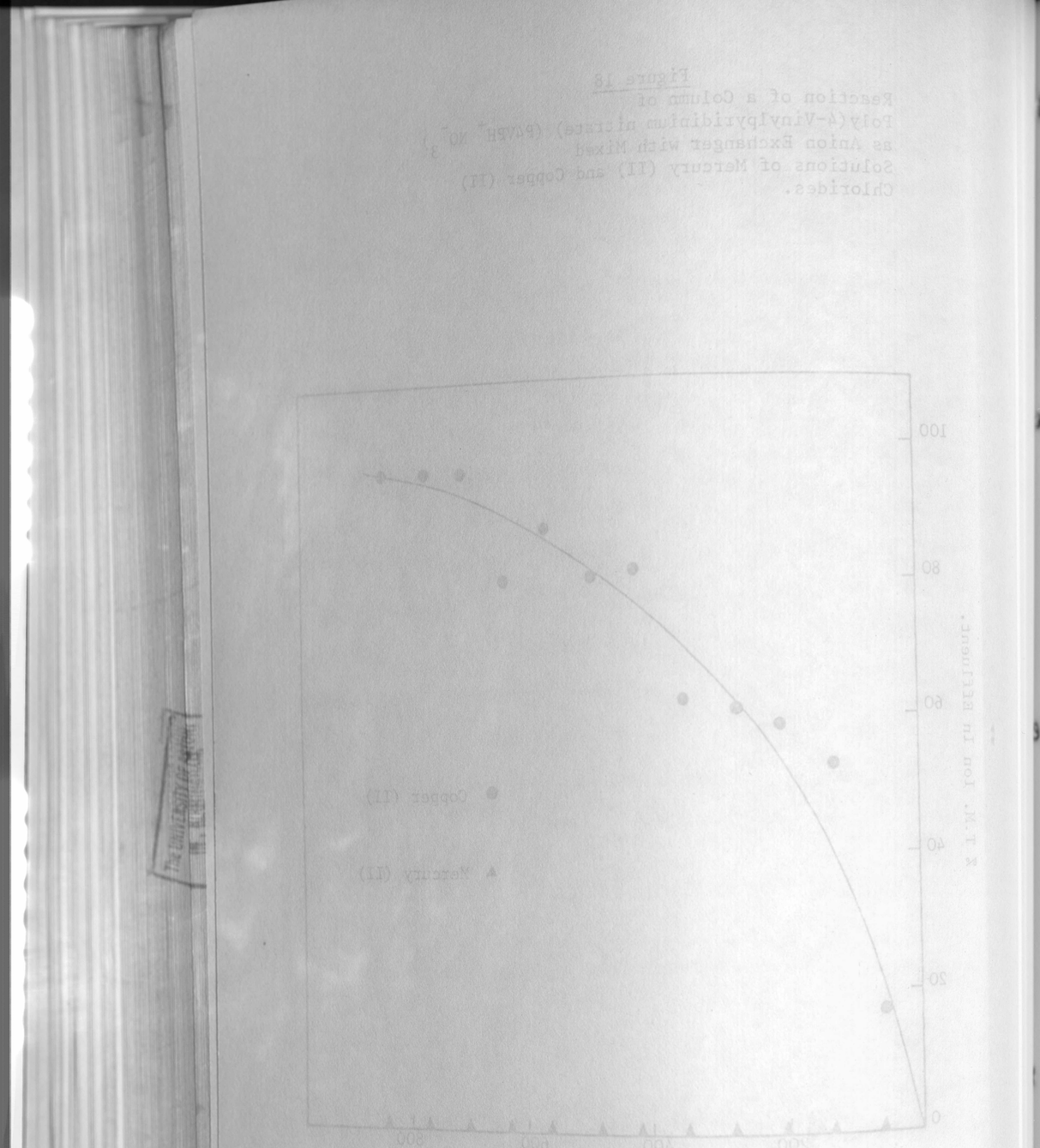
$$Hg^{2+} + 4\,NO_3^- \longrightarrow Hg(NO_3)_4^{2-}$$

and possibly the 'polymer effect' causes sufficient concentration of the nitrate ion in the 'solid' phase to allow this reaction, followed by substitution of chloride for nitrate in the complexes. More probably the situation is a little more complicated with absorption of mixed complexes reflecting differing anion in the solution and in the resin, thus

Figure 18

Reaction of a Column of Poly(4-Vinylpyridinium nitrate) ($P4VPH^+ NO^-_3$) as Anion Exchanger with Mixed Solutions of Mercury (II) and Copper (II) Chlorides.





$$P4VPH^+,NO_3 + Cl^- \rightleftharpoons P4VPH^+,Cl^- + NO_3^-$$

$$Hg^{2+}(+ 4\ (NO_3^-) \rightleftharpoons Hg(NO_3)_4^{2-}$$

$$Hg^{2+} + 4(Cl^-) \rightleftharpoons HgCl_4^{2-}$$

$$P4VPH^+,NO_3^- + Hg(NO_3)_4^{2-} \rightleftharpoons P4VPH^+,Hg(NO_3)_4^{2-},\ P4VPH^+$$

$$\text{or } P4VPH^+,Cl^- + HgCl_4^{2-} \rightleftharpoons P4VPH^+,HgCl_4^{2-},P4VPH^+$$

Intermediate stages in the above equilibria are assumed and ommitted here to simplify the expressions. That chloride does exchange fully with the nitrate was confirmed by chloride analyses (mecurimetric titration) of the effluent. That Copper (II) cations remain as the hydrated cations without formation of the chloride complex $CuCl_4^{2-}$ is evident from the continuing blue colouration throughout, no obvious yellow bands appear on the polymer.

The above show that P4VP can be quite versatile in its reactions and although not able to act as a cation exchanger in the normal sense (it can exchange by absorption of more strongly complexed cations in place of others, Copper (II) in place of Co (II) for instance, as we have seen) it is a cation complexing agent which can be modified to yield an anion exchanger. Clearly in the above case separation of Copper (II) from Hg (II) is possible using such columns. Regeneration of the resin could be effected by acid washing. In a similar manner it may be possible to use $P4VPH^+$ (cross-linked) in order to separate Co (II) (as $CoCl_4^{2-}$) from Ni (II)[101] after the initial separation of these two cations from Cu (II) using the neutral P4VP. Total separation of the cations may then be possible using a single column.

III.2.5 Anion Dependance of T.M. Ion Absorption

Although we are not so concerned with anion exchange, absorption of anions by the polymers is of great concern to us. In

the introduction it was pointed out that P4VP and P4VPNQ are complexing resins rather than cation exchangers and that this means that an equivalent amount of an anion must be absorbed into the polymer network with the cation in order to maintain electrical neutrality. This was simply confirmed by separate measurement of cation and anion concentrations in solutions over the polymer.

It could be expected that the character of the anion will play some part in the absorption of the particular metal salt. The situation regarding such 'anion effects' is considerably more complicated than is the case for T.M. cations and associated preferences. In particular difficulty can be encountered in attempting to differentiate between effects due to pH variation and those due to change of the counterion. Previously (figure 5) we came to the conclusion, that when the counterion present was Cl^-, although there was a considerable 'pH effect' for the rather poorly absorbed species Co (II), Ni (II) there appeared to be none for the Cu (II) cation, the absorption maximum for the latter being a plateau between pH 2.5-5.0. The same is apparently not true for $CuSO_4$ solutions and under similar conditions we can see (figure 19) that pH variation of the initial solution can have some effect, in this case less pronounced than for Ni (II) and about equal to that for Co (II) (figure 5), with approximately 15% increased Cu (II) absorption at some stages.

A series of experiments using a cross-linked (2 mole% DVB) fine particled resin showed (figure 20) an appreciable order of absorption for Copper (II) salts from aqueous solutions. In all

Figure 19

Reaction of Copper (II) Sulphate Solution (100ml of 0.1 Molar) with Poly(4-Vinylpyridine) (2g)

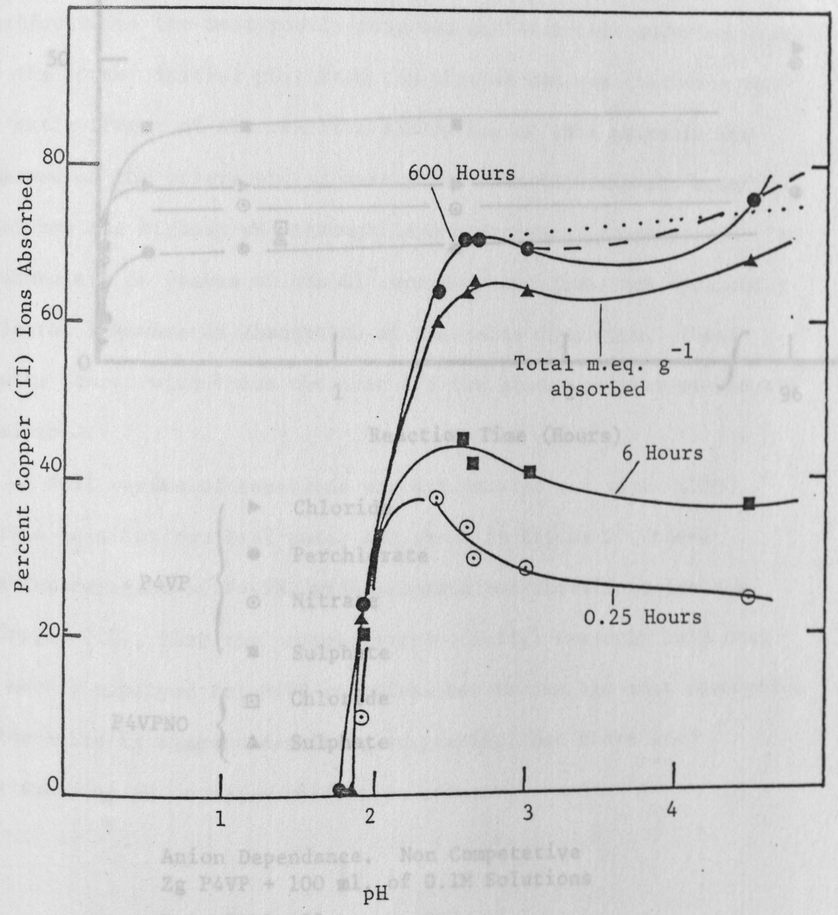
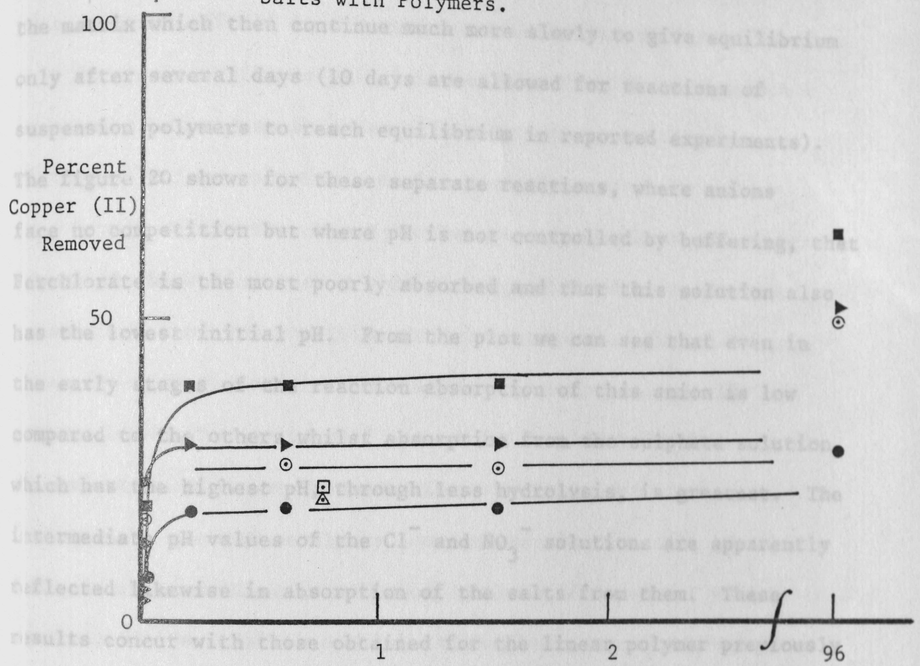


Figure 20

Reaction of Various Copper (II) Salts with Polymers.



Anion Dependance. Non Competetive
Zg P4VP + 100 ml. of 0.1M Solutions

Data Table 25

cases the characteristic initial fast reaction is complete after a short time (~0.5 hours). Here it seems most probable that we are seeing reaction of the surface and easily accessable regions in the beads prior to the onset of diffusion controlled reactions in the matrix which then continue much more slowly to give equilibrium only after several days (10 days are allowed for reactions of suspension polymers to reach equilibrium in reported experiments). The figure 20 shows for these separate reactions, where anions face no competition but where pH is not controlled by buffering, that Perchlorate is the most poorly absorbed and that this solution also has the lowest initial pH. From the plot we can see that even in the early stages of the reaction absorption of this anion is low compared to the others whilst absorption from the sulphate solution which has the highest pH, through less hydrolysis, is greatest. The intermediate pH values of the Cl^- and NO_3^- solutions are apparently reflected likewise in absorption of the salts from them. These results concur with those obtained for the linear polymer previously considered.

A full series of reactions was not carried out with P4VPNO in this case but two test cases are shown in figure 20, these were for reaction of P4VPNO with sulphate and chloride solutions of Copper (II), here the polymer sample (1.21g) was only half that (in moles) employed for P4VP reactions but we can see that absorption of the salts is almost identical, suggesting that there are apparently no pH or anion absorption effects.

The data for P4VP then suggests that generally, decreasing pH indicates increasing degree of protonation of the polymer, a reaction which effectively competes with Cu^{2+} absorption and that other factors such as change in ease of access with decreasing pH and 'anion effect' in absorption are in effect dominated by it.

In order to divorce pH related effects from anion dependance in absorption processes Copper (II) solutions containing a mixture of anions were reacted with the polymers.

Copper salts were chosen for the reaction because the higher degree of absorption over a wide pH range allowed more accurate measurement than was possible with other cations. The pH value under these conditions is obviously the same for all species present but such experimental procedures complicate methods of determination of anion concentration. No longer of course could the anion be assesed merely by complexiometric titration of the T.M. cations remaining in solution, methods of assesment which are specific for the various anions, Sulphate, Perchlorate, Chloride and Nitrate, were required having accuracy equal to that of the EDTA titrimetric methods previously used for cation determination. Initially a combination of volumetric and gravimetric methods was considered, Chloride analysis using a Mecuric nitrate titrimetric method proved entirely successful (Chapter II), not so a gravimetric method of Sulphate determination which in our hands gave erratic results and clearly required more practise for successful application. An alternative volumetric method for this anion proved successful if a little

protracted (Chapter II). Having gained a preference for volumetric over gravimetric methods of determination the choice of methods available for Perchlorate and Nitrate is limited. One reported method for Perchlorate [80] was examined and found to be unsuccessful, the reasoning and chemical theory were apparently sound however and some modification of the experimental procedure provided an accurate but again rather time consuming method of analysis (Chapter II). No suitable method of Nitrate determination was available and it was decided that where necessary a different method would be employed.

Several separate experiments, using the mixed Copper (II) salt solutions with the polymers, were carried out the intention being detection and estimation if possible of any variation in anion absorption. The results of the experiments appear in Tables 26-28 of the appendix.

Initially using solutions having total Copper (II) concentration of 0.1M and which were as near equi-equivalent as possible in anion the results in Table 26 were obtained, here Perchlorate is given as a difference value. Perchlorate is absorbed more quickly during the early stages of the reaction but this absorption slows after some hours. At termination (not necessarily equilibrium) of the reaction the percentage of Perchlorate ion removed from solution exceeds that of Copper (II) removed and is more than double that of the other anions absorbed. A partial explanation for the differences may be that the perchlorate anion being non-complexing makes fewer demands on the arrangement of the Copper (II) polymer complex during the absorption process whilst

Chloride and Sulphate become involved as ligands perhaps slowing complex formation, in essence a situation similar to that occurring for poorly absorbed cations where the conformations are unsuitable for complex formation. Attempts to determine the coordination state of Sulphate ions on the Cu^{2+}/P4VP complexes were made (Chapter IV) with only limited sucess. There appears then in these stationary experiments to be some element of the 'kinetic' effect proposed by Haines.

The common (Cu^{2+}) cation experiments were continued and it was decided to examine the result of passing the mixed anion solution through a P4VP column in a dynamic experiment similar to those previously described. The results in Table 27 (appendix) were obtained, here the same column has been used in both cases with regeneration using $HCl/NH_3/H_2O$ washes. In retrospect rather more runs at different flow rates might have been useful. Samples 1 and 2 shown were isolated at different effluent volumes. The results show that at the higher flow rate Sulphate is moderately well absorbed with Chloride and Perchlorate reacting only slightly, the situation changes for the slower run and here there is an appreciable difference between samples (1 and 2) collected at different effluent volumes. Perchlorate is slightly absorbed with first the Sulphate and then the Chloride being more strongly absorbed by the column. There is then a considerable contrast with the static experiments described above, though it must be remembered that the column experiments do generally involve a lower reaction time and higher polymer to solution ratio.

The results of further experiments involving reaction of slightly more concentrated solutions of the mixed Cu^{2+} salts with both P4VP and P4VPNO are shown in Table 28. These reactions were allowed to reach equilibrium (4 weeks) and here we can see that the anions are absorbed in approximately equal proportions by P4VP with Perchlorate slightly preferred. The same is not true for P4VPNO where Cu^{2+} absorption is much less with Perchlorate absorption dominating that of Chloride and Sulphate. Explanation for the difference in behaviour of these polymers is not easily found though it is again possible that involvement of Chloride and Sulphate as ligands provides arrangements less suited to the polymer conformation to an extent which is reflected even in the equilibrium state for P4VPNO.

Earlier it was stated that the intention of the common cation experiments was to divorce pH related effects from preferential absorption of anion. It may not be possible to do this effectively if the anions all have different absorption/pH profiles. We have already seen that chloride and Sulphate do differ in this respect and another possible explanation of the changes in absorption in the experiments described is that they are due to such pH effects. pH measurements were not made at the time and so we are not able to confirm this.

Generally there has been little precedent involving examination of the role played by anions during absorption of cations by complexing polymers, one remotely related paper has been published.[60] In that work protonated P4VP derivatives were reacted with Copper (II) solutions at various ionic strengths,

the conclusions contrast somewhat with the results of this study as might be expected for such anion exchangers.

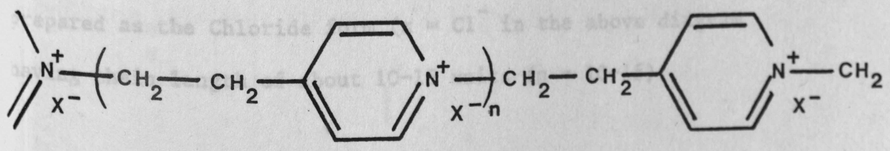
An order of anion absorption:-

$$AcO^- > SO_4^{2-} > Cl^- > NO_3^-$$

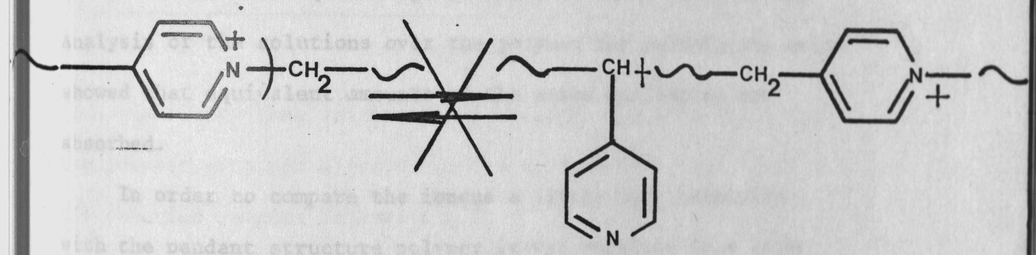
was determined there, the Copper (II) ion being absorbed poorly from solutions of Copper (II) Nitrate having ionic strength 0.1 and 1.0 adjusted by sodium nitrate addition. Russian workers had previously suggested that partial protonation of P4VP resulted in increased ability to complex T.M. cations generally however data from that work indicates that Copper (II) Nitrate is absorbed from 0.1M solutions by 'neutral' P4VP considerably more strongly than by the protonated species, there appears then to be some contradiction there. It does appear however that pH variation can affect the degree of Copper (II) absorption in some but not all cases.

III.2.6 The Ionene Polymers

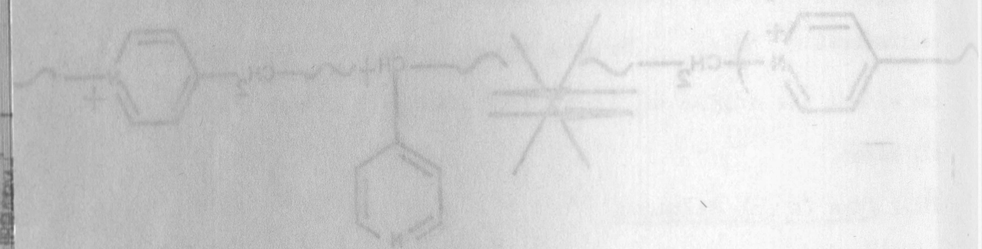
4-Vinylpyridine can polymerise to give an isomeric form of P4VP, these new polymers have different structures to the pendant forms we have dealt with so far and are commonly called ionene polymers though more correctly they are poly(1,4-pyridylethylene) cations which have associated anions



usually these polymers are only of a few units chain length and are produced by nucleophilic polymerisation mechanisms initiated by protonation of the monomer 4VP. From the structure of the polymer we expected that it would operate well as an anion exchange polymer but should not function at all as a cation exchanger because of the strong N^+-C bond which unlike the protonated pyridinium ring polymers mentioned above cannot be expected to give an equilibrium concentration of the neutral ring which



might then form complexes with T.M. cations by acting as ligands. Generally then no reaction was expected to take place between T.M. cations and the ionene polymers. Surprisingly this was not always the case. Initially the ionene polymers were prepared as the Chloride form (x = Cl^- in the above diagram having chain length of about 10-15 units (n = 10-15).



This polymer was very easily water soluble and so it was not possible to carry out two phase reactions in aqueous media as we had with the cross-linked $P4VPH^{+}Cl^{-}$ beads. Acetone was chosen as a suitable non-solvent for the polymer and reactions with the T.M. perchlorates in acetone solution were carried out. The results were unexpected, considerable amounts of the cations were removed from solution. The results are shown in Table 29. These show that absorption by the ionene is much less selective than for P4VP but it absorbs far more strongly from acetone than the isomeric $P4VPH^{+}Cl^{-}$ did from aqueous solutions. The reaction is not very fast in all cases and can require days or weeks to reach equilibrium. Analysis of the solutions over the polymer for perchlorate anion showed that equivalent amounts of the anion and cation are absorbed.

In order to compare the ionene a little more carefully with the pendant structure polymer it was required in a water insoluble form, by carrying out an anion exchange reaction in aqueous solution with Sodium perchlorate we obtained the insoluble perchlorate form in 99% yield. Attempts to absorb transition metal cations on this polymer failed entirely, no reaction occured with aqueous solutions.

Detailed analysis of the acetone solutions over the chloride form of the polymer during reactions with the T.M. perchlorate solutions was not carried out but if possible

explanations are considered and the colour changes in the reaction noted

Polymer Colour			Solution Colour		
Initial	Intermediate	Final	Initial	Final	Salt
White	Green	Yellow	Blue	Green-Yellow - Colourless	$Cu(ClO_4)_2$
White	Sky Blue	Blue	Red	Deep Blue - Colourless	$Co(ClO_4)_2$
White	White	White	Green	Pale Green - Colourless	$Ni(ClO_4)_2$
White		Green	Scarlet	Deep Green	Co/Cu perchlorate mixture

it seems likely that initially a fast anion exchange occurs on the polymer with perchlorate displacing chloride. Formation of the chloride complex follows e.g.,

$$Cu(ClO_4)_2 \longrightarrow Cu^{2+} + 2ClO_4^-$$

$$Polymer/Cl^- + ClO_4^- \longrightarrow Polymer/ClO_4^-$$

$$Cu^{2+} + 4Cl^- \longrightarrow CuCl_4^{2-}$$

$$Polymer/Cl^- + CuCl_4^{2-} \longrightarrow Polymer/CuCl_4^{2-}$$

explaining the blue ($CoCl_4^{2-}$) and yellow ($CuCl_4^{2-}$) colours on the polymer. That the solutions also change colour suggests that the chloride complexes occur in solution as well.

III.2.7 Comparison with Results of Previous Work

In general, resins previously considered as complexing-chelating macromolecular ligands for T.M. cations in aqueous media have themselves had a considerable affinity for the solvent,

this includes the partially protonated forms of P4VP examined by Russian workers. Thus P4VP differs in the context we have studied it in having no real affinity for the solvent whilst P4VPNO resembles more those resins previously considered. We have already mentioned in general terms the ability of various resins to absorb T.M. cations and the degree of selectivity which can be expected. It is necessary to know how P4VP and P4VPNO compare in a quantitative manner with other resins in terms of capacity for various cations and degree of selectivity.

Some direct comparison with previous work on P4VPs is possible, Kopylova et al have determined a series of sorption capacities for their resins.[57,58] These values are compared to those calculated for the 8% and 2% DVB cross-linked polymers used for this work in Table 30. For the poorly absorbed cations we have compared the absorptions at optimum reaction pH, this as we have already pointed out is not the single value implied by Kopylova et al but rather varies with the cation concerned; this is clearly seen by comparison of Cu^{2+} sorption which is greater for our polymers than those protonated forms used by the Russian workers. Generally then it appears that the polymers prepared are more selective for Cu^{2+} absorption than are those used by Kopylova but show nearly equal selectivity for other ions at optimum conditions.

Comparison with the other major work on absorption of T.M. cations by P4VP is also possible, here rather than examine

sorption capacities at optimum pH we look at values for pH 5.0 - 5.5 (Table 30). Once again the preference for Copper (II) seems rather greater for the polymers we have used whilst Nickel (II) and Cobalt (II) ions are absorbed to a similar degree in both cases.

Comparison with other Complexing Resins

Examination of some of the work published recently allows us to compare the sorption capacity and degree of selectivity shown by the 4VP based polymers with that of other chelating ion exchange and complexing resins. As P4VP absorbs Copper (II) in preference to most ions comparison with systems recommended for absorption of this cation is most useful. Examples of such selective resins are the modified imino diacetic acid ligands described by Sinyavskii[117] and 'tuned' polymers (c.f. those prepared by Nishide [61]) prepared by Kabanov.[116] Further examples are the Hydroxamic acids based polymers produces by Vernon.[48] Table 31 shows sorption capacities and times to half saturation ($t_{\frac{1}{2}}$) where available and we can see that P4VP compares favourably, on the former count, with most if the conditions are suitable.

One serious drawback for P4VP is its lack of affinity for the aqueous solvent, ironically this also appears to be one of the major contributing factors in its selectivity; we are however often reminded of how important this affinity and the resulting faster attainment of equilibrium is.

P4VP does have an initial fast reaction with Cu^{2+} (figure 20) in which generally more than 50% of capacity sorption is reached, $t_{\frac{1}{2}}$ then generally compares favourably with those for other polymers. The equilibrium may however take hours to effect. This then is where P4vP compares poorly with other species which continue to react more quickly and may only require minutes to reach equilibrium and though we may not only reduce the degree of absorption but also the selectivity (figure 21) this is especially serious in column operations. With polymers such as we have described the only means of regaining the selectivity is to allow time for the reaction to more nearly attain equilibrium. slowing flow rate etc. There is another approach to the problem, by increasing the available surface area of the polymer available for reaction we would limit diffusion control, this is precisely what happens with macroreticular polymers,[83] in fact attempts were made to prepare a macroreticular form of P4VP (Chapter II) without success, the resulting beads were the normal solid suspension product. The reported preparative method is now acknowledged as being unsuitable. It is expected that production of a macroporus product, akin to those produced from styrene, in the future will largely eliminate problems due to limiting reactions.

III.2.8. Conclusions

1) P4VP and P4VPNO act as macromolecular ligands for most lst row T.M. cations but not alkaline or alkaline earth ions.

2) An order of reaction of $VO^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$ has been established in agreement with previous work.

3) Decreasing pH (indicating increasing degree of polymer protonation) can cause increased absorption of some cations by P4VP but not by P4VPNO. Cu^{2+} absorption decreases or remains constant with drop in pH in some but not all cases.

4) P4VP (but not P4VPNO) is suitable for selective absorption of Cu^{2+} from most first row T.M. cations in aqueous solution at near neutral pH provided extraneous precipitation does not occur. VO^{2+} is an exception. Use of polymer columns in chromatographic separations at high flow rates is possible.

5) $P4VPH^{+}Cl^{-}$ and $P4VPNOH^{+}Cl^{-}$ are excellent anion but poor cation exchangers.

6) The anion present during cation absorption can play a role in the reaction. An order of preference for anion removal is not clearly defined and may change during the reaction and be cation related. The preference for Cu^{2+} seems to be $SO_4^{2-} > Cl^{-} > NO_3^{-} > ClO_4^{2-}$ though this can change. When pH effects are ruled out anion absorption is equal at equilibrium.

7) Reactions of P4VP are diffusion controlled and full equilibrium is slow; reaction to equilibrium for P4VPNO is considerably faster. The drawbacks can be countered to some extent by using low levels of cross-linking and small bead polymers, this can have deleterious effect. $t_{\frac{1}{2}}$ values are suitably low for purposes of cation complexation and removal.

8) Stability constants of the Cu^{2+} chloride complexes of P4VP and P4VPNO were calculated and found to differ (being lower)

with those previously determined by other workers.

9) There is no evidence to suggest initial formation of Co (II) - P4VP complexes as kinetic products in preference to Cu (II) complexes which are shown to be thermodynamically preferred products.

10) Absorption of Ni (II) and Co (II) can occur on P4VP columns of sufficient length that these ions are exposed to large excess of the polymer in the absence of competing Cu (II) cations. These complexes will be broken down as Cu (II) passes the reaction zone and displaces other ions (VO^{2+} excepted).

11) The maximum amount of Cu (II) cations which the polymer will absorb is one half its own molar quantity.

12) P4VP competes effectively(in degree of absorption and in $t_{\frac{1}{2}}$ (time to half equilibrium) values.) with other chelating complexing resins.

APPENDIX TO CHAPTER III.

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Table 1

Potentometric Titration of (2% DVB) Cross-Linked P4VP Derivatives

200mg Samples P4VP v's 10^{-2}M HCl			1.4g of 2% DVB P4VPH^{+} Cl^{-} v's 0.5M NaOH	
Volume of 10^{-2}M Hydrochloric Acid Added	pH at Equilibrium		Volume of 0.5M Sodium Hydroxide	pH at Equilibrium
	2% Cross L'd	Linear		
0	5.62	5.62	12.0	4.70
0.05	5.04	4.72	14.0	5.30
0.20	4.61	4.40	14.3	5.325
0.30	4.45	4.20	14.5	5.60
0.52	4.24	3.88	14.8	6.70
1.00	4.02	3.62	14.9	8.70
2.05	3.66	3.40	15.0	10.40
2.45	3.60	3.28	15.1	10.85
4.00	3.41	3.09	15.3	11.25
6.00	3.26	2.93	15.6	11.50
7.00	3.23	2.87	16.0	11.75
8.00	3.20	2.83		
9.00	3.16	2.78		
10.00	3.14	2.72		

Table 1b

Potentiometric Titration of P4VPNO with 1.0M HCl

Results of 1.21g of 2% DVB P4VPNO

Volume of 1.0M HCl added	pH at Equilibrium
0	10.26
0.5	9.81
1.0	9.20
1.5	7.77
1.7	7.34
2.0	6.97
2.4	6.66
2.8	6.43
3.2	6.19
3.5	6.00

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Table 3

Static Reaction of P4VP(Linear) with T.M. Cations

Transition Metal Salt	T.M. Ion Concentration at			
	Initial Concn.	24 Hours	220 Hours	1248 Hours
Copper (II) Chloride	0.0997M	0.0774M	0.0159M	0.01289M
Copper (II) Sulphate	0.0997M	0.0712M	0.01192M	0.0052M
Copper (II) Perchlorate	0.1007M	0.0799M	0.04613M	0.03864M
Nickel (II) Chloride	0.1084M	0.1074M	0.1074M	0.1074M
Nickel (II) Perchlorate	0.1073M	0.1029M	0.09491M	0.09438M
Cobalt (II) Chloride	0.1029M	0.1019M	0.1016M	0.1007M
Cobalt (II) Sulphate	0.1093M	0.0982M	0.0823M	0.0644M
Cobalt (II) Acetate	0.1082M	0.1072M	0.1000M	0.09015M

10g Polymer reacted with 50ml of solutions

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Table 4

Static Reaction of P4VP(Linear) with T.M. Cations

		T.M. Ion Concentration in Solution			
Transition Metal Salt	Initial	24 Hours	48 Hours	72 Hours	720 Hours
Copper (II) Sulphate	0.09953M	0.05260M	0.03378M		0.004M
Copper (II) Nitrate	0.09040M	0.04422M	0.03378M		0.0263M
Copper (II) Perchlorate	0.1008M	0.06521M	0.05760M		0.02233M
Copper (II) Chloride	0.1003M			0.0144M	0.00449M
Nickel (II) Sulphate	0.1003M	0.0993M	0.09894M		0.0806M
Nickel (II) Nitrate	0.0992M	0.0983M	0.09734M		0.09237M
Nickel (II) Perchlorate	0.09932M	0.08637M	0.08143M		0.0715M
Cobalt (II) Sulphate	0.1015M			0.07351M	0.0404M
Cobalt (II) Nitrate	0.0999M	0.09635M	0.09533M		0.0910M
Cobalt (II) Perchlorate	0.1023M	0.09232M	0.08738M		0.0715M

2g of Polymer reacted with 25ml of solutions

Table 5

Order of Absorption from Various Salts by P4VP

Cu (II) Absorption

Time	Perchlorate	Chloride	Sulphate	Nitrate
20 Hours	IV	III	II	I
48 Hours	III	II =	I	I
214 Hours	III	II =	I	IV
1 Month	III	II =	I	IV

Co (II) Absorption

20 Hours	II	IV	I	III
48 Hours	II	IV	I	III
213 Hours	II	IV	I	III

Nickel (II) Absorption

20 Hours	I	IV	II =	III
48 Hours	I	IV	II	III
213 Hours	I	IV	II	III

Order of Absorption from Aqueous Solutions by solid, Linear P4VP 'chips'. (Samples (5ml) were extracted from the reaction mixture (consisting of 2g of P4VP with 25ml of 0.1M solutions) at the times shown.

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Table 6. Reaction of Cross-Linked (8% DVB) P4VP Derivatives with First Row T.M. Cations Polymer

			P4VP		$P4VPH^{+}.Cl^{-}$		P4VPNO		$P4VPNOH^{+}.Cl^{-}$	
Reaction Time	T.M. Ion	Initial Concn.	Final Concn.	meq g^{-1} Absorbed	Final Concn.	meq g^{-1} Absorbed	Final Concn.	meq g^{-1} Absorbed	Final Concn.	meq g^{-1} Absorbed
2 Hours	Fe^{3+}	0.097M	0.0970M	0	0.0970M	0	0.0860M	1.10	0.0940M	0.3
	CO^{2+}	0.1015M	0.0980M	0.35	0.1020M	0	0.0880M	1.35	0.1010M	0
	Ni^{2+}	0.099M	0.0970M	0.20	0.1030M	0	0.0870M	1.20	0.1000M	0
	Cu^{2+}	0.1025M	0.0655M	3.70	0.1020M	0	0.0845M	1.80	0.0980M	0.45
6 Days	Fe^{3+}	0.0970M	0.0960M	0.10	0.0970M	0	0.0860M	1.10	0.0940M	0.30
	Co^{2+}	0.1015M	0.0980M	0.35	0.1020M	0	0.0880M	1.35	0.1025M	0
	Ni^{2+}	0.099M	0.0950M	0.40	0.1020M	0	0.0870M	1.20	0.1000M	0
	Cu^{2+}	0.1025M	0.0590M	4.35	0.1020M	0	0.0830M	1.95	0.0995M	0.30
12 Days	Fe^{3+}	0.0970M	0.0960M	0.10	0.0960M	0.10	0.0860M	1.10	0.0940M	0.30
	Co^{2+}	0.1015M	0.0980M	0.35	0.1010M	0	0.0880M	1.35	0.1025M	0
	Ni^{2+}	0.099M	0.0950M	0.40	0.1020M	0	0.0870M	1.20	0.1000M	0
	Cu^{2+}	0.1025M	0.0550M	4.75	0.1020M	0	0.0830M	1.95	0.0980M	0.45

Reaction of Cross-Linked P4VP (8% DVB) Derivatives with T.M. Cations

(1g Polymer Samples with 50ml of approx: 0.1 Molar solutions)

Table 7

Sorption pH Profiles:- Data for Figure

Reaction of 2% DVB Cross-Linked P4VP and P4VPNO with 0.1 Molar Solutions of Chloride Salts. P4VP 105mg with 50ml P4VPNO 121mg with 50ml.

Volume of M HCl Added	Equilibrium pH	Initial Concentration	Final Concentration	Absorption	
				% M^{2+}	meq g^{-1}
$VOCl_2$/P4VP					
0	2.92	0.1070	0.0431	59.7	6.39
3	2.20	0.1070	0.0551	47.0	5.10
7	1.85	0.1070	0.0941	12.0	1.3
10	1.30	0.1070	0.1059	4.5	0.55
$VOCl_2$/P4VPNO					
0	3.05	0.1070	0.0463	56.7	6.07
$CuCl_2$/P4VP					
0	4.20	0.1010	0.047	53.5	5.40
0.5	3.65	0.1010	0.049	51.5	5.20
1.0	3.59	0.1010	0.05175	48.8	4.92
2.0	3.19	0.1010	0.0540	46.5	4.70
3.0	2.79	0.1010	0.0590	41.6	4.20
4.0	2.49	0.1010	0.0650	35.6	3.60
5.0	2.32	0.1010	0.0750	25.7	2.6
6.0	2.16	0.1010	0.0850	15.8	1.60
7.0	2.10	0.1010	0.0920	8.9	0.90
8.0	1.84	0.1010	0.0980	2.97	0.30
9.0	1.52	0.1010	0.1020	0	0
10.0	0.50	0.1010	0.1060	0	0
0	(4.95) NaAcO adjust	0.1010	0.0465	54.0	5.45
$NiCl_2$/P4VP					
0	5.35	0.1016	0.0975	3.9	0.41
0.5	5.00	0.1016	0.0912	10.2	1.04
1.0	4.40	0.1016	0.0774	23.82	2.42
1.5	4.20	0.1016	0.0744	26.8	2.72
2.0	3.85	0.1016	0.0760	25.20	2.56
2.5	3.95	0.1016	0.0756	25.59	2.60
3.0	3.70	0.1016	0.0800	21.26	2.16
4.0	3.55	0.1016	0.0892	12.20	1.24
5.0	3.45	0.1016	0.0892	12.20	1.24

Continued

Table 7 (Cont'd)

Volume of M HCl Added	Equilibrium pH	Initial Concentration	Final Concentration	Absorption	
				% M^{2+} Removed	meq g^{-1}
$CoCl_2$/P4VP					
0	6.40	0.1035	0.0995	3.86	0.4
0.5	4.90	0.1035	0.0915	11.59	1.2
1.0	4.40	0.1035	0.0880	14.97	1.55
2.0	4.25	0.1035	0.0900	13.04	1.35
3.0	4.125	0.1035	0.0940	9.10	0.95
5.0	3.75	0.1035	0.0975	5.80	0.60
6.0	3.45	0.1035	0.1015	1.90	0.20
10.0	1.45	0.1035	0.1060	0.0	0
$CoCl_2$/P4VPNO					
0	6.9*	0.1035	0.049	51.0*	5.45*
0.5	6.7*	0.1035	0.057	42.0*	4.65*
3.0	5.75	0.1035	0.080	21.0	2.35
4.0	5.00	0.1035	0.082	19.0	2.15
5.0	3.90	0.1035	0.095	7.0	0.85
$ZnCl_2$/P4VP					
0	6.15	0.0945	0.0520	45.0	4.25
1	3.50	0.0945	0.0674	28.7	2.71
2	3.48	0.0945	0.0858	9.2	0.87
3	3.30	0.0945	0.0858	9.2	0.87
5	2.85	0.0945	0.0919	2.75	0.26
7	2.42	0.0945	0.0980	-3.70	Solvent absorption
$MnCl_2$/P4VP					
0	6.9	0.0982	0.0982	0	0
1.0	5.5	0.0982	0.0982	0	0
2.0	4.75	0.0982	0.0982	0	0
3.0	4.70	0.0982	0.1027	0 Solvent	0
4.0	4.6	0.0982	0.1027	0 absorptn	0

*with precipitation

Table 10

Reaction of Polymers with Various Copper (II) Concentration Solutions

Initial Cu^{2+} Concentration	Final Cu^{2+} Concn. over P4VP	Final Cu^{2+} Concn. over P4VPNO	Cu^{2+} / Polymer P4VP	Cu^{2+} / Polymer P4VPNO	Cu^{2+} in Solution / Cu^{2+} on Polymer P4VP	Cu^{2+} in Solution / Cu^{2+} on Polymer P4VPNO
0.0906M		0.0853M		1.16		16.09
0.06794M	0.0659M	0.06435M	0.382	0.78	32.95	18.1
0.0453M	0.0432M		0.400		20.57	
0.02265M		0.01924M		0.75		5.60
0.01132M	0.00946M	0.008961M	0.355	0.52	5.08	3.80
0.00453M	0.00346M	0.003905M	0.2042	0.138	3.234	6.25
0.00227M	0.001512M	0.001811M	0.145	0.100	1.995	3.95
0.001134M	0.00063M	0.000620M	0.096	0.110	1.25	1.21

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Table 11

Reaction of Polymers with More Concentrated Aqueous Solutions of T.M. Salts

Polymer Solution						Absorption	
Species	Weight	Salt	Initial Concn.	Volume	Final Concn.	Meq g^{-1} absorbed	Empirical Formula
1. Linear P4VP	6g	$CuSO_4$	1.5838M	50ml	1.0410M	9.047	$Cu(P4VP)_{2.12}SO_4$
2. Linear P4VP	3g	$CoCl_2$	0.835M	50ml	0.835M	0	-
3. Linear P4VP	3g	$Co(AcO)_2$	1.040M	50ml	0850M	6.34	$Co(P4VP)_{3.0}(AcO)_2$
4. Linear P4VP	3g	$CoSO_4$	0.880M	50ml	0.715M	5.50	$Co(P4VP)_{3.46}SO_4$
5. Linear rep'pted	3.5g	$Cu(ClO_4)_2$	0.915M	50ml	0.810M	3.00	$Cu(P4VP)_{6.35}ClO_4$
6. Linear fine bead	5g	$CuCl_2$	2.873M	50ml	2.525M	6.96	$Cu(P4VP)_{2.74}Cl_2$
7. 8% DVB N Oxide	1g	$CuCl_2$	2.873M	20ml	2.68M	7.72	$Cu(P4VPNO)_{2.14}Cl_2$
8. 8% DVP P4VP	2g	$CoCl_2$	0.2125M	100ml	0.1987M	1.38	$Co(P4VP)_{12.7}Cl_2$
9. 8% DVB P4VP	2g	$Co(NO_3)_2$	0.1825M	100ml	0.1700M	1.25	$Co(P4VP)_{14.0}(NO_3)_2$
10. 8% DVP P4VPNO	1.22g	$CoCl_2$	0.2125M	100ml	0.1800M	5.328	$Co(P4VPNO)_{3.29}Cl_2$
11. 8% DVB P4VPNO	1.22g	$Co(NO_3)_2$	0.1825M	100ml	0.1550M	4.508	$Co(P4VP)_{3.89}(NO_3)_2$
12. 8% DVB P4VPNO	1.22g	$Ni(NO_3)_2$	0.1840M	100ml	0.1562M	4.557	$Ni(P4VP)_{3.85}(NO_3)_2$

Table 12

Reaction of P4VP (2% DVB Cross-Linked with 0.5M $CuSO_4$: A Time Study

Initial Concn.	Final Concn.	meq g^{-1} Absorbed	Reaction Time	Empirical formula
0.5018M	0.4440M	5.505	20 mins.	$Cu(P4VP)_{3.29}SO_4$
0.5018M	0.4405M	5.838	40 mins.	$Cu(P4VP)_{3.11}SO_4$
0.5018M	0.4355M	6.314	60 mins.	$Cu(P4VP)_{2.87}SO_4$
0.5018M	0.4160M	8.171	90 mins.	$Cu(P4VP)_{2.22}SO_4$
0.5018M	0.4085M	8.886	120 mins	$Cu(P4VP)_{2.041}SO_4$
0.5018M	0.4070M	9.029	180 mins.	$Cu(P4VP)2.0\ SO_4$

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Table 13

Reaction of Polymers with more Concentrated T.M. Ion Solutions

Polymer		T.M. Ion Solution				Absorption	
Species	Weight	Salt	Initial Concn.	Volume	Final Concn.	meq g^{-1} Absorbed	Empirical Formula
P4VPNO (8% DVB)	1.22g	$CuCl_2$	1.50M	20ml	0.880M	22	$Cu(P4VPNO)_{0.8}Cl_2$
-"-	1.22g	$CuCl_2$	1.50M	30ml	0.915M	28.7	$Cu(P4VPNO)_{0.6}Cl_2$
-"-	1.22g	$CuCl_2$	1.50M	10ml	0.725M	12.7	$Cu(P4VPNO)_{0.7}Cl_2$
-"-	1.00g	$CuCl_2$	1.50M		0.91M		
-"-	1.22g	$CoCl_2$	1.03M	10ml	0.90M	2.13	$Co(P4VPNO)_{7.7}Cl_2$
-"-	1.22g	$CoCl_2$	1.03M	20ml	0.965M	2.13	$Co(P4VPNO)_{7.7}Cl_2$
-"-	1.22g	$CoCl_2$	1.03M	30ml	0.9875M	2.10	$Co(P4VPNO)_{7.8}Cl_2$

Table 14

Dynamic Experiment ; Reaction of Mixed Co (II)/Cu (II) Perchlorates Solutions with P4VP Columns

	T.M. Ion Concentration In Effluent	
Flow Rate(seconds ml^{-1})	Copper (II) Concentration	Cobalt (II) Concentration
0.45	2800 ppm	3000 ppm
0.45	2200 ppm	3000 ppm
1.05	1200 ppm	3000 ppm
1.40	1000 ppm	2800 ppm
Initial Concentration	3200 ppm	3000 ppm
Column 12.5g P4VP 20 cm x 1 cm l.d tube		

Table 15

Dynamic Experiment : Reaction of Mixed Co (II)/Ni (II)/Cu (II) Chlorides Solutions with P4VP Columns

	T.M. Ion Concentration In Effluent		
Flow Rate(seconds ml^{-1})	Cobalt (II)	Nickel (II)	Copper (II)
0.0			
0.52	1902 ppm	1709 ppm	1209 ppm
0.54	1818 ppm	1918 ppm	1618 ppm
1.00	1756 ppm	2085 ppm	1286 ppm
1.02	2018 ppm	1801 ppm	1209 ppm
1.40	2061 ppm	1668 ppm	1014 ppm
3.00	1993 ppm	1751 ppm	967 ppm
4.00	1943 ppm	1751 ppm	622 ppm
4.80	2077 ppm	1708 ppm	34 ppm
7.02	1935 ppm	1601 ppm	229 ppm
Initial Concentration	2106 ppm	2189 ppm	2147 ppm

Columns 12.5g Linear P4VP dimension 20 cm x 1 cm (1.d)

Table 16

Dynamic Experiment: Reaction of Mixed Co (II)/Ni (II)/Cu(II) Solutions with P4VP Columns

Flow Rate ($seconds\ ml^{-1}$)	Cation Concentration in Effluent (ppm)		
	Copper (II)	Nickel (II)	Cobalt (II)
The Chlorides			
0.95	797	1155	1383
1.45	665	889	1298
2.12	597	568	1230
3.35	500	747	1199
3.50	413	687	1303
6.05	286	480	1430
20.40	233	594	1174
Initial Concn.	2121	1934	1941
The Perchlorates			
0.60	980	955	1319
1.1	910	862	1091
1.2	812	683	1200
2.7	548	692	609
3.75	417	564	734
4.02	426	700	629
4.8	362	434	669
5.55	370	337	522
Initial Concn.	2114	1941	1981

50g of P4VP as column reacted with 150ml of Solutions

Table 17

Dynamic Experiment:-

Reaction of Cross-Linked P4VP with Mixed Sulphates of VO^{2+}, Cu^{2+} and Zn^{2+}

Total Effluent Volume (ml)	Cation Concentration (ppm)		
	VO^{2+}	Cu^{2+}	Zn^{2+}
0	940	1580	2260
55	0	0	13.1
115	0	0	326.4
175	0	0	826.0
235	0	0	690
295	2.4	0	775
355	22.2	0	1678
415	49.0	0	1756
475	93.4	6.98	1762
535	150.4	49.0	1810
595	172.4	115.4	1858
655	262.2	217.0	2208
715	363.4	346.4	2108
775	456.2	465.8	1988
820	578.6	596.8	2036
865	627.4	747.0	2348
905	742.6	876.8	2304
975	802.0	966.0	2264
1035	866.0	1066.0	2456
1096	851.4	1152.0	2276
1155	900.0	1280.0	2260
1215	915.2	1519.0	2408
1275	936.0	1470.0	2548
1335	914.6	1570.0	

Table 18

Dynamic Reaction of Mixed Fe (III), Co (II), Ni (II) and Cu (II) Nitrates with the P4VP Column

Volume of Effluent (ml)	Cation Concentration (ppm)		
	Fe (III)	Co (II)	Cu (II)
55	122	92.4	1.6
105	701	790	2.0
160	926	1147	2.0
215	1107	1290	2.0
270	1238	1400	2.0
325	1539	1770	2.0
380	1593	1900	50
435	1456	1860	56
490	1600	1950	167
Initial Conc^{n}	1609	1920	1881

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Table 19

Dynamic Reaction of Mixed Solutions of Copper (II) and Chromium (III) As Nitrates with P4VP Column

Total Cation Content of Input Solution 0.1 Molar

Flow Rate

Total Effluent Volume (ml)	Cation Concentration In Effluent (ppm)	
	Copper (II)	Chromium (III)
47.5	5.1	347.5
102.5	78.6	1496.5
157.5	93.5	1600.0
212.5	153.5	1760.0
272.5	650.0	2100.0
327.5	1400.0	2400.0
382.5	1850.0	2850.0
437.5	2100.0	2725.0
Input Concentration	3400.0	3095.0

Table 20

Dynamic Reaction of Mixed Solution of Mn(II), Co(II), Ni(II) and Zn(II) as Nitrates with P4VPNO Column

Total Cation Content of Solution = 0.1M

Total Effluent Volume	Cation Concentration in Effluent (ppm)			
	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}
45	0	0	0	0
95	0	0	0	0
145	338	0.3	0.2	119
195	1364	1364	1276	
245	1196	1406	1312	930
295	1152	1566	1452	894
377	1338	1764	1870	1192
429	1302	1872	1920	1382
484	1266	1822	1899	1302
539	1284	1886	1970	1126
606	1193	1900	1970	1154
661	1246	1900	1951	1074
	(0.0227M)	(0.0324M)	(0.0331M)	
Initial Solution	1302	1850	1966	1252

figure 12 - shows a plot based on the above data.

Table 21

Dynamic Reactions of Mixed Ni (II), Co (II), Cu (II) Nitrates with P4VPNO Column

Volume of Effluent	Concentration of cations in solutions (ppm)		
	Cobalt (II)	Nickel (II)	Copper (II)
37.5	0.9	0	0
94.0	1.55	0.35	0
149.0	61	47.15	0
194.0	2446	2282	0
249.0	2794	2791	0
304.0	2721	2666	255
359.0	2200	1902	1592
414.0	2098	1989	1890
479.0	2059	1841	1771
544.0	2369	2169	2032
Initial Concn.	2974	2900	2116

Flow Rate 0.385 mins. ml^{-1}

Table 22

Dynamic Reaction of Mixed Solutions of Copper (II) And Chromium (III) As Nitrates With P4VPNO Column

Total Cation Concentration of Input Solution 0.1 Molar

Flow Rate

Total Effluent Volume (ml)	Cation Concentration In Effluent (ppm)	
	Copper (II)	Chromium (III)
47.5	4.225	172.6
103.5	2.0	972.0
159.5	3.5	1266.5
192.0	15.5	1426.4
Input Concentration	3400.0	3095.0

Table 23

Reaction of $P4VPH^+$, NO_3^- As an Anion Exchanger in Dynamic Experiments with Mixed Cu (II), Hg (II) Aqueous Solutions of the Chlorides.

Total Effluent Volume (ml)	Cation Concentration (ppm)	
	Hg^{2+}	Cu^{2+}
Initial Concentrations	10555	3004.8
60	0	506
130	0	1593
200	0	1752
270	0	1823
340	0	1842
410	0	2454
480	0	2410
550	0	2613
620	0	2417
690	0	2874
760	0	2890
830	0	2881

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Table 24

Data for Figure 19

Reaction of 0.1M $CuSO_4$ with P4VP at various pH values

Initial pH of Solution	Conc.^{n} of Cu^{2+} in solution after Time (Hours)						Total M^{2+} sorbed
	0.25	0.834	4.0	6.0	64.0	600	meq g^{-1}
4.50	0.75	0.0772	0.0662	0.06312	0.030	0.0237	6.86
3.00	0.716	0.0706	0.0662	0.0587	0.0312	0.0300	6.42
2.62	0.716	0.0700	0.0612	0.0581	0.0306	0.02937	6.48
2.60	0.656	0.0653	0.0512	0.0531	0.0300	0.0287	6.40
2.40	0.622	0.0631	0.0556	0.0544	0.0356	0.0362	6.02
1.90	0.090	0.0900	0.8375	0.0788	0.0756	0.0762	2.24
1.85	0.1012	0.0994	0.0987	0.0987	0.1000	0.1025	0.212

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Table 25

Reaction of Cross-linked P4VP with Aqueous Copper (II)

	Reaction Time (Hours) In	Copper (II) Ion Concentration 1M			
		Chloride	Perchlorate	Nitrate	Sulphate
Initial Concn.	0	0.1005M			0.1010M
	0.017	0.0875M	0.0915M	0.0820M	0.0820M
	0.2	0.0710M	0.0806M		0.0620M
	0.6	0.0700M	0.0800M	0.0730M	0.0620M
	1.5	0.0700M	0.0805M	0.0730M	0.0615M
	96	0.0500M	0.0700M		0.0355M
	Initial pH	4.3	2.5	4.2	5.0
Reaction of P4VP (2.1g) with 0.1M aqueous solutions (100ml)					
	0	0.1005M			0.1010M
	0.75	0.0780M			0.0805M

Reaction of P4VPNO (1g) with Cu(II) solutions (50ml)

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Table 26

Comparison of Anion Absorption by P4VP From Copper (II) Solution

Reaction Time (Hours)	Cu^{2+} Concentration Over Polymer (Molar)	Anion Concentration Over Polymer (g.eq. $(^{-1})$			Percent Absorption Based on Initial Values			
		Chloride	Sulphate	Perchlorate	Cu^{2+}	Chloride	Sulphate	Perchlorate
0	0.09944	0.06594	0.0660	0.0670				
0.02	0.09500	0.06590	0.0588	0.0588	4.46	0.21	1.1	12.2
0.0625	0.0940	0.06540	0.05876	0.05876	5.47	0.80	3.5	12.3
0.20	0.0917	0.06320	0.05380	0.05380	7.78	4.1	0.5	19.7
0.75	0.0890	0.06300	0.0520	0.0520	10.5	4.4	4.7	22.0
4.30	0.0855	0.06010	0.0488	0.0488	14.0	9.0	5.93	27.16
17.0	0.0840	0.05940	0.0486	0.0486	15.5	9.9	9.2	27.5

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Table 27

Relative Absorption of Anions in a Dynamic, Column Experiment

	Flow Rate Min ml^{-1}	Initial Solution	Sample 1 Initial 30ml	Sample 2 Second 30ml	Concentration of Ions in effluent as Percentage of Initial Values.							
					Perchlorate 1	Perchlorate 2	Chloride 1	Chloride 2	Sulphate 1	Sulphate 2	Cu^{2+} 1	Cu^{2+} 2
	0.75											
Cu^{2+} Concn.		0.1009	0.0844	0.0843								
$(ClO^{-}_4)_2$ Concn.		0.0342	0.0340	0.0345	99.4	100	94.7	94.7	56.6	55.4	83.6	83.5
$(Cl^{-})_2$ Concn.		0.03327	0.0315	0.0315								
SO_4^{2-} Concn.		0.03340	0.01890	0.0185								
	1.00											
Cu^{2+} Concn.		0.1009	0.0774	0.0753								
$(ClO_4^{-})_2$ Concn.		0.0342	0.0300	0.0300	87.8	87.8	67.6	81.1	74.5	54.8	76.7	74.6
$(Cl^{-})_2$ Concn.		0.03327	0.0225	0.0270								
SO_4^{2-} Concn.		0.03340	0.0249	0.0183								

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Table 28

Absorption of Anions at Equilibrium

	Anion Concentration			
	Cu^{2+} Concentration	Sulphate (equiv.)	Chloride (equiv.)	Perchlorate (eqiuv.)
P4VP (2.1g)/100ml				
Initial	0.230	0.0788	0.07685	0.07435
Final	0.155	0.05385	0.05355	0.0476
% Absorption	32.6	31.7	30.3	35.98
P4VPNO (2.42g)/100ml				
Initial	0.230	0.0788	0.07685	0.07435
Final	0.1987	0.0776	0.06832	0.05278
% Absorption	13.6	1.50	10.6	29.0

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Table 29

Two Phase Reactions of Transition Metal Perchlorates in Acetone Solution with Ionene Polymer

Weight of Ionene (g)	Perchlorate	Vol. of Solution	Initial T.M. concn.	Final T.M. concn.	Reaction Time	% T.M. Absorption	mg T.M./g on Polymer
5	Copper (II)	50ml	0.0733M	0.0030 M	13 days	96 %	45
5	Cobalt (II)	50ml	0.0703M	0.0029 M	13 days	95.9%	43
5	Nickel (II)	50ml	0.097 M	0.0023 M	28 days	98 %	60
2.5	Copper (II)	25ml	0.0976M	0.00778M	5 days	92 %	57
2.5	Cobalt (II)	25ml	0.1018M	0.0588 M	5 days	41 %	22
2.5	Cobalt (II)	25ml	0.1018M	none detected	4 weeks	100 %	48
2.5	Cobalt (II)	25ml	0.1018M	0.03735M	5 days	63 %	38
	Copper (II)	25ml	0.0976M	0.01889M	5 days	81 %	50

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Table 30

Nickel (II) Sorption

	Salt, Concentration	(optimum pH)	Sorption Capacity (mg equiv. g^{-1})
P4VP 2% DVB	0.1 Molar $NiCl_2$	4.0	2.65
P4VP NO 8% DVB	0.1 Molar $NiCl_2$		1.30
*P4VP 8% DVB	0.05 Molar		2.40
α = 0.6			

* Data of Kopylova et al

CHAPTER IV

THE STRUCTURE AND COMPOSITION OF COMPLEXES OF P4VP AND P4VPNO WITH THE FIRST ROW TRANSITION METAL IONS

IV.1 Introduction

We come now to consider the products from reactions of polymers of 4-Vinylpyridine (4VP) with T.M. cations. It was considered that information concerning the structures of these products might enable a clearer understanding of the absorption processes occurring in experiments previously described, and point towards areas of practical application for the polymers.

Several different approaches to preparation of T.M. complexes having polymeric derivatives of the above mentioned ligands are possible, these include:

a) Reaction of P4VP or P4VPNO in solution with T.M. ion containing solutions

b) Reaction of solid polymeric derivatives with aqueous cation containing solutions, the so called two phase reactions mentioned in the quantitative sections of Chapter III.

c) Reaction of 4VP with T.M. cations in solution, followed by polymerisation of the resulting complex, generally by free radical addition reactions.

We have already mentioned some of the work previously carried out involving products from reactions falling in groups a and b above. The considerable amount of information available to us is reviewed briefly below and in more detail where relevant throughout this Chapter, it has allowed us to make valuable comparisons in many areas, in addition simplifying interpretation of the new data obtained.

A) Solution Reactions of the Polymers

i) P4VP

Solution reactions involving cations from the first row

IV.1 Introduction

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a) Solution Reactions of the Polymers

i) P4VP

Solution reactions involving cations from the first row

transition metals (T.M.) have been studied by Biederman et al [50] and by Agnew et al.[85] Products from reactions with other T.M. cations have been considered by Rhoda et al.[53,54]

Biederman examined products from reactions of both P4VP and P2VP with di-valent T.M. chlorides in solution in low alcohols and found that generally the products precipitated from solution, the solids having colours characteristic of the di-valent ion concerned. Formulae of $M(P4VP)_2Cl_2.2H_2O$, where (P4VP) indicates coordination of a pendant aromatic ring from the P4VP macromolecule, were generally found for reactions involving the hydrated salts whilst the anhydrous salts under dry conditions gave more complex products in some cases,in particular those from reaction of Copper (II) and Iron (III). Generally all the monomer units of the polymer chains were found to be coordinated to the T.M. cation but it was found that reaction conditions could effect the composition of the products to a small extent.[50e] The studies were extended to consider complexes of the P4VP ligand with mixtures of cations to give products containing potential redox systems which may provide a route to novel catalysts.[52] The stoichiometry of these mixed cation products is more complex than those of the single cation containing complexes,with composition of the final products reflecting the preference of the polymer for complex formation with Copper (II) and Iron (III) among others. We have not examined further these mixed cation solution reactions, primarily because of the associated complexity of the products, preferring to consider in greater detail the products from single cation reactions. At a later stage in this chapter however we have attempted to relate preferences shown by the polymer in

solution to those shown in the two phase reactions of the solid polymers.

ii) P4VPNO

Less work has been carried out on complexes of P4VPNO with T.M. cations and that by Holt et al[71] provides the information most useful to us. Reactions of the polymer carried out in aqueous solution were reported to give two series of products depending on relative reagent concentrations, $M(P4VPNO)Cl_2$ and $M(P4VPNO)_2Cl$ where (P4VPNO) represents a coordinated monomer unit in the polymer chain. No work involving reactions of the P4VPNO ligand with solutions of mixed T.M. cations has been reported.

b) Reactions of Solid Polymers with Aqueous Solutions of T.M. Cation

We have already mentioned work by Kopylova et al[56] and Nishida et al[61] who considered absorption of T.M. cations from dilute aqueous solutions. The results of a quantitative study concerning such absorption are reported in Chapter III of this report and results of studies on the products are reported in this Chapter.

Few if any workers have considered absorption by the solid polymers from concentrated aqueous solutions, we have examined in some detail products from such reactions. We have already mentioned that the results of Chapter III indicate that the stoichiometry of the reaction products from the two phase reactions of the polymers tends to irregularity, reflecting perhaps inflexibility in the arrangement of the solid ligand and limiting permeability leading to diffusion control. The products then, could be expected to contain many unreacted monomer units and the resulting lack of uniformity means that study of the arrangement about the cations is somewhat more difficult than is the case for T.M. - Pyridine reaction products for instance where the unreacted ligand is removed by purification.

A comparison of T.M. complexes of 4VP with those having P4VP as

ligand was expected to prove useful.

IV.2 Experimental Section

1. Preparation of Poly(4-Vinylpyridine) Complexes of Transition Metal Complexes having Fully Reacted Monomer Units.

Procedure

A solution of P4VP (1.05g) in methanol (200ml) was added drop wise with stirring to a solution of five times molar excess of the T.M. chloride or nitrate hydrate concerned in methanol (100ml). Immediate precipitation usually occured (VO^{2+} reactions seemed slower). The mixture was stirred for one hour followed by heating to reflux temperature (except Fe (III) and VO^{2+}) for a further one hour. After cooling to room temperature the diffuse coloured precipitates were filtered at the pump through porosity three sintered glass crucibles, washed carefully with ethanol and finally dried under vacuum at $50^{o}C$. The resulting products were fine powders having colours characteristic of the reacting T.M. cation VO^{2+} and Fe (III) products were isolated from their reaction mixtures without Reacting.

Reacting

Anion	Cation	Product Colour	Product Weight
Chloride	VO^{2+}	Dark Green, Grey	1.70g
"	Mn(II)	White	1.60g
"	Fe(III)	Brown	2.60g
"	Co(II)	Blue	1.96g
"	Ni(II)	Green	1.95g
"	Cu(II)	Grass Green	1.648g
"	Hg(II)	Off White	
Nitrate	Co(II)	Pink	2.80g
"	Ni(II)	Green	1.85g
"	Cu(II)	Blue	1.91g
Sulphate	VO^{2+}	Grey	2.17g

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Reacting

Anion	Cation	Product Colour	Product Weight
Chloride	VO^{2+}	Dark Green, Grey	1.70g
"	Mn(II)	White	1.69g
"	Fe(III)	Brown	2.60g
"	Co(II)	Blue	1.96g
"	Ni(II)	Green	1.94g
"	Cu(II)	Grass Green	1.948g
"	Hg(II)	Off White	
Nitrate	Co(II)	Pink	2.80g
"	Ni(II)	Green	1.88g
"	Cu(II)	Blue	1.91g
Sulphate	VO^{2+}	Grey	2.17g

2. Preparation of Poly(4-Vinylpyridine-N-oxide) Complexes of Transition Metal Ions.

Procedure

A solution of P4VPNO (1.21g) in water (75ml) was added dropwise with stirring to a solution of five times molar excess of the T.M. salt concerned in water (100ml). In those cases where precipitation occurs immediately (Cu (II), VO^{2+} and Fe (III)) the mixture was stirred for six hours and the precipitate isolated by filtration through a porosity three sintered glass crucible followed by washing with water and with ethanol followed by drying under vacuum at $50^{o}C$. In those cases where precipitation did not occur the mixture was rotary evaporated to 25ml and an equal amount of alcohol added followed by cooling for two days at $5^{o}C$. The resulting precipitate was filtered off on a sintered glass crucible (porosity three) and washed with ethanol and dried as previously. The products were fine powders and again had colours characteristic of the reacting T.M. cations.

T.M. Salt	Product Colour	Product Weight
$VOCl_2.2H_2O$	Dark Green	1.30g
$VOSO_4.5H_2O$	Dark Green	1.13g
$MnCl_2.4H_2O$	White	
$FeCl_3$	Brown	
Ferric Ammonium Sulphate	Brown	1.61g
$CoCl_2.6H_2O$	Grey	
$Co(NO_3)_26H_2O$	Pink	1.16g
$NiCl_2.6H_2O$	Green	

T.M. Salt	Product Colour	Product Weight
$Ni(NO_3)_2 6H_2O$	Green	1.48g
$CuCl_2, 2H_2O$	Green	1.20g
$Cu(NO_3)_2 . 6H_2O$	Blue	1.07g

3. Preparation of 4-Vinylpyridine - Transition Metal Complexes.

Generally we have attempted to prepare complexes having the lowest possible number of 4VP units coordinated to cations, the situation we expected to encounter in the polymer matricies, exceptions have been $Co(4VP)_4Cl_2$ and $Ni(4VP)_4Cl_2$. The procedure for the bis complexes of Cu(II), Co(II) and Ni (II) has generally been to add the ligand to excess T.M. salt solution and for the tetra 4VP derivative vice versa, thus:-

Preparation of Bis 4-Vinylypyridine Cobalt (II) Chloride

Pure 4VP (5g = 0.0476 moles) was added dropwise to a solution of Cobalt (II) chloride hexahydrate (8g = 0.0336 moles) in methanol (50ml). The resulting deep blue solution was rotary evaporated to 30ml and cooled to $-5^{o}C$ for two days during which time blue crystals were deposited. These were filtered off at the pump and washed with chilled methanol followed by drying under vacuum at room temperature to give 9.2g (57%) of a blue crystalline (plates) solid soluble in alcohols, chloroform and acetone but insoluble in water. This melted at $128^{o}C$. Corresponding yields for $Ni(4VP)_2Cl_2$ and $Cu(4VP)_2Cl_2$ were 64% and 98% respectively. $Cu(4VP)_2Cl_2$ was insoluble in most common solvents but could be purified by placing the crude product in a soxhlet thimble and extracted with chloroform, pure plate-like crystals quickly form in the receiving flask.

4. Polymerisation of the Monomer 4VP/Transition Metal Complexes

Polymerisation of Tetrakis 4VP Cobalt (II) chloride: Tetra 4VP Cobalt (II) chloride (30g) was dissolved in chloroform (150ml) and Azobisisobutyronitrile (0.3g) was added as free radical initiator. The blue solution was placed in a pyrex glass ampoule and degassed by attaching to a vacuum line, freezing to liquid nitrogen temperature and evacuating followed by thawing to allow release of dissolved gasses, this freeze thaw cycle was repeated twice before sealing the ampoule. Polymerisation was carried out by immersing the ampoule in a water bath at 60°C for forty eight hours. The blue solid product was isolated by filtration at the pump through a porosity two sintered glass crucible followed by washing with Ethanol and finally drying under vacuum at 50°C to yield 28.46g of an intensely blue very finely divided solid. The elemental analysis data for the product appears in Table 4 .

Polymerisation of Bis 4-Vinylpyridine Cobalt (II) Nitrate Tetrahydrate.

Procedure

A solution of monomer 4VP (purified as above) (5g) in ethanol (50ml) was added to a solution of excess Cobalt (II) nitrate hexahydrate (10g) in ethanol (50ml). To the resulting red solution was added AIBN (0.05g) a free radical initiator and the mixture flushed of oxygen by bubbling nitrogen gas through it at room temperature for half an hour. The polymerisation was carried out by heating the solution to 60°C for four hours under a nitrogen atmosphere. A pink precipitate soon formed during the reaction and this was filtered off (after cooling) at the pump through a porosity two sintered glass crucible and washed with ethanol. After drying

2.52g of a pink solid was obtained.

Preparation of Bis 4-Vinylpyridine Nickel (II) Nitrate Tetrahydrate and Polymerisation

Procedure

As for the Cobalt complex 4VP (10.5g) was reacted with excess of the T.M. nitrate (18.5g) followed by polymerisation to give a green solid (15.5g (70%)) powder insoluble in all organic solvents and in water but soluble in dilute acid. The neutral ligand could be precipitated from acidified solutions by pouring into aqueous ammonium hydroxide.

5. Preparation of the Cross-linked Polymerised, Monomer Complexes.

Following the general procedures set out for preparations above but with incorporation of 10 mole % p-divinylbenzene as cross-linking agent to give insoluble polymer matricies from which the T.M. ion could be removed to give selective complexing resins. Thus:-

Polymerisation of bis 4VP Cobalt (II) chloride to give cross-linked bis P4VP Cobalt (II) chloride

A solution of 4VP (10.5g) with AIBN (0.25g) as free radical initiator in methanol (150ml) was added to a solution of Cobalt (II) chloride hexahydrate (15g) in methanol (250ml). The blue solution was heated to reflux on a water bath for twenty four hours during which time a blue solid formed, this was isolated by filtration at the pump through a porosity two sintered glass crucible. Drying under vacuum gave 17.3 (97%) of an intensely blue finely divided powder insoluble in all common solvents but which turned white in aqueous acid without dissolving.

IV.3. Results and Discussion

The investigation of the structure of the T.M. cation containing polymers commenced with a brief examination of 4VP itself and the related polymeric ligands.

IV.3.1. The Ligands

1. 4-Vinylpyridine

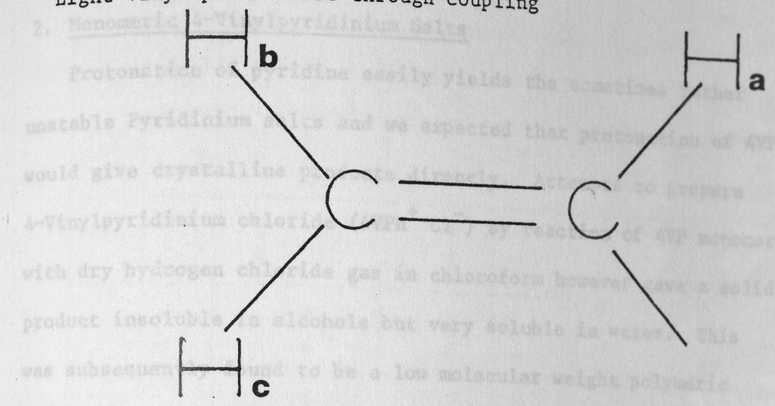
We have said that this is a vinyl heterocyclic aromatic monomer showing the characteristics of both pyridine and styrene, this was confirmed as follows.

Proton Nuclear Magnetic Resonance

As expected for such a γ substituted pyridine derivative the ^1H NMR spectrum was considerably less complicated than that of Pyridine or related α and β substituted species resembling instead the simple spectrum obtained for sytrenes. This simplification is directly attributable to disappearance of the γ hydrogen which then no longer couples with other ring protons to cause splitting of signals. The spectrum (figure 1) shows two peaks in the aromatic region, each due to two protons. Those on α carbons absorb downfield of those on β carbons and the difference is more pronounced than for styrene becuase of the additional deshielding effect of the electrophillic nitrogen atom at the α carbon. Coupling of moments for the ring protons has caused splitting of each signal to give two doublets and similarly coupling of the vinyl group protons has given rise to a series of eight peaks in the vinyl region of the spectrum. This is in agreement with the accepted structure of the monomer.

FIGURE 1 THE ^{1}H NMR SPECTRUM OF 4-VINYLPYRIDINIUM TRIFLUORO-ACETATE

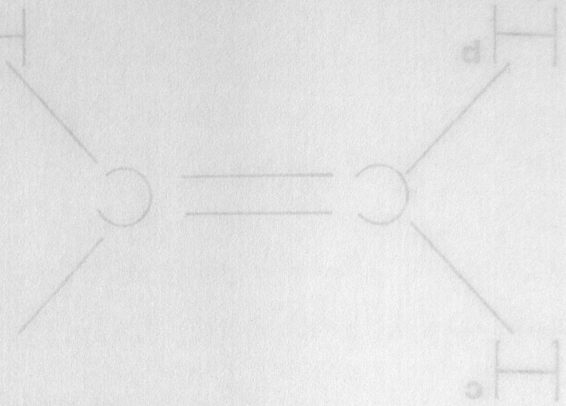
Eight vinyl peaks arise through coupling



of Ha to the now inequivalent H_b and H_c giving four equal peaks for Ha which in turn splits signals for both H_b and H_c into two. Finally a small coupling occurs between the two inequivalent hydrogen atoms on the same carbon atom as this allows us to identify these signals more easily. Integration of the spectrum confirms that there are four aromatic protons and three vinyl protons. Data from the spectrum including splitting constants is given in Table 1.

Infra-Red Spectrum of the Monomer

The infra-red spectrum of the monomer as might be expected is quite complex, resembling closely that of Pyridine itself. Intense absorption occurs at 1596 cm^{-1} and is assigned to C = C and C = N stretching vibrations in both the Pyridine ring and the vinyl group. Bands which characterise the aromatic ring (C-H stretch aromatic) appear around 3000 cm^{-1} with bending vibrations of the ring appearing between 400-700 cm^{-1}. A complete assignment of the absorption bands for the monomer has previously been made [87] and we shall make use of those interpretations this work.



2. Monomeric 4-Vinylpyridinium Salts

Protonation of pyridine easily yields the sometimes rather unstable Pyridinium salts and we expected that protonation of 4VP would give crystalline products directly. Attempts to prepare 4-Vinylpyridinium chloride ($4VPH^+ Cl^-$) by reaction of 4VP monomer with dry hydrogen chloride gas in chloroform however gave a solid product insoluble in alcohols but very soluble in water. This was subsequently found to be a low molecular weight polymeric derivative of 4VP belonging to a class of compounds labelled 'ionenes' by their American discoverers Fitch, Snider and Salamore.[91] The mechanism of the reaction and characterisation of further related products are described below.

Preparation of the monomeric vinylpyridinium salts ($4VPH^+ X^-$) then was difficult with more commonly encountered gegen ions. When 4VP is reacted with Trifluoroacetic acid in a suitable solvent however a stable crystalline monomeric product could be obtained provided excess acid was present during reaction of the monomer. More difficult but still possible was the preparation of $4VPH^+ HSO_4^-$ and $4VPH^+$ both of which can be prepared under suitable conditions (See Chapter II). Both these latter salts were characterised by comparison with the 4VP/triflouroacetic acid salt. Preparation of these salts has not previously been described, they are much less stable than the TFA derivative in both the solid form and in solution.

Proton Nuclear Magnetic Resonance of the $4VPH^+$ Cation

^1H NMR spectra show the effect of introducing the charge by protonating the Pyridine ring. Once again the spectra are far

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Table 1

^1H NMR Data for 4-Vinylpyridine and Protonated Derivatives

Compound	Solvent	Aromatic	Vinyl			J,Hz			$-CH_2-$
			H_a	H_b	H_c	J_{ac}	J_{ab}	J_{bc}	
4-Vinylpyridine	CCl_4	8.48,7.10;4H,2d,J=4Hz.	6.55	5.3	5.8	18.0	10.0	1.5	
4-Vinylpyridinium chloride	D_2O	8.75,8.10;4H,2d,J=6Hz.	7.05	6.04	6.48	17.3	10.0	0.8	
4-Vinylpyridinium bisulphate	D_2O	8.71,8.05;4H,2d,J=6Hz.	7.03	6.0	6.45	17.4	10.5	1.0	
4-Vinylpyridinium acetate	Acetic acid	8.70,7.80;4H,2d,J=6Hz.	6.90	5.8	6.2	16.0	10.0	2.0	
4-Vinylpyridinium trifluoroacetate	D_2O	8.67,8.03;4H,2d,J=6Hz.	6.99	5.99	6.4	18.5	10.0	1.5	
Ionene Polymers from Reaction of 4-Vinylpyridine with									
a) Hydrochloric acid	D_2O	8.88,8.12;multiplet	7.06	6.05	6.5	17.0	10.3	1.0	5.1,3.8
b) Sulphuric acid	D_2O	8.90,8.15;multiplet	7.10	6.07	6.51	17.5	10.0	1.0	5.1,3.8
c) Acetic acid	Acetic acid	8.85,8.05;multiplet	7.05	5.98	6.4	18.0	10.0	1.0	5.0,3.7
d) Trifluoroacetic acid	D_2O	8.75,8.10;multiplet	7.05	6.05	6.5	17.5	10.7	1.0	5.0,3.7

simpler than for the corresponding unsubstituted Pyridinium chloride, further de-shielding of protons on β ring carbons occurs with a consequent shift of the signals to lower field whilst the increase in de-shielding is much less pronounced at the α position and this results in a reduced shift for the proton there. Similarly the effect and resulting shift are much reduced for the signals in the vinyl region of the spectra. The shifts for various salts ($4VPH^+/TFA^-$, $4VPH^+/HSO_4^-$ and $4VPH/Cl^-$) together with values for the coupling constants determined for the spectra are given in Table 1 and generally as can be seen they appear to be independent of the anion concerned implying little interaction in solution. The spectra of the salts is similar to that of the unreacted monomer.

Infra-Red Spectra of $4VPH^+$

Infra-red spectroscopy also clearly reflects the effect of protonation and the presence of the counterion in the 4VP salt. The peak at 1599 cm^{-1} for the monomer assigned to C = C and C = N in the vinyl and aromatic groups shifts to 1640 cm^{-1} reflecting strengthening of these bonds which occurs upon gain of a positive charge by the ring. Bands due to counterion appear (sulphate 1000 cm^{-1} broad non-coordinated, TFAcetate 1700 cm^{-1} broad) confirming salt formation. Generally however spectra of the protonated species resemble that of the unreacted monomer.

The Polymeric Ligands

3. P4VP

Free radical polymerisation of 4VP has previously been widely studied[23] and both linear and cross-linked products described.

The structure of the unreacted polymer is known and we have confirmed it using ^{1}H NMR and infra-red spectroscopies.

Proton NMR

The linear polymer was soluble in chloroform and solution NMR shows a spectrum with much reduced resolution compared to that for the monomer. Two peaks of equal area appear in the aromatic region of the spectrum and these are assigned to protons on the α (δ = 8.2) and β (δ = 6.3) ring carbons, the rather great breadth of the peaks is probably due to failure to resolve the split peaks observed for the monomer. No peaks appear in the vinyl region but signals which we can assign to methylene and methine protons appear well upfield (δ = 1.5 - 2.5) confirming the change from unsaturated monomer to the fully saturated backbone chain of the polymer. Integration of the signal confirms the ratio of four aromatic to three aliphatic protons in each unit, further the methine peak integrates as one half the methylene signal.

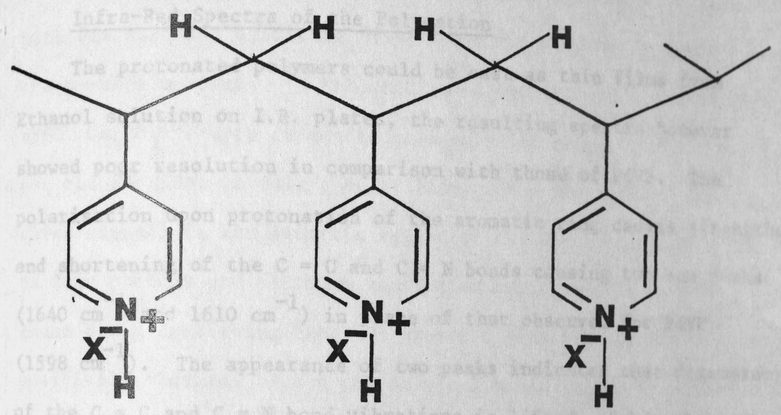
Infra-Red Study Of Poly(4-vinylpyridine)

By evaporation of a dilute solution of P4VP in chloroform on an infra-red transparent plate, a thin good quality film of the polymer suitable for I.R. spectroscipy was obtained. The resulting well resolved spectrum closely resembled that of the monomer.

Generally those absorptions of greatest interest to us for the investigation are those associated with C = C and C = N vibrations in the ring and vinyl groups, we shall see that these can provide information concerning the situation of the monomer or polymer as ligand.

Protonation of P4VP by reaction with acid gave a pendant

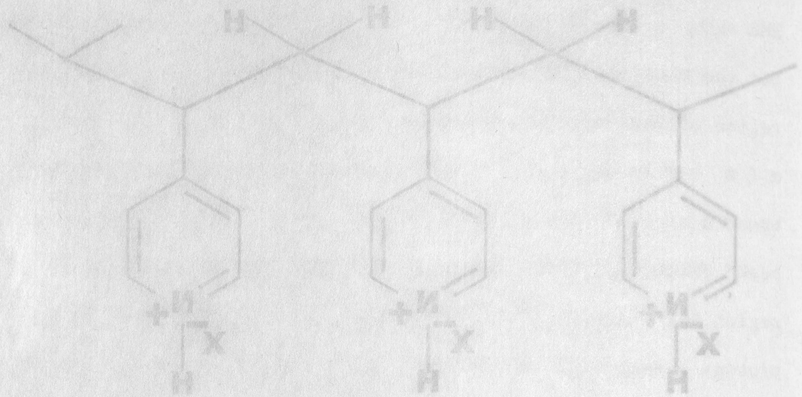
polymer corresponding to the $4VPH^+$ cation, the linear polymeric products are polyelectrolytes that is a polycation with associate monomeric counterions maintaining electrical neutrality.



Just as the $4VPH^+$ monomeric species can be related to the 'neutral' monomer so too can the polycation to the unreacted polymer.

Proton NMR of the Polyvinylpyridinium cation. ($P4VPH^+$)

Protonation increases the electron withdrawing power of the nitrogen atom upon which the positive charge mainly resides, thus,as for the monomers increased de-shielding of protons on the aromatic ring occurs, with those on the β carbons being most strongly affected through delocalisation. The ^1H NMR spectrum then,shows two peaks in the aromatic region shifted downfield (δ8.5, 7.5) relative to those for the unreacted polymer. Again these peaks are broad through failure to fully resolve splitting caused by coupling. Vinyl proton absorption peaks are totally



absent with methine and methylene peaks appearing at 1.5 - 2.6 ppm confirming the pendant structure of the product. As for the monomeric analogues the counterion present in solution has no effect on the spectrum of the poly-cation.

Infra-Red Spectra of the Polycation

The protonated polymers could be cast as thin films from Ethanol solution on I.R. plates, the resulting spectra however showed poor resolution in comparison with those of P4VP. The polarisation upon protonation of the aromatic ring causes strengthening and shortening of the C = C and C = N bonds causing two new peaks (1640 cm^{-1} and 1610 cm^{-1}) in place of that observed for P4VP (1598 cm^{-1}). The appearance of two peaks indicates that degeneracy of the C = C and C = N bond vibrations is lifted. Other changes occur as for the monomer analogues.

4. The N-Oxidized Derivatives

Pyridine-N-Oxide (PyNO) is simply prepared from Pyridine by the method of Ochai[68] using an oxidizing mixture of Hydrogen peroxide in Acetic acid. The resulting N-oxide which is a very hygroscopic solid is, like Pyridine capable of acting as a ligand to T.M. cations and some such complexes have previously been characterised.[67,84] With perchlorate as non-complexing counterion isolation even of hexakis complexes is possible[67] with other counterions complexes with fewer N-oxide ligands often results.

Several attempts were made in the course of this project to produce 4-Vinylpyridine-N-oxide (4VPNO) from 4VP by the method of Ochai, and previously a patent dealing with such reactions and claiming that N-oxidation of monomer vinylpyridines including

4VP was possible had been registered.[92] It soon became obvious that the claims of that patent were not fully valid, dissolving monomer 4VP in acetic acid as required produces initially the protonated species $4VPH^+ CH_3CO_2^-$ and if this were stable, reaction with the peroxide oxidizing mixutre would indeed be expected to give the N-oxide monomer. ^1H NMR studies of this reaction showed that $4VPH^+ CH_3CO_2^-$ reacts in acetic acid solution to yield a new species, not the N-oxide, in only a short time. This new species still gives signals in the aromatic region of the spectrum which integrate as four protons and although resolution drops no shift occurs for these peaks confirming that the aromatic ring remains intact and positively charged. Peaks due to vinyl bonds initially present however disappeared whilst new peaks appear at δ 3.7 and δ 5.5 each peak integrated as two protons. We have assigned these peaks then to $-CH_2-$ methylene groups and this shows that the product was the previously mentioned ionene type polymer, a very closely related polymer was used in pure form in reactions described in Chapter III, Table 2, this chapter shows relevant data.

5. Poly(4-Vinylpyridinium-N-oxide) (P4VPNO).

Whilst problems occur in N-oxidation of 4VP the reaction of P4VP with the Hydrogen peroxide/acetic acid mixture follows the more simple pathway of pyridine. In order to prepare P4VPNO it was necessary to use Holts modification of the Ochai method.[68,69]

The linear polymer, yellow in colour was rather hygroscopic and this meant that its isolation from aqueous solution during preparation was difficult and required large excess of the alcohol

Table 2

^{1}HNMR Shifts for Derivatives of Poly(4-Vinylpyridine)

Polymer	Protons on C2 Carbon Atoms	Protons on C3 Carbon Atoms	Protons on Backbone Chain
Poly(4-Vinylpyridine) ($CDCl_3$)	8.2	6.3	1.5 - 2.5
Poly(4-Vinylpyridine-N-Oxide	8.5	6.95	1.4 - 2.6
Poly(4-Vinylpyridinium Chloride	8.5	7.5	1.3 - 2.6

precipitant used. Oxidation of cross-linked P4VP was much more simple, with the pale yellow products absorbing only small amounts of moisture from the atmosphere. Characterisation of the linear product is quite straight forward:-

Proton Nuclear Magnetic Resonance

Proton spectra in D_2O resemble those of the unreacted polymer of the $P4VPH^+$ species. Once again the addition of an electron withdrawing unit causes further de-shielding of the protons on the ring carbons and peaks in the aromatic region are again shifted downfield (Table 1) relative to those in P4VP. Aliphatic protons on the backbone chain can be identified from the absorption at δ = 1.4 - 2.6. Integration confirms that the ratio aromatic/aliphatic = 4/3 and broadening of the peaks occurs as for the other polymers. Table 2 shows the relevant data.

Infra-red Study

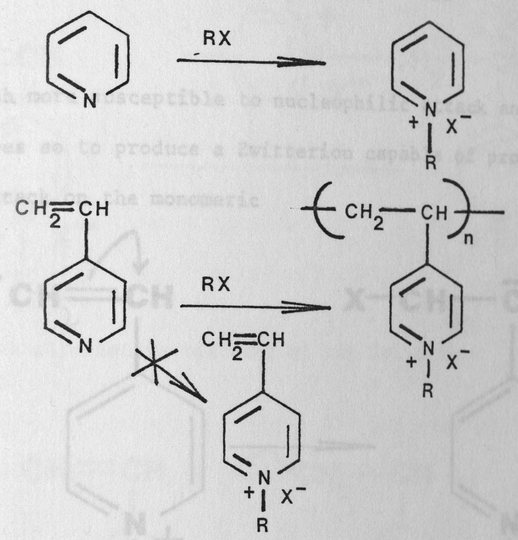
The infra-red spectrum of P4VPNO is still more poorly resolved than that of $P4VPH^+Cl^-$ with rather broad absorption from 1570 - 1630 cm^{-1} due to C = C and C = N vibrations of the aromatic ring whilst N = O stretching vibrations appear at 1235 cm^{-1} and N - O in plane bonding vibrations at 842 cm^{-1}. Once again the peaks in the spectrum are broad and quoted frequencies will generally refer to greatest peak height. In this work the N-oxide bonds in the I.R. are of greater interest to us than are the C = C, C = N bonds because as will be seen from these we can tell the state of coordination of the N-oxide ligand. The remaining absorption bands are similar to those of P4VP though less well resolved.

Of some interest was the observation that N - O stretching vibrations for P4VPNO appear at 1235 cm^{-1} in the I.R. whilst for

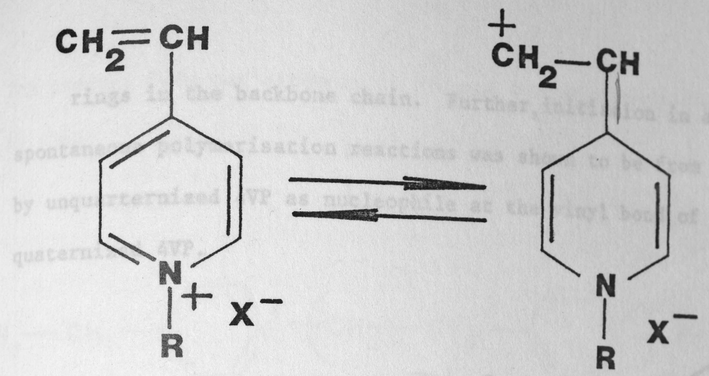
PyNO they appear at 1260 cm^{-1}. [84]

6 The Ionene Polymers.

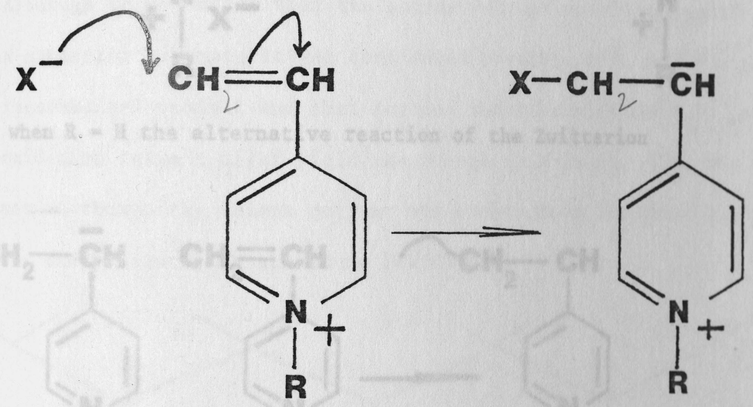
Early work on 4VP by Russian workers[88] showed that reaction of the monomer with quaternizing agents which would normally be expected to give monomeric salts as for Pyridine in a Menschutkin type reaction gave instead a polymeric species:-



and that isolation of the monomeric species III was generally not possible save in a few rather exotic cases[90]. Kabanov et al also examined the reaction of 4VP with acids, once again they obtained polymeric products, which were electrolytes, in place of the monomeric salt and by analogy with the Menschutkin reaction these workers proposed a similar pendant ring structure to the products (R = H above). It was suggested that the reason for spontaneous polymerisation was that introduction of a positive charge onto the ring activates the vinyl bond through induction and resonance.



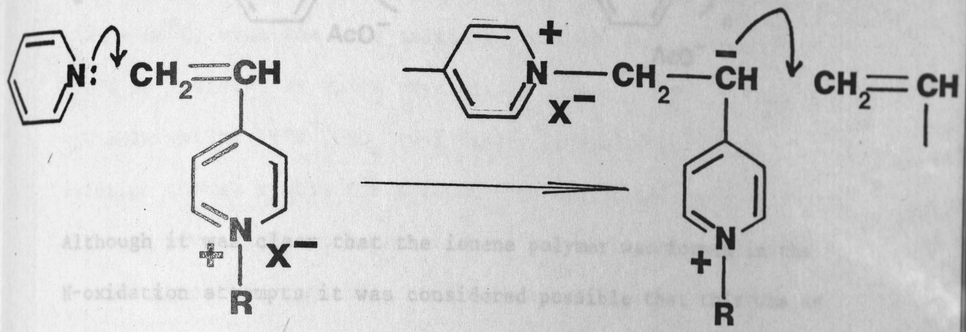
making it much more susceptible to nucleophilic attack and that free anion does so to produce a Zwitterion capable of propagation by further attack on the monomeric



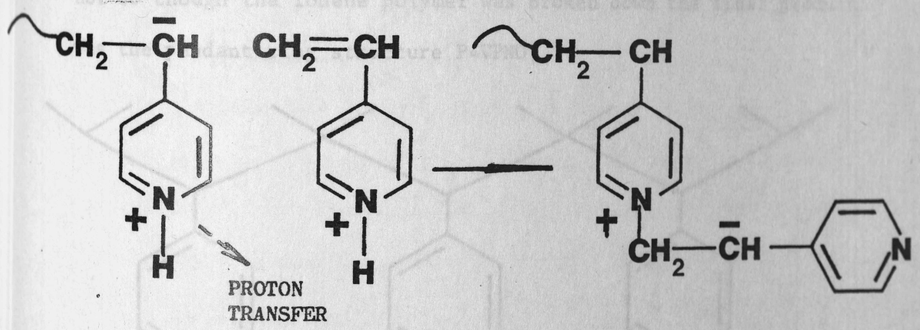
salt yielding ultimately a high molecular weight fully quaternised pendant ring structure polymer.

This assumption that the reaction with protonic acids followed the same course was shown by American workers Fitch et al to be in error. They showed quite clearly that generally protonation of 4VP did indeed give a polymer but the structure was an isomeric form of the pendant poly(4-Vinlypyridinium) cation labelled 'ionene' by the Americans and having a linear structure with Pyridine

rings in the backbone chain. Further, initiation in all the spontaneous polymerisation reactions was shown to be from attack by unquarternized 4VP as nucleophile at the vinyl bond of the quaternized 4VP.

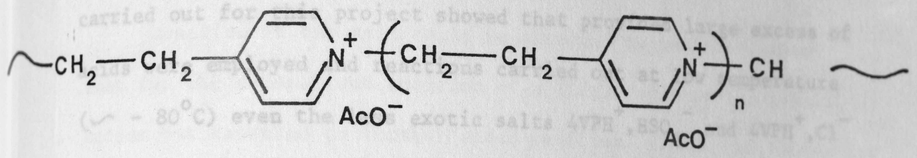


when R = H the alternative reaction of the Zwitterion

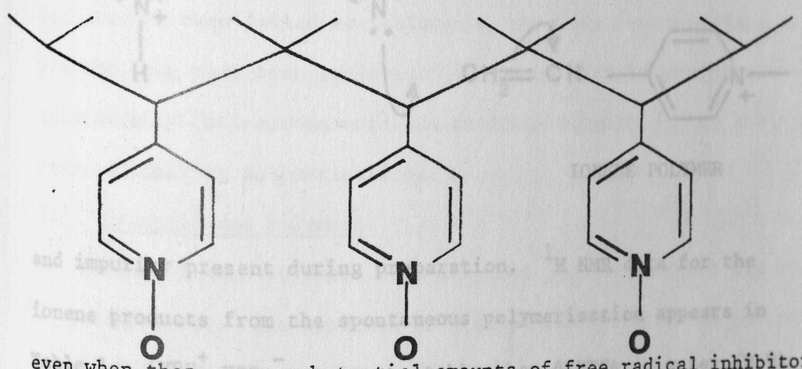


is preferred, this species is then capable of attack as nucleophile once again on the protonated monomer to propogate, yielding the ionene polymer

The product from our attempts to prepare 4-Vinylpyridine-N-oxide is then



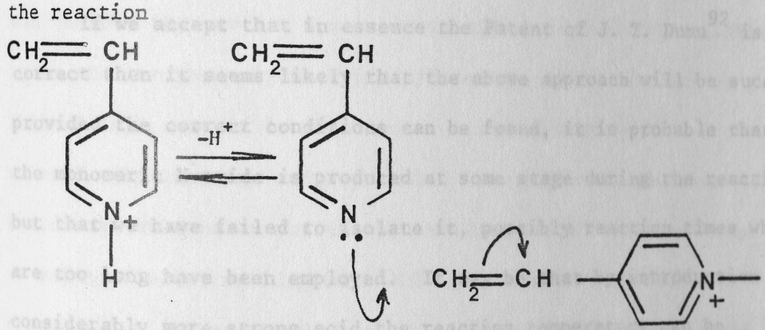
Although it was clear that the ionene polymer was formed in the N-oxidation attempts it was considered possible that this was an intermediate product and that further reaction with the H_2O_2/AcOH oxidation reagent might yield the monomeric N-oxide. This was not so though the ionene polymer was broken down the final product was the pendant ring structure P4VPNO,



even when these were substantial amounts of free radical inhibitor present.

Fitch, Snider et al had shown that if excess of a sufficiently

strong acid such as Trifluoroacetic acid was used in the protonation reaction of 4VP, then very little monomer was present as nucleophile and that the resulting crystalline monomeric product could be isolated. This was stable as a solid and in solution. Work carried out for this project showed that provided large excess of acids were employed and reactions carried out at low temperature ($\sim$ - 80°C) even the less exotic salts $4VPH^+,HSO_4^-$ and $4VPH^+,Cl^-$ could be isolated as white crystalline solids. $4VPH^+,Cl^-$ was quite unstable whilst $4VPH^+,HSO_4^-$ was nearly as stable as 4VPTFA. In solution though stable for a short time the products gradually react to give ionene polymer after a time. This may be due to a combination of production of free monomer capable of initiating the reaction



IONENE POLYMER

and impurity present during preparation. ^1H NMR data for the ionene products from the spontaneous polymerisation appears in Table 1. $4VPH^+,HSO_4^-$ was more stable than 4VPTFA in water (D_2O) whilst $4VPH^+,Cl^-$ reacted more quickly.

The great stability of the $4VPH^+,HSO_4^-$ and 4VPTFA salts

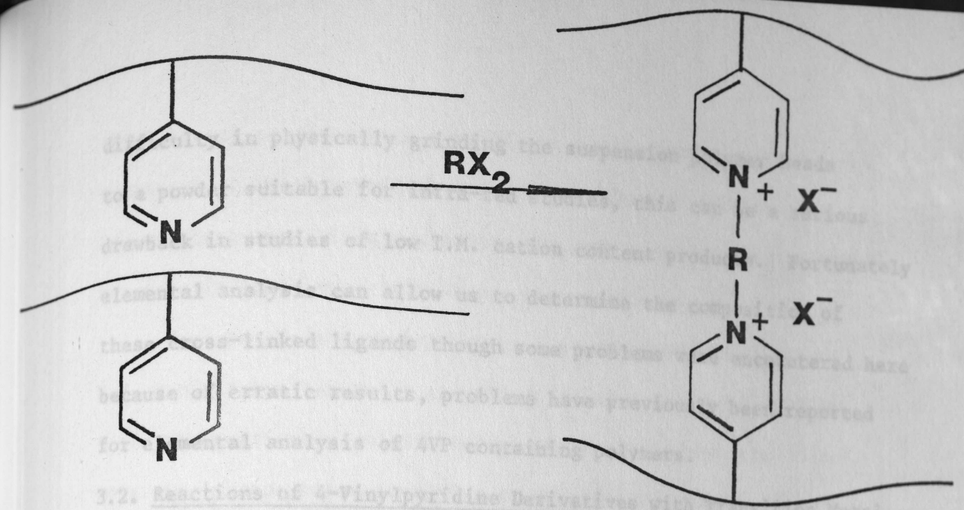
suggested an alternative approach to the N-oxidation of 4VP. Using these salts in place of neutral 4VP we expected to be able to overcome the ionene formation and obtain monomeric 4-Vinylpyridine-N-oxide (4VPNO).

Reaction of the salt could be expected to be faster than that for the monomer and addition of a little acid to the reaction medium was expected to further speed reaction. 4VPTFA was chosen for the reaction having a more suitable counterion. The results were disappointing, once again the final product could not be isolated by vacuum low temperature distillation and ^{1}H NMR showed the product to be the corresponding polymer P4VPNO even though free radical inhibitors (t-butyl catechol) were used.

If we accept that in essence the Patent of J. T. Dunn[92] is correct then it seems likely that the above approach will be successful provided the correct conditions can be found, it is probable that the monomeric N-oxide is produced at some stage during the reaction but that we have failed to isolate it, possibly reaction times which are too long have been employed. It may be that by introduction of considerably more strong acid the reaction temperature can be reduced limiting polymerisation.

7. Cross-Linked Polymers

Cross-linked polymers were prepared from 4VP for use and study in this project. The approach of Nishide and Tsuchida was considered, this consisted of quaternization of the pendant pyridine units of PrVP by reaction with a dihalo alkane to give polymeric products having some units related to those of the monomer Pyridine species previously described.



Such an approach to cross-linking does allow close control of the degree of cross-linking but we considered that the long term stability of such species may be questionable, especially in situations which may involve washing or contamination with strong base. It was decided then to use a more conventional divinyl cross-linking agent and the commonly used divinyl benzene (DVB) was chosen. This divinyl monomer is supplied as a 55-60% mixture with ethenyl ethyl benzene and separation is a difficult process, following the usual practise then the monomer mixture was used as supplied after washing with 10% aqueous sodium hydroxide to remove inhibitor and with water followed by drying. This means that the products are in fact ter-polymers of 4VP, DVB and ethenyl ethyl benzene. Provided the level of the benzene is sufficiently low (2 - 10%) this retains the chemical characteristics of the major fraction.

The cross-linked products generally however are a little more difficult to characterise than are the related linear polymers. Proton NMR for example is no longer possible because the products are insoluble as intended. Similarly thin film deposition on I.R. plates is impossible and we have previously mentioned the

difficulty in physically grinding the suspension polymer beads to a powder suitable for infra-red studies, this can be a serious drawback in studies of low T.M. cation content products. Fortunately elemental analysis can allow us to determine the composition of these cross-linked ligands though some problems were encountered here because of erratic results, problems have previously been reported for elemental analysis of 4VP containing polymers.

3.2. Reactions of 4-Vinylpyridine Derivatives with Transition Metal Cations of the First Row.

1. 4-Vinylpyridine Containing Monomer Analogue Complexes.

Pyridine has long been known as an organic ligand and reactions with divalent T.M. cations from the first row have been very widely studied. Two series of products can generally be obtained in the solid form with most anions, depending on reagent concentration, thus $M(Py)_2X_2$ and $M(Py)_4X_2$ where x = Cl^-, NO_3^- etc., are known. With non-complexing ligands such as perchlorate and nitrate higher numbers of the ligand units may coordinate to the central cation. The tetrakis species $Cu(Py)_4^{2+}$ has been particularly well characterized in solution[96] using u.v.-visible spectrophotometry and e.s.r. techniques and this has provided us with useful information in our investigation of the structures in the complexes of the polymers.

Like Pyridine (Py) 4VP was expected to form complexes with first row transition metal cations and although the brief for this project was to examine reactions and structure of polymers of 4VP with T.M. ions it seemed probable that examination of the 4VP/T.M. complexes would provide information helpful in subsequent investigations. In order to model the macromolecular reaction products described in

this chapter as closely as possible we would normally consider complexes of 4-ethylpyridine rather than those of 4VP, we were however interested in the products not only as models but as vinyl monomers in their own right, hence the compromise.

Some previous work has involved study of 4VP complexes of T.M. cations and generally the chloride salts have been used in their preparation, possibly because the products then are rather more simple than those involving other anions, sulphate, for example (See below). Generally the chlorides have been used for this work also, complexes involving other counterions were prepared and studied in a few cases to aid investigation of differing structures in the polymeric products and to allow comparison with the chloride structure, these too are described in this chapter.

1.i. Complexes From Reaction Of 4-Vinylpyridine With Cobalt (II), Nickel (II) and Copper (II) Chlorides.

We were initially concerned with the separation of these three divalent cations and the structures of polymers containing them and so chose to prepare their monomer analogues to start. The preparations (experimental section) are fairly simple with water or alcohols as solvents for the reagents. Excess 4VP was initially employed for the reactions with Methanol as solvent and the T.M. complexes precipitated quite quickly. Generally 90% or better yields were obtained if the mixtures were cooled to $0^{o}C$ prior to filtration. By adding 4VP solutions to excess T.M. cations a second series of complexes could be prepared. The two series proved later to be the tetrakis and bis 4VP complexes, Copper (II) however reflects its preferred coordination number of four, forming only

the bis complex $Cu(4VP)_2Cl_2$. Differences in the bis and tetrakis Nickel (II) complexes were apparent, the former being yellow-green and insoluble in chloroform whilst the latter was a deeper green and soluble. There was a more dramatic difference for Cobalt (II) complexes with $Co(4VP)_4Cl_2$ being pink-red in colour suggesting an octahedral arrangement of the ligands about the Cobalt (II) cation whilst the bis complex had the intense blue colour usually associated with the tetrahedral arrangement. Study of $Co(4VP)_4Cl_2$ proved extremely difficult because of its rather poor stability, attempts to dissolve the red crystals always yielded blue solutions and attempts to press discs suitable for I.R. spectroscopy with the complex dispersed in a polyethylene matrix again gave a blue colouration, further, nearly all common solvents in which this product was insoluble (ethers etc.) caused a change in its colour to blue upon contact with it. It seems probable that individual 4VP units are displaced by solvent to give the tetrahedral bis complex. A similar situation arises with $Ni(4VP)_4Cl_2$, this is initially easily dissolved in chloroform however a precipitate of the bis complex is soon thrown down.

Elemental Analysis for the Monomer Complexes.

Elemental analysis and EDTA complexiometric titration in dilute acid using Alizarin complexone indicator allowed confirmation of the empirical formulae which were in agreement with the results of Agnew et al.[97, 112] $Co(4VP)_4Cl_2$ and $Ni(4VP)_4Cl_2$ were sufficiently stable for these analyses, though drying above room temperature or at pressures much below 20 m m. Hg caused formation of blue 'patches' on the pink solid. The analytical data appear in Tables 3-6.

1.ii. Complexes Involving Counterions other than Chloride.

Little work dealing with complexes in which the anion is other than chloride or psuedo-halide has been reported for monomer 4VP. In this work preparations of various complexes with 4VP have been carried out to provide models of related polymers. In some cases the products have not been isolated but rather reacted further, generally as vinyl monomer. Thus we observed that reaction of 4VP with excess of Nickel (II) or Cobalt (II) nitrates in Methanol gives the soluble bis complexes $M(4VP)_2(NO_3)_2.4H_2O$, M = Co (II), Ni (II) and Copper (II) gives a similar complex which precipitates slowly on standing (Table 5). With the nitrate ion sharing a typically low tendancy to complex the central cation we could obtain the tetrakis Copper (II) complex when the 4VP ligand was present in excess and expected this to be so for Cobalt (II) and Nickel (II).

Reaction of monomer 4VP with Copper (II) sulphate in Methanol gave a product having an empirical formula approaching that of the complex $Cu(4VP)SO_4$. The Copper content however is rather low giving an actual formula of $Cu(4VP)_{1.45}SO_4.3H_2O$ and this is independant of reagent ratios. Sulphate salts of T.M. cations are known for their ability to yield complexes having irregular stoichiometry and tend to be studied less frequently than chlorides, nitrates and perchlorates. Complexes of 4VP with other sulphates were not prepared.

One problem arose during our studies of the 4VP/T.M. complexes, elemental analyses based on Carbon, Hydrogen and Nitrogen values

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Table 3

Complexes of Transition Metal Ions

Reactions of Vanadyl Salts with 4-Vinylpyridine and some Derivatives

Ligand	Salt	Colour	Elemental Analysis				Empirical formula	Preparative Method
			V	C	H	N		
4VP	$VOCl_2.2H_2O$	Grey - Green	24.5	33.5	2.6	5.5		
	Calculated		23.0 21.0	30.3 34.5	2.5 2.8	5.0 5.7	$(VOCl_2)_5(4VP)_4$- $VO(4VP)Cl_2$	1
4VP	$VOCl_2 2H_2O$	Green	23.0	23.0	2.5	3.5		
	Calculated		22.5	24.7	2.9	3.5	$(VOCl_2.H_2O)_3(4VP)_2$	2
4VP	$VOSO_4.5H_2O$	Grey	22.5	25.0	3.0	3.9		
	Calculated		21.8	24.0	2.8	4.0	$(VOSO_4.H_2O)_3(4VP)_2$	1
4VP	$VOCl_2/ClO_4^-$	Olive - Green		32.6	2.9	5.0		
	Calculated			32.8	3.4	5.4	$VO(4VP)ClO_4.2H_2O$	3
P4VP	$VOCl_2.2H_2O$	Grey	9.5	38.9	4.5	6.3		
	Calculated		9.2	38.1	4.3	6.3	$(VOCl_2.3H_2O)_2(P4VP)_5$	1
P4VP	$VOSO_4.5H_2O$	Grey Green	13.2	28.7	4.0	4.8		
	Calculated		13.6	29.8	4.6	5.0	$(VOSO_4.4H_2O)_3(P4VP)_4$	1

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Table 4

Products from Reaction of Cobalt (II) Salts with 4-Vinylpyridine and some Related Polymeric Ligands

Ligand	Salt	Colour	Elemental Analysis (% weight)						Empirical Formula
			Co		C	H	N	Cl	
			EDTA	AA					
4VP	$CoCl_2 6H_2O$	Blue	17.1	18.5	48.7	4.5	8.2	19.0	
	Calculated		17.32		49.4	4.1	8.2	20.9	$Co(4VP)_2Cl_2$
4VP	$CoCl_2 6H_2O$	Red			61.3	5.3	10.2	14.1	
	Calculated				61.1	5.1	10.2	12.9	
P4VP	$CoCl_2 6H_2O$	Blue	17.8	17.2	42.5 42.4	4.7 4.3	7.0 7.0	18.7	
	Calculated		15.7		44.7	4.8	7.4	18.9	$Co(P4VP)_2Cl_2 2H_2O$
Polymerised $Co(4VP)_2Cl_2$		Blue	13.7 13.8	14.1 15.9	42.8 44.3 48.1	4.5 4.0 4.8	6.2 7.3 8.2	19.3 19.0	
	Calculated		17.32		49.4	4.1	8.2	20.9	$(Co(P4VP)_2Cl_2)_n$

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Table 4 (Cont'd)

Ligand	Salt	Colour	Elemental Analysis (% weight)					Empirical Formula
			Co		C	H	N	Cl	
			EDTA	AA					
Polymerised $Co(4VP)_4Cl_2$		Blue	10.1	11.4	55.0 56.2	5.1 4.9	9.1	14.2	
Calculated			10.7		61.1	5.1	10.1	12.9	$(Co(P4VP)_4Cl_2)_n$
P4VP	$Co(NO_3)_2 6H_2O$	Red	14.9		38.2 36.1	4.2 4.7	12.3 12.0		
Calculated			12.7		36.1	4.7	12.0		$Co(P4VP)_2(NO_3)_2 4H_2O$
Polymerised $Co(4VP)_2(NO_3)_2 4H_2O$		Red	13.9	10.1	40.8	4.0	11.8		
Calculated			12.7		36.1	4.7	12.0		$(Co(P4VP)_2(NO_3)_2 4H_2O)_n$
Calculated			13.7		39.1	4.2	13.0		$(Co(P4VP)_2(NO_3)_2 2H_2O)_n$
Polymerised $Co(4VP)_2Cl_2$ - co Divinylbenzene		Blue	13.9		50.2	3.2	7.1	19.2	

Table 4 (Cont'd)

Ligand	Salt	Colour	Elemental Analysis (% weight) Co		C	H	N	Cl	Empirical Formula
			EDTA	AA					
Polymerised $Co(4VP)_2(NO_3)_2 4H_2O$-co Divinylbenzene		Red	13.21		45.5		12.1		
P4VPNO	$CoCl_2 6H_2O$	Grey	9.72		42.7	4.6	6.8		
Calculated			9.8		41.9	5.3	6.9		$Co(P4VPNO)_3Cl_2 6H_2O$
P4VPNO	$Co(NO_3)_2 6H_2O$	Pink	8.7		45.2	5.0	9.2		
Calculated			8.4		47.0	4.84	11.7		$Co(P4VPNO)_4(NO_3)_2 2H_2O$

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Table 5

Reaction Products of Copper (II) with 4-Vinylpyridine and some Polymeric Derivative

Ligand	Salt	Colour	Elemental Analysis				Empirical Formula	Prep. Method
			Cu	C	H	N		
4VP	$Cu(NO_3)_2 6H_2O$	Blue		51.0	4.8	12.7		
	Calculated			52.0	4.9	13.0	$Cu(4VP)_4(NO_3)_2 2H_2O$	1
4VP	$Cu(NO_3)_2 6H_2O$	Blue-Green		37.9	3.7	11.8		
				37.3	3.8	12.2		2
	Calculated			35.8	4.7	12.0	$Cu(4VP)_2(NO_3)_2 4H_2O$	
	Calculated			38.7	4.1	12.9	$Cu(4VP)_2(NO_3)_2 2H_2O$	
4VP	$CuCl_2 2H_2O$	Green	18.3	49.2	4.2	8.3		
	Calculated		18.43	48.8	4.1	8.1	$Cu(4VP)_2Cl_2$	
4VP	$CuSO_4.5H_2O$	Pale-blue Green	17.1	33.3	3.7	5.4		
			16.4	32.1	4.0	5.3		
	Calculated		16.46	32.0	4.7	5.34	$Cu(4VP)_{1.47}SO_4.4H_2O$	
	Calculated		24.5	32.0	2.6	5.3	$Cu(4VP)\ SO_4$	

Table 5 (cont'd)

Ligand	Salt	Colour	Elemental Analysis				Empirical Formula	Prep. Method
			Cu	C	H	N		
P4VP	$Cu(NO_3)_2 6H_2O$	Blue		38.4	3.5	12.5		
	Calculated			38.7	4.1	12.9	$Cu(P4VP)_2(NO_3)_2 2H_2O$	3
P4VP	$CuCl_2 2H_2O$	Green	16.8	39.3	3.8	6.4		1
			16.5	39.2	3.9	6.5		
P4VP	$CuCl_2 . 2H_2O$	Green	16.5	42.7	4.2	7.0		3
	Calculated		17.6	42.0	4.6	7.0	$Cu(P4VP)_{1.8}Cl_2 2H_2O$	
	Calculated		16.7	44.1	4.7	7.3	$Cu(P4VP)_2Cl_2 2H_2O$	
P4VPNO	$CuCl_2 2H_2O$	Green	11.7	42.8	4.1	7.1		
	Calculated		11.9	42.6	5.0	7.1	$Cu(P4VPNO)_{2.7}\ Cl_2 . 2H_2O$	1
P4VPNO	$Cu(NO_3)_2 6H_2O$		9.97	42.2	4.5	9.1		
	Calculated		10.8	43.0	4.26	11.9	$Cu(P4VPNO)_3(NO_3)_2 . 2H_2O$	1
P4VP								

Table 6

Elemental Analysis Data for

Manganese (II), Iron (III) and Nickel (II) Complexes

Ligand	TM Salt	% C	% H	% N	% Cl	% M
4VP	$FeCl_3$	34.7	2.64	5.52	31.2	19.9
P4VP	$FeCl_3$	28.8	2.8	4.4	36.4	19.0
P4VPNO	$FeCl_3$	25.0	4.5	4.0		
P4VP	$NiCl_2 6H_2O$	41.1	5.1	6.9		17.2
P4VP	$Ni(NO_3)_2.6H_2O$	42.0	4.6	12.0		9.13
P4VPNO	$NiCl_2 6H_2O$	26.0	3.9	4.3		14.5
$MnCl_2$ Pd'd Complex	$MnCl_2 4H_2O$	46.2	4.5	7.6		

could prove quite erratic with variation in the latter of several percent. Carbon analyses were reliable but could still vary by greater than one percent for the same sample in some cases. Such complications have previously been reported in elemental analyses of polymers of 4VP[94] and though none have been noted for the related Pyridine complexes some have been observed by Larkworthy and Agnew for the complexes of P4VP derivatives with some T.M. chlorides.[85] It seems quite possible that the errors in these cases are related to thermal polymerisation of the monomeric complexes and incomplete ignition of the resulting resinous products. Errors were found to be most significant for % N values.

Infra-red Studies.

Infra-red studies were possible for the bis complexes but as mentioned problems occur with tetrakis complexes. We could extract considerable information concerning the structure of the products from the spectra obtained, a full analysis of changes in the I.R. spectra associated with complex formation has not been attempted. The information obtained can be described in two sections and a similar approach will be used in examination of related complexes having polymeric ligands at a later stage.

i) Absorption Associated with the Monomer 4-Vinylpyridine Ligand.

Generally the whole of the I.R. spectrum above 400 cm^{-1} can be assigned to various vibrations of the 4VP ligand. The number of absorption bands increases for the ligand upon complexation reflecting lower symmetry with degeneracy being lifted for some vibrations. Resolution remains excellent. In plane deformation of the aromatic ring gives rise to a peak at 643 cm^{-1} and this

remains constant for the complexes.

Nakamoto[98] has said that complex formation by Pyridine does not lead to appreciable changes in the higher frequency region of the spectra, the same is not true for 4VP monomer, one of the observations made in this project is that significant shifts do occur for peaks due to C = C and C = N bond stretching vibrations. (1596 cm^{-1} for unreacted monomer) upon complex formation. These shifts are reported in Table 7. Here it seems the (M - N) coordinate bond strength is reflected in the extent of the shift.

ii) Metal Ligand Bond Vibrations.

It is possible in some cases to detect vibrations of metal-ligand (M - L) bonds in the region of the spectrum below 400 cm^{-1}, though care is necessary not to confuse vibrations of the ligand with those of coordinate bonds. 4VP for instance shows a peak at 220 cm^{-1} which we are unable to confidently assign.

Band positions in this region are reported for various complexes of the monomer in Table 8. Little previous work has been reported for the 4VP complexes in this region of the spectrum making definitive assignment of ν(M - Cl) and ν(M - N) vibrations difficult. In some cases comparison with data for related complexes proved useful:- thus $Co(Py)_2Cl_2$ is known to exist in both tetrahedral (blue) and polymeric octahedral bridged (lilac) forms, the blue form shows (Co - Cl) at 347 cm^{-1} and 306 cm^{-1} with ν(M - N) appearing at 253 cm^{-1} whilst the octahedral form has ν(Co - Cl) below 200 cm^{-1} (186 cm^{-1} and 174 cm^{-1}) and ν(M - N) near that of the blue form (243 cm^{-1} and 235 cm^{-1}). There is then close

Table 7

C = C and C= N Stretching Vibrations for Complexes of 4VP and P4VP Prepared by Solution Reaction

T.M. Ion	Polymer Complexes		Unreacted Units	Monomer complex (bis) (cm^{-1})
	Chloride	Nitrate		
VO (II)	1638		1600	1640
Fe (III)	1633	1634	1600	1635
Cu (II)	1618	1617		1617
Ni (II)	1613	1613		1614
Co (II)	1610	1611		1612
Fe (II)	1607	-		-
Zn (II)	1607	1605		1607
Mn (II)	1605	-		1602
4VP	1598		P4VP	1596

Table 8

Metal-Ligand Bond Vibrations in the Far Infra-Red for T.M. Complexes of 4VP and P4VP

Ligand Added	T.M. Cation	Counterion	Vibrations cm^{-1}
4VP	VO (II)	Chloride	400, 352, 325w
4VP	Fe (III)	Chloride	360, 350sh, 280, 267
4VP bis	Co (II)	Chloride	300, 264, 247
4VP bis	Ni (II)	Chloride	
4VP	Cu (II)	Chloride	345, 315, 250
P4VP	Vo (II)	Chloride	340w
P4VP	Mn (II)	Chloride	280w
P4VP	Fe (III)	Chloride	362, 315, 275
P4VP	Fe (II)	Fe (III) Sulphate	275
	Co (II)	Chloride	320, 285, 355
	Co (II)	Nitrate	285w
	Cu (II)	Chloride	310, 295, 270
Polymerised	$Co(4VP)_4Cl_2$		318, 282, 350
	$Co(4VP)_2Cl_2$		318, 282, 350
	$Co(4VP)_2(NO_3)_2 4V_2O$		276w

similarity of $Co(Py)_2Cl_2$ and $Co(4VP)_2Cl_2$ prepared in this project and the latter too is a monomeric tetrahedral species. Further the I.R. spectrum for the blue 'polyethene' discs produced from pink $Co(4VP)_4Cl_2$ samples gave a spectrum identical to that of $Co(4VP)_2Cl_2$ and $Co(Py)_2Cl_2$. This suggests that change from octahedral to tetra hedral arrangement of ligands occurs with loss of 4VP ligand.

The I.R. spectrum of $Cu(4VP)_2Cl_2$ showed three peaks between 400-200 cm^{-1} and from comparison with data for $Cu(Py)_2Cl_2$ a polymeric octahedral complex which showed (Cu - N) at 268 cm^{-1} we could expect the peak at 250 cm^{-1} for $Cu(4VP)_2Cl_2$ to be a Cu^{2+} - N bond vibration. Peaks at 315 and 345 cm^{-1} might then be assigned to ν (Cu^{2+} - Cl) vibrations, Van Ooigen however, assigns bands below 200 cm^{-1} to Cu - Cl bridging groups and it may be that those at 315 and 345 are terminal Cu - Cl bond vibrations which we would expect in this area. The data then concurs with that of Van Ooijen pointing to an octahedral chloride bridged polymer of few units chain length.

Infra-red spectra of complexes having sulphate and nitrate counterions also show that coordinate bond formation occurs with shifts from 1596 cm^{-1} (4VP) to above 1600 cm^{-1} for the ν (C = C) and (C = N) vibrations. For these complexes however examination of the far infra-red region does not always reveal sharp bands due to ν (M - N) or ν (M - Cl).

Infra-red spectrophotometry shows that generally the nitrate ion does not form coordinate bonds to the central T.M. ion whilst sulphate tends to act as a bidentate ligand.

^{1}H NMR Studies of the Tetrakis Complexes.

Previous experience involving ^{1}H NMR spectroscopy in the presence of T.M. cations has shown that coupling leads to shift of absorption peaks with severe broadening in many cases. This was indeed the case for the complexes studied in this work ($Co(4VP)_4Cl_2$ and $Ni(4VP)_4Cl_2$), the Copper (II) complex was insoluble. Shifts are reported below.

Complexes of 4-Vinylpyridine With Other Cations.

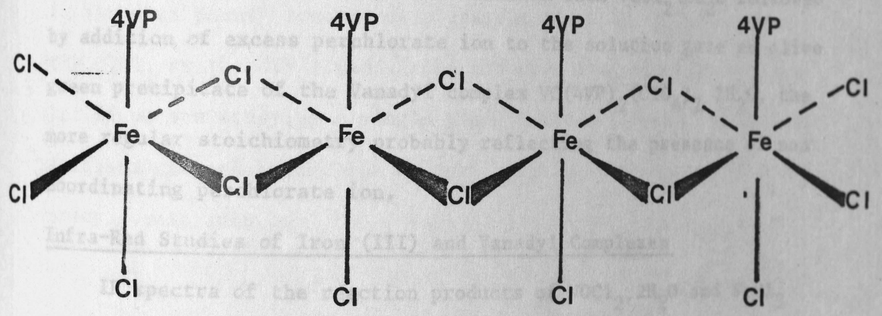
Following the successful isolation of the Cobalt (II), Nickel (II) and Copper (II) complexes attempts were made to prepare the bis 4VP complexes of Iron (III) and VO^{2+} by reaction of the monomer with excess of these ions as chlorides. The method was as previously used (II.2) and the elemental and complexiometric titration results appear in Tables 3 and 6. Clearly there are differences here and the bis complexes are not normally produced.

The reactions of divalent Iron with the monomer have previously been described and the structure of the product discussed.[102] Little if any work involving reaction of trivalent Iron has been reported however. Larkworthy et al have commented upon the tendency of the Iron (II) complexes with 4VP to undergo atmospheric oxidation, this was verified in this

Complex	Shifts (δ)
$Ni(4VP)_4Cl_2$	10.3 (d); 9.6 (d); 3.8:
$Co(4VP)_4Cl_2$	5.15 (M); 5.0; 4.4; 4.0 - 4.3:

project in solution reactions of 4VP in Methanol and water, further, this tendency to oxidation is common for reaction products of Iron (II) with related polymers.

Analysis suggested an empirical formula approaching $Fe(4VP)Cl_3$ but the possibility of there being present some Iron (III) cations not having monomer 4VP as ligand could not be discounted. From this it seemed that a bridged octahedral structure similar to that of the Cu (II) and Fe (II) complexes might be preferred. The new complex was very readily soluble in water suggesting that if a bridged polymeric structure did obtain then vacant coordination sites facilitate solvation.



A similar reaction of hydrated Iron (III) nitrate with the monomer in Methanolic solution gave an orange brown precipitate on warming, this was paler when dry and was initially thought to be a hydrated Fe (III) oxide. Elemental analysis showed presence of monomer presumably as ligand and an empirical formula of $Fe(4VP)_2(NO_3)_3$ $nH_2O(n=4)$ indicating an octahedral arrangement about the central cation is possible.

Similar reactions of 4VP with excess $VOCl_2.2H_2O$ in aqueous ethanol (1:20, water/ethanol, V/V) gave no immediate precipitate but the solution changes from green to a dark blue-green. After standing for twelve hours a grey-green precipitate had formed. Elemental analysis after drying as previously showed that this product contained both the Vanadyl cation and 4VP ligand (Table 3) but the empirical formula of the product $(VO)_5((4VP)(OH)Cl(H_2O))_4$ shows that the structure may be complicated. A similar problem arises for reaction products of Vanadyl sulphate with 4VP in Ethanolic solution. Elemental analysis data indicates an empirical formula of $(VOSO_4\ H_2O)_3(4VP)_2$ for the dried, grey product which may suggest that bridging by sulphate ion is occuring.

Reaction of 4VP in alcoholic solution with $VOCl_2.2H_2O$ followed by addition of excess perchlorate ion to the solution gave an olive green precipitate of the Vanadyl complex $VO(4VP)_2(ClO_4)_2\ 2H_2O$, the more regular stoichiometry probably reflecting the presence of non coordinating perchlorate ion.

Infra-Red Studies of Iron (III) and Vanadyl Complexes

IR spectra of the reaction products of $VOCl_2.2H_2O$ and $FeCl_3$ with 4VP monomer could be compared with those of other complexes involving chloride counter-ion:-

Vibrations of the C = C and C = N bonds are once again shifted to higher frequency and in these cases the shifts are considerably greater than for the complexes previously considered (Table 7). The explanation of these differing shifts may be that coordinate (M - N) bond strengths vary for the complexes examined. It is interesting to see that the shift of ν(C = C) and ν(C = N) are

nearly independant of counterion.

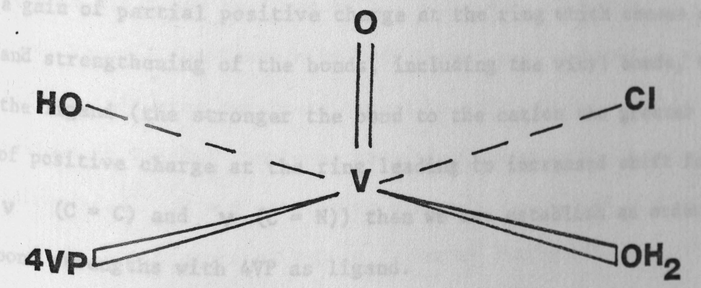
It is relevant to mention a second possible reaction pathway considered but discarded for VO^{2+} and Fe (III) ions. Reactions of the former employed hydrated salts, under some conditions hydrolysis reactions may occur. This would cause increase of solvated proton in the medium and may cause polymerisation of the ligand to give an ionene

$$4VP + H^+ \longrightarrow 4VPH^+ \xrightarrow{4VP} \text{Ionene}$$

probably in the chloride form. We might then expect anion exchange to occur with negatively charged species containing the Vanadyl unit if they were to be present. It seems unlikely that $VO(OH)(H_2O)_2Cl^-$ exists in the final product

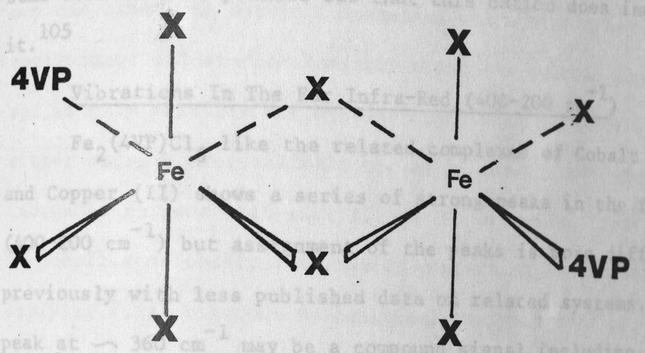
$$\text{Ionene cation}^+ \; / \; VO(OH)(H_2O)_2Cl^-$$

and the data point towards displacement of water as ligand from $VO(H_2O)_2Cl_2$ by the 4VP ligand. The chloride analysis figure shows that if we are studying a single product then chloride is expelled as ligand through hydrolysis at some stage. In this case we might expect a unit such as



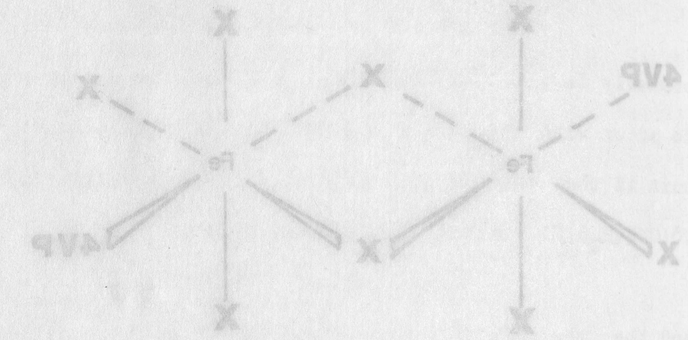
in the product, perhaps with bridging through hydroxy or chloride groups.

The situation for reaction of the monomer with Iron (III) Chloride is slightly more simple, here under anhydrous conditions hydrolysis does not occur. The elemental analysis showed that chloride present was again lower for the complex than for the chloride salt and that no ligand other than chloride and 4VP were present in the complex suggesting a dimeric structure.



Possible Basic Structure

If we accept that shift of ν (C = C, C = N) in the I.R. spectra upon complex formation is related to that occuring upon protonation, the common explanation being that formation of bonds between the nucleophilic Nitrogen and positively charged central ion leads to a gain of partial positive charge at the ring which causes shortening and strengthening of the bonds, including the vinyl bonds, throughout the ligand (the stronger the bond to the cation the greater the gain of positive charge at the ring leading to increased shift for ν (C = C) and ν (C = N)) then we can establish an order of M - N bond strengths with 4VP as ligand.



H $^{+}$N > VO^{2+} N > Fe(III) N > Cu(II) N >
1640cm^{-1} 1638cm^{-1} 1633cm^{-1} 1618cm^{-1}

Ni(II) N > Co(II) N > Mn(II) N > Zn(II) N
1614cm^{-1} 1612cm^{-1} 1605cm^{-1}

This of course resembles the Irving-Williams series and this is to be expected. VO^{2+} is not often quoted in that series but some workers have pointed out that this cation does indeed head it.[105]

Vibrations In The Far Infra-Red (400-200 cm^{-1})

$Fe_2(4VP)Cl_6$ like the related complexes of Cobalt (II), Nickel (II) and Copper (II) shows a series of strong peaks in the far infra-red (400-200 cm^{-1}) but assignment of the peaks is more difficult than previously with less published data on related systems. A broad peak at ~ 360 cm^{-1} may be a compound signal including contributions from ν (Fe(III) - N) and ν (Fe(III) - Cl) vibrations. Assignment of a peak at 267 cm^{-1} is not possible with certainty, it may be due to ν (Fe(III) - Cl) bridging bonds.

I.R. spectra of the monomer complex with Ferric nitrate showed little detail in this area of the Infra-red spectrum, a weak band at about 360 cm^{-1} may be a ν (Fe - N) vibration.

Vanadyl complexes similarly showed only weak-medium peaks in the far infra-red but these cannot be confidently assigned. Recent reviews of Vanadyl complexes have reported no bands in the far infra-red.[105] V = O stretching vibrations give rise to strong characteristic peaks at 990 cm^{-1}, rather little detailed information can be obtained here, the peak is rather insensitive to changes of the coordination sphere.

Nitrate counterion in the reaction product of 4VP with hydrated

Iron (III) nitrate is shown by I.R. to be non-coordinating with only a single (ν (N - O)) band.

Electron Paramagnetic Resonance In Complexes With 4VP Ligand.

Electron paramagnetic resonance (epr) has provided a powerful tool for examination of complexes of some of the first row transition metals (TM) cations. Generally, using this technique, one can expect to obtain information concerning change of the environment and stereo-chemistry about the central ion. Clearly epr is only possible for systems containing unpaired electrons, either organic free radicals or, as in cases considered here, inorganic cations with part filled d orbitals. Fortunately it is possible to obtain information concerning TM complexes without applying fully rigorous mathematical analysis used by some workers, this is because there is a body of knowledge previously established upon which we may draw for comparison with the results of our studies. The systems we have chosen to study are among the most simple abailable with Copper (II), d^9 , we are able to interpret the spectrum in terms of a single position via the 'hole formalism', the VO^{2+}, d^1 system is of course still more simple. There has been a large collection of data published for both cations and this has been useful for comparisons.

We can divide the ions of the first row into two groups, those which give well resolved spectra under suitable conditions at room temperature and those which do not. Into the former group fall Fe(III) d^5, Mn(II) d^5, Cu(II) d^9 and VO^{2+}(d^1) whilst Cr(III), Co(II) and Ni(II) are in the latter. The difference here is that the lattice relaxation times (T) are shorter for the latter group resulting in

uncertainty in the energy level which manifests itself as broadening of absorption lines in the spectrum. Reducing the temperature (to that of liquid Helium in some cases) which reduces line width appreciably in most cases allows detection of an epr signal if this is not possible at room temperature.

EPR In Complexes of Copper (II) With 4VP As Ligand

The epr specturm of the product from reaction of 4VP with Copper (II) sulphate (hydrate) consisted only of a single extremely broad line implying interaction of neighbouring electronic and nuclear spins had occurred in the system which was not magnetically dilute. A g average value of 2.08 was determined.

Previous workers have examined $Cu(4VP)_2Cl_2$ using a variety of techniques some of which have previously been mentioned. The epr spectrum we obtained for the powdered recrystallized complex was surprising in showing three g values; at such high Cu (II) concentration and at room temperature exchange coupling was expected to give broad lines with poor resolution.

Values of

$g_1 = 2.246$, $g_2 = 2.10$ and $g_3 = 2.02$

were determined in this project with hyperfine splitting being apparent for g_1, $A_1 = 112$ Gauss

These values should be compared with those of

$g_1 = 2.26$, $g_2 = 2.08$ and $g_3 = 2.04$

obtained by Ooijen et al.[100] Both sets of data show that $Cu(4VP)_2Cl_2$ does indeed have a rhombic rather than merely an axial (tetragonal)

distortion. Data in this project suggests that the distortion is a little less pronounced than previously suggested.

A second study of the $Cu(4VP)_2Cl_2$ complex has been made[108] and the conclusion there was that the data is compatible with a tetragonally distorted halide bridged structure. A chloride bridged octahedral structure with Cu - Cl bonds of different lengths would be compatible with a three g value epr spectrum.

The $Cu(4VP)_2(NO_3)_2 2H_2O$ complex, like that of the sulphate gave a poorly resolved epr spectrum, with severe broadening of a single line (g_{av} = 2.06). The onset of precipitation of the complex is slow and epr studies of the reaction solution were carried out for various Cu/4VP ratios. g_{av} values are shown in Table 9. A shift of g_{av} from 2.08 to 2.15 is seen as the excess of 4VP increases and the two species $Cu(H_2O)_6^{2+}$ and a derivative of the monomer, probably $Cu(4VP)_2(H_2O)_4^{2+}$, appear to exist together in solution. Increasing complexity of the spectrum with addition of 4VP monomer may reflect presence of a variety of complexes prior to precipitation.

The Vanadyl Complexes

Having said that complexes containing VO^{2+} cation often show good resolution (where one might not initially expect it) because of high lattice relaxation times, it was disappointing to find that the $VOSO_4$/4VP and $VO(ClO_4)_2$/4VP reaction products gave epr spectra showing very poor resolution; no particularly useful information could be obtained, the line width in the $VOSO_4$/4VP complex was of the order of 500 gauss. Presumably the poor resolution is due to exchange coupling with neighbouring

Table 9

Data for Copper (II)/4-Vinylpyridine Solutions

Solution	4VP Added	g Average
$Cu(NO_3)_2 6H_2O$ in Methanol		
10ml of 10^{-3} Molar		2.10
10ml of 10^{-2} Molar	$10^{-3} \div 4$ Mol.	2.08
10ml of 10^{-3} Molar	10^{-3} Mol.	2.03
10ml of 10^{-3} Molar	$10^{-3} \div 4$ Mol.	2.10
10ml of 10^{-3} Molar	10^{-2} Mol.	2.09
10ml of 10^{-1} Molar	10^{-3} Mol.	2.08
10ml of 10^{-1} Molar	2×10^{-3} Mol.	2.08
10ml of 10^{-1} Molar	3×10^{-3} Mol.	2.075
10ml of 10^{-1} Molar	4×10^{-3} Mol.	2.07

paramagnetic species. g_{av} values are given in Table 10.

The situation is different for the Vanadyl chloride/4VP complex however, here the spectrum shows quite good resolution (figure 2) why this difference between $VO(4VP)_2(ClO_4)_2 2H_2O$ and the $VOCl_2$/4VP complex should occur is rather unclear. The spectrum of the latter shows a quite complicated pattern of lines and from it we are able to obtain three g values a situation not commonly found for the Vanadyl cation, indeed we are aware of only one published work reporting three such distinct g values. It may be then that here we are seeing more than one unit in the complex, something we have already considered possible. In that case although some g and A values might be rather insensitive to minor changes more lines would be expected in the epr. The spectrum shown (figure 2) indicates rhombic (approaching tetragonal) distortion in the complex and the g values for perpendicular and parallel directions are shown in Table 10. No published data concerning complexes of 4VP or Pyridine with VO^{2+} was available and it was necessary to make comparison with that available for other complexes.[105,107] g_z for $VO(OH)(4VP)Cl\ H_2O$ has a value considerably below the free electron value with a large hyperfine splitting factor ($A_{||}$) of 187 gauss, g_x and g_y values are also below 2 reflecting the positive value of the spin orbit-coupling constant for Vanadium. The data is compatible with a square pyramidal structure with the single electron in the d_{xy} orbital and localized on the cation; not surprisingly then no super hyperfine structure is observed (d_{xy} does not interact with incoming ligands).

Solution Reactions

Just as we considered the reaction of 4VP with Copper (II)

Table 10

Data from Electron Paramagnetic Resonance Spectra of Powdered High Transition Metal Content Complexes.

Ligand	T.M. Salt	g_x	A_x	g_y	A_y	g_z	A_z
4VP	$VOCl_2.2H_2O$	1.994	77	1.976	80.25	1.952	187.2
P4VP	$VOCl_2.2H_2O$	2.02	76.0	1.981	79.0	1.954	184.4
P4VP	$VOSO_4.5H_2O$	2.02	79.0	1.983	68.5	1.951	185.0
4VP	$CuCl_2.2H_2O$	2.02		2.10		2.246	

		$g_\perp$	A	g_{II}	A
P4VPNO	$VOCl_2.2H_2O$	1.975	73.7	1.93	190.5
P4VPNO	$VOSO_4.5H_2O$	1.989	78.0	1.926	195.0

		g average
P4VP	$CuCl_2.2H_2O$	2.095
4VP	$CuSO_4.5H_2O$	2.12
P4VP	$CuSO_4.5H_2O$	2.10
4VP	$Cu(NO_3)_26H_2O$	2.06
P4VPNO	$CuCl_2.2H_2O$	2.10
P4VP	$MnCl_24H_2O$	2.005

Table 11

Solution	4VP Added	g Average
$VOCl_2 \cdot 2H_2O$ in Methanol		
10ml of 10^{-2} Molar		1.995
10ml of 10^{-1} Molar	10^{-3}	1.995
10ml of 10^{-1} Molar	2×10^{-3} Mol.	1.995
10ml of 10^{-1} Molar	3×10^{-3} Mol.	1.995
10ml of 10^{-1} Molar	4×10^{-3} Mol.	1.995

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Figure 2

Electron Spin Resonance Spectrum

of Product from Reaction of 4VP with

$VOCl_2 \cdot 2H_2O$

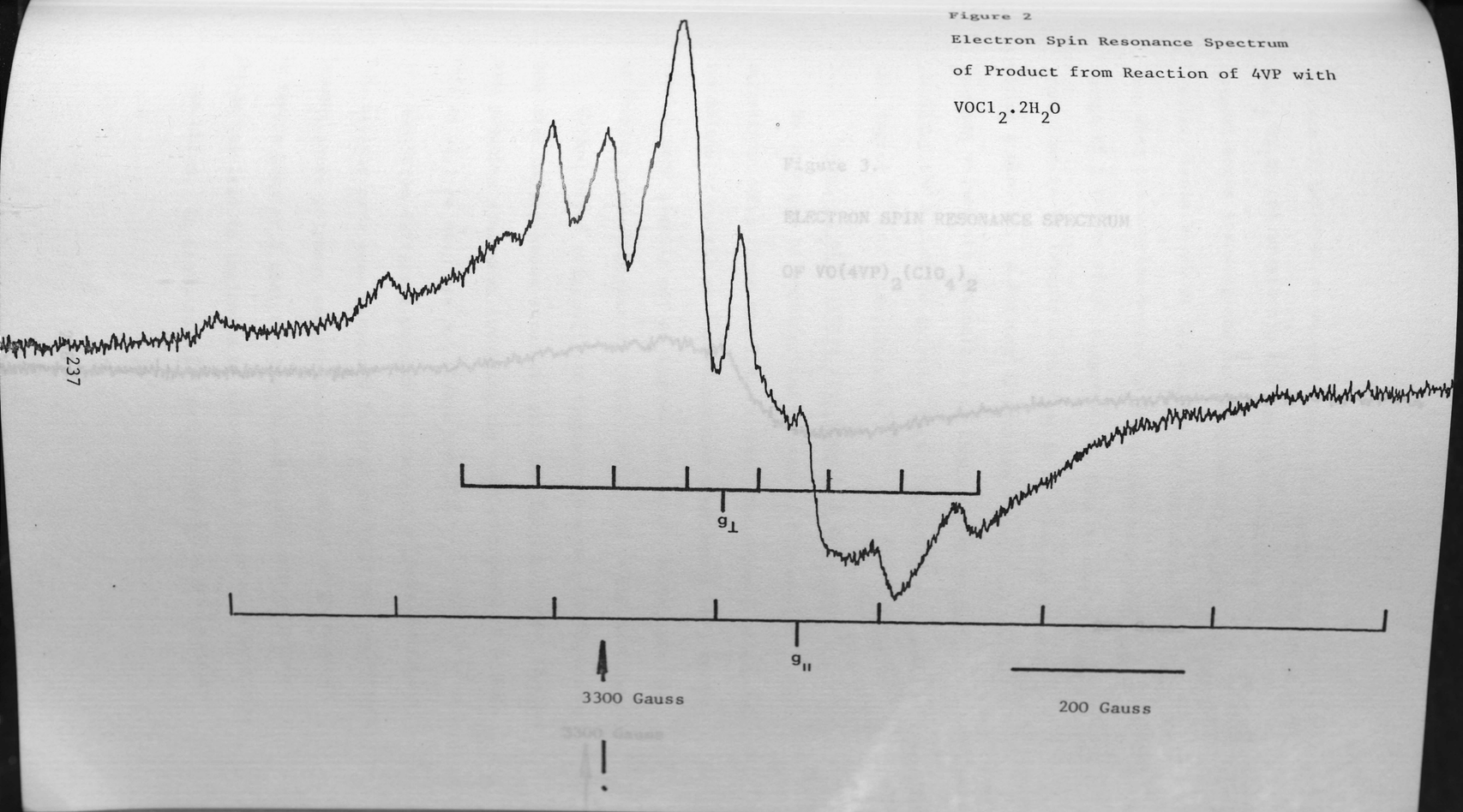


Figure 3.

ELECTRON SPIN RESONANCE SPECTRUM

OF $VO(4VP)_2(ClO_4)_2$

nitrate in Methanol so we could study the similar reaction of $VOCl_2$ $2H_2O$. As previously the complex precipitates only after several hours standing and so the system was suitable for epr studies, Table 11 shows the results for the complex formation. Even when the complex begins to precipitate we see very little change of g values which suggests that when the complex forms precipitation is immediate and that in solution the solvated cation dominates. A further alternative - that g and hyperfine coupling values are insensitive to change in the complex's chemistry and structure exists. Selbin has previously mentioned some degree of such insensitivity.[105]

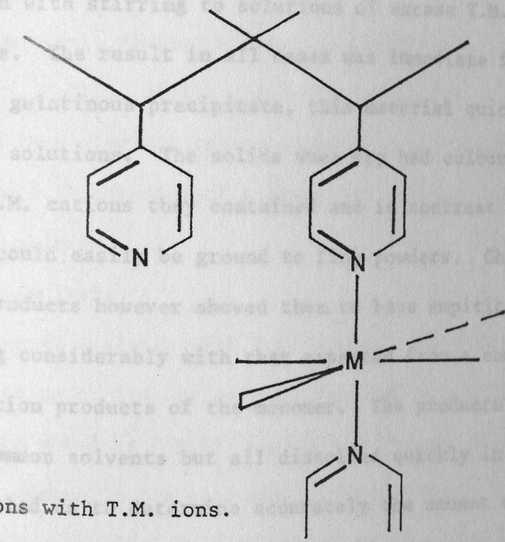
3.3 Reaction of Polymers with Transition Metal Ions

We come now to consider the reaction of P4VP and its derivatives with first row T.M. cations. The attempts to prepare low molecular weight analogue complexes described in the previous section were clearly not an unqualified success though there was no problem with complexes of Co(II), Ni(II) and Cu(II) chlorides.

We had hoped originally to simply compare data for the monomer complexes having known structure with that for the polymers to allow some positive statement involving the reaction products to be made, this as will be seen was not always possible.

The three different methods of obtaining polymers containing T.M. cations have been noted and there is one quite major difference between these polymers and products from reaction of the monomer: We saw in Chapter I that reaction of individual units of polymer chains can lead to inclusion of side reaction products as impurities on the chain. In contrast side reaction impurities are generally

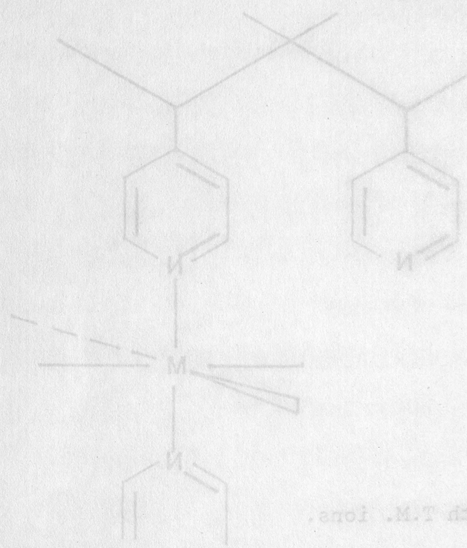
easily removed in reactions of the monomers. The same tends to be true for reaction of the chelating P4VP or P4VPNO with T.M. ions, in the two phase systems clearly unreacted units of the pendant lig d remain as impurity and the same may be true for reactions carried out in solution. We can imagine for instance, that if concentration of the linear polymer solution added to a T.M. salt solution is high, then reaction may not occur uniformly throughout the added macromolecule because as mixing commences rapid precipitation of reaction product may occur with solid forming at some critical stage not necessarily when all ligand units have reacted. Hence both methods (a) and (b) may give copolymers of the type:-



in reactions with T.M. ions.

3.3.1. Transition Metal/Poly(4-vinylpyridine) Complexes from Solution Reactions.

We chose however to attempt to prepare such products having fully reacted ligand units with the expectation that they may provide more effective models for the products from our later studies of the two phase reaction products. It was considered



that under the correct reaction conditions the macromolecules have far greater freedom of movement in solution than do those in the solid with the probability that during the reaction the monomer units are more able to adjust to form complexes because of this increased flexibility.

The number of solvents suitable for reaction of P4VP with simple salts of T.M. ions is limited, in this project the low alcohols, usually methanol or ethanol have been used.

Results

Initially solutions of a linear P4VP (molecular weight 260,000) having a concentration of 105 $g.l^{-1}$ were prepared and this solution was added with stirring to solutions of excess T.M. ions as chlorides. The result in all cases was immediate formation of coloured gelatinous precipitate, this material quickly hardened in the T.M. solutions. The solids when dry had colours characteristic of the T.M. cations they contained and in contrast to the unreacted polymer could easily be ground to fine powders. Chemical analysis of the products however showed them to have empirical formulae differing considerably with that expected from a comparison with the reaction products of the monomer. The products were insoluble in all common solvents but all dissolved quickly in dilute acid. This enabled us to determine accurately the amount of T.M. ion in the products by complexiometric titration using Alizarin complexone as indicator.[77] This confirmed that the concentration of the metal ion in the polymer could be varied over approximately 20% by changing rates of stirring, addition, temperature or concentration. Of additional interest here was the observation that titration

using Alizarin complexone at pH 3.5 gave results which were identical to those using murexide indicator at pH 10. This shows that under these basic conditions the polymer (P4VP) which precipitates in finely divided form does not compete effectively with EDTA for complex formation with the cations. Clearly then we might expect that EDTA could effectively strip T.M. cations from the solid polymer compexes provided sufficient time is allowed for reaction.

The Fully Saturated Polymers

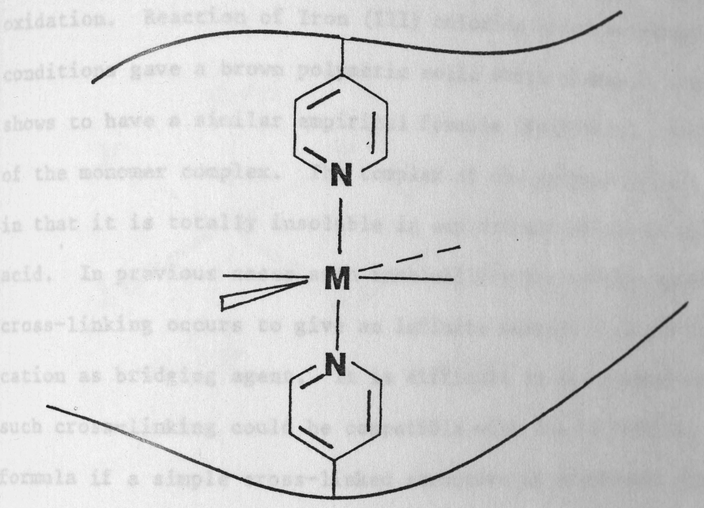
As the reagents were diluted, in particular the polymer solutions, the stoichiometry of the products gradually approached that of the bis 4VP T.M. chlorides and the ratio of M^{2+} to P4VP monomer unit reached a limit in $M(P4VP)_2Cl_2\ 2H_2O$ for M = Mn(II), Co(II), Ni(II) and Zn(II) chlorides. Generally it was found that slow (dropwise) addition of a 1% solution of the polymer to a 5% solution of excess T.M. salt gave the fully saturated species.

Elemental Analysis

Elemental analysis with T.M. cation content determined by EDTA titration or A A analysis of the products in dilute acid gave the results shown in Tables 3-6 for the various cations. It seems then that generally the reaction products have all of the ligand units reacted to give the bis complex, as with the reaction conditions as they were, we could not expect three ligand units from P4VP to complex some cations whilst others remain unreacted.

Molecular models show that if two monomer units from coordinate bonds to each cation then these units must come from separate chains,

or at least from units separated by a considerable distance along a chain, thus the most likely arrangement for the complex involves cross-linking of the linear chains by the T.M. cations:



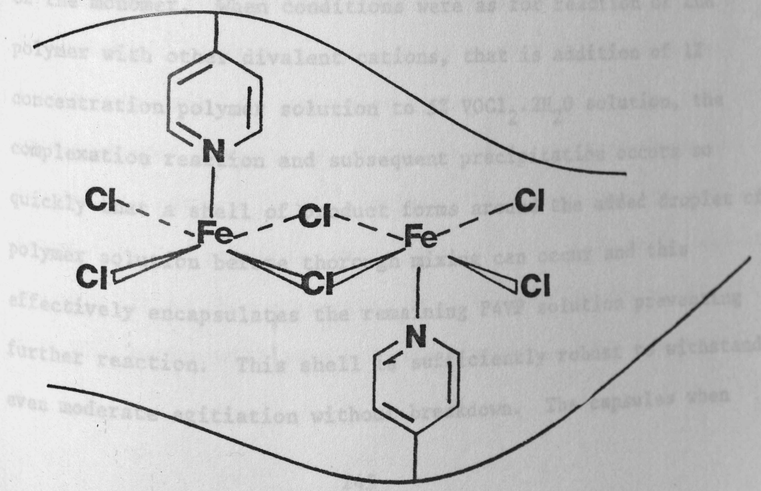
this would explain the total insolubility of these complexes in solvents which do not cause their breakdown.

The empirical formulae based on elemental and cation analyses for polymers from solution reactions involving excess T.M. ion show that preparation of the fully reacted polymers is possible (preparative method 1 Tables 3-6) generally we have obtained

$M(P4VP)_2Cl_2 2H_2O$ and $M(P4VP)_2(NO_3)_2\ 2H_2O$

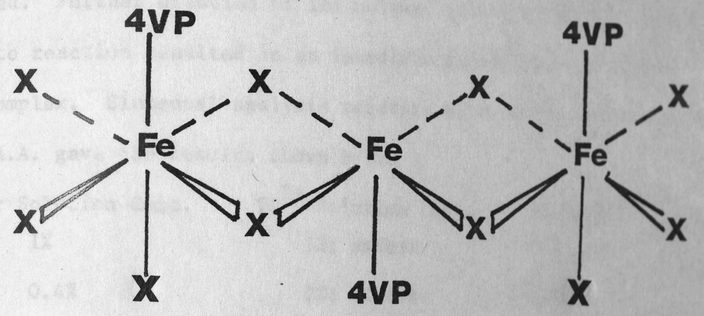
where M = Mn(II), Co(II), Ni(II) and Zn(II). Copper (II) gave $Cu(P4VP)_2(NO_3)_2\ 2H_2O$ but the chloride gave a product $(P4VP)_2(CuCl_2\ H_2O)_3$ where apparently less than two ligand units coordinate to each cation in some cases.

Iron (II) sulphate did react with P4VP in solution giving a pale green precipitate which quickly changed to brown; attempts to prepare this Iron (II) complex under dinitrogen gave a pale green solid which was dried under vacuum, exposure to the atmosphere caused a change to dark brown once again indicating oxidation. Reaction of Iron (III) chloride under anhydrous conditions gave a brown polymeric solid which elemental analysis shows to have a similar empirical formula ($Fe(P4VP)Cl_3$) to that of the monomer complex. The complex of the polymer differs however in that it is totally insoluble in any solvent except mineral acid. In previous cases such insolubility has usually meant that cross-linking occurs to give an infinite network with the T.M. cation as bridging agent. It is difficult to see however how such cross-linking could be compatible with the $Fe(P4VP)Cl_3$ formula if a simple cross-linked structure as previously obtained, instead here the possibility of a slightly different form of cross-linking occurs involving both chloride bridging of the Fe(III) ions and formation of a coordinate bond by each pendant Pyridine unit to a metal ion to give



Here the assumption is made that as previously all ligand units are able to coordinate to cation.

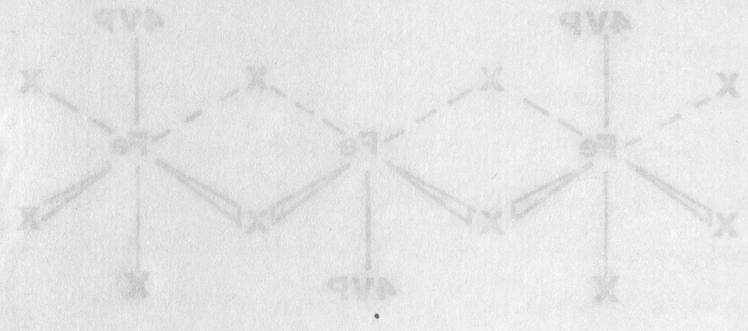
The ease with which the complex of monomer 4VP with Iron (III) chloride dissolves in water suggests that it may not have a polymeric chloride bridged structure



X = Chloride

but rather the dimeric structure mentioned earlier.

The product from reaction of Vanadyl chloride with P4VP in Ethanolic solution precipitated immediately in contrast to that of the monomer. When conditions were as for reaction of the polymer with other divalent cations, that is addition of 1% concentration polymer solution to 5% $VOCl_2.2H_2O$ solution, the complexation reaction and subsequent precipitation occurs so quickly that a shell of product forms around the added droplet of polymer solution before thorough mixing can occur and this effectively encapsulates the remaining P4VP solution preventing further reaction. This shell is sufficiently robust to withstand even moderate agitiation without breakdown. The capsules when



filtered were spherical and released unreacted P4VP solution when crushed. It was then, necessary to further dilute the reagent in order to be sure of obtaining products having the maximum possible degree of complex formation. Dilution of the polymer solution to 0.4% with $VOCl_2\ 2H_2O$ at 2% concentration and with five times excess also gave an immediate precipitate, here however no encapsulation occurred. Further dilution of the polymer solution, to 0.2% w/v, prior to reaction resulted in an immediate precipitate of a pale grey complex. Elemental analysis together with cation determination using A.A. gave the results shown below

Polymer Solution Conc.	VO^{2+} Solution Conc.	P4VP/VO^{2+}
1%	5%; excess	2.56
0.4%	2%; excess	2.532
0.2%	2%; excess	2.502

clearly the difference in reaction conditions has an effect which though appreciable is not as great as our observations may have lead us to expect. The limiting empirical formula is

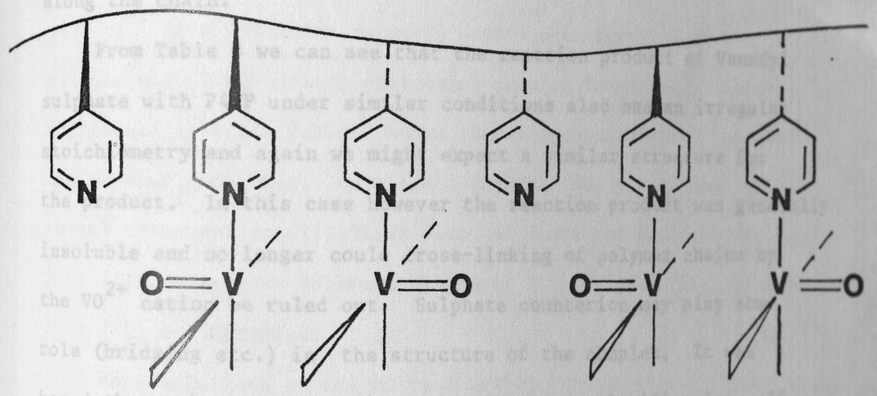
$$(VOCl_2 nH_2O)_2(P4VP)_5$$

where n = 2 or 3 and a simple structure related to those previously is difficult to envisage. The immediate precipitation of the product might suggest that rapid cross-linking takes place within the polymer in this case. The dried product was found to be easily water soluble, this must suggest that either the complexes breakdown upon dissolution or that there is no cross-linking of the polymer network by VO^{2+} cations. This being the case and remembering our previous comment that if two ligand units complex a single cation then cross-linking will result we can see that each VO^{2+} cation will have only one ligand unit from the polymer

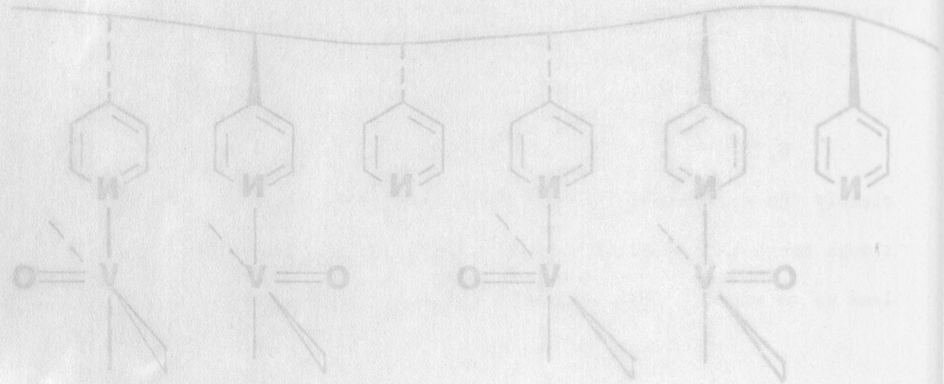
coordinated to it. This must mean that a substantial proportion (one third?) of the units from the polymer chain remain unreacted.

The possibility that water would displace the polymer ligand units from the VO^{2+} complex seems remote if we consider the spectrochemical series and breakdown of the complex seems an improbable explanation for its water solubility.

That the limiting formula has VO^{2+}/P4VP = 2/5 suggests then that there may be units such as are shown in our simplistic diagram



Possibly resembling those in the complex of the 4VP monomer which had a similar empirical formula but which was not soluble. Such an arrangement would explain why not all ligand units form coordinate bonds if every third unit experiences severe hinderance to approach of a cation and such a hinderance may arise from the



V = O bonds themselves. The system however is rather more complicated than is immediately obvious with conformation of the polymer playing a role in the arrangement and change of conformation upon complex formation is probable with energy gained from the M - N bond allowing this change.[55] It may be instead a simple electrostatic interaction with repulsion of incoming positively charged ions by those attached adjacent to the ligand though clearly in this case we might have expected a preference for reaction of alternate ligand units with further reaction of ligands between complexes causing a great increase in repulsion effects along the chain.

From Table 3 we can see that the reaction product of Vanadyl sulphate with P4VP under similar conditions also has an irregular stoichiometry and again we might expect a similar structure for the product. In this case however the reaction product was generally insoluble and no longer could cross-linking of polymer chains by the VO^{2+} cation be ruled out. Sulphate counterion may play some role (bridging etc.) in the structure of the complex. It was hoped that subsequent studies would allow some clarification. If in fact cross-linking of P4VP chains by the VO^{2+} cation is absent then clearly we might expect fewer unreacted pyridine groups in the product.

Infra-Red Studies

Having studied some of the monomer complexes using IR spectroscopy we were able to identify immediately changes in the spectrum of the polymers which might be indicative of complex formation, thus we were particularly interested in the regions 3000 - 4000 cm^{-1}, 1500 - 1700 cm^{-1} and 200 - 400 cm^{-1}. The lower

limit of 200 cm^{-1} for the IR spectrophotometer used in this work has meant that some M - Cl bond vibrations could not be observed. Unsuccessful attempts were made to study these vibrations using an interferometer.

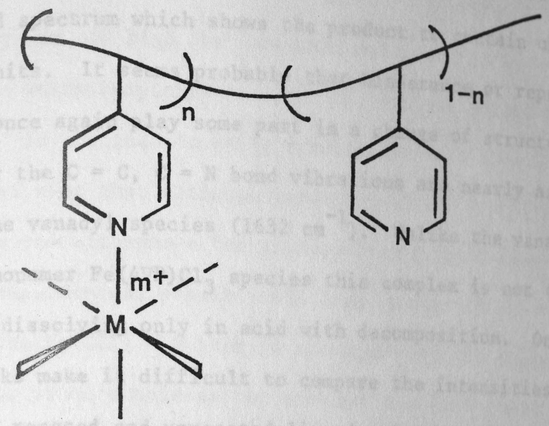
Generally bands in the IR spectra of polymers were broader than those seen for monomer complexes and in many cases resolution was considerably poorer.

Spectra of Products from T.M. Chlorides and Nitrates

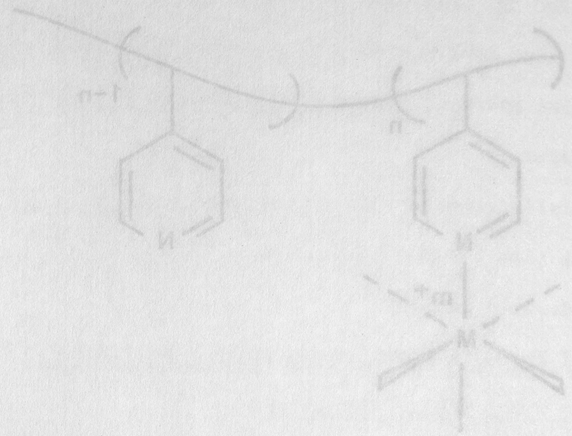
C = C, C = N Stretching Vibrations

Just as for the monomer a shift in the C = C, C = N band at 1598 cm^{-1} (for unreacted polymer) occurs upon reaction of the polymer with T.M. cations indicating complex formation. These shifts are shown in Table 7 where they are compared with those of the monomer complexes. Once again Vanadyl has the highest shift though there are complications here and these are discussed below, Iron (III) came next followed by Copper (II), Nickel (II), Cobalt (II), Zinc (II) and Manganese (II).

When solutions of the polymer having concentrations appreciably above the 1% used in our attempts to prepare the fully coordinated polymers (homopolymers of the bis complex) were employed for reactions, the spectra of the products in the 1600 cm^{-1} region are different:- In place of the single peak above 1600 cm^{-1} we observed two peaks one in the same position as for the reacted polymer but a second close to that for the unreacted P4VP. This clearly shows the differences which can occur when precipitation is so fast that full reaction of the units in the macromolecular chains is impossible giving a copolymer of the metal complex with 4VP. This confirms the findings of elemental analysis.



The complex of P4VP with $VOCl_2$ $2H_2O$ was unique among the divalent chloride derivatives in that this was the only complex which gave two peaks for C = C and C = N vibrations even for products from reaction of very dilute polymer solutions. We have already suggested that the unusual empirical formula of $(VOCl_2\ H_2O)_2(P4VP)_5$ indicates only partial complex formation and the I.R. spectrum confirms that earlier comment with the two peaks which can indeed be assigned to reacted and unreacted ligand vibrations. Although resolution in spectra of the polymers is rather reduced relative to complexes of monomer 4VP we do see that the proportion of complexed and uncomplexed units based on the band intensities has a ratio of about 3:2. This contradicts our previous conclusion that one pendant unit coordinates to each VO^{2+} cation leaving three units uncomplexed in which case, we should expect the inverse ratio of that obtained from the I.R. study. It may be that some absorption due to coordinated water at 1640 cm^{-1} distorts the picture.



Like the Vanadyl complex that of Iron (III) chloride has an infra-red spectrum which shows the product to contain unreacted ligand units. It seems probable that hinderance or repulsion effects once again play some part in a change of structure. The shift for the C = C, C = N bond vibrations are nearly as great as for the vanadyl species (1632 cm^{-1}). Unlike the vanadyl species and the monomer $Fe(4VP)Cl_3$ species this complex is not (water) soluble, dissolving only in acid with decomposition. Once again broad peaks make it difficult to compare the intensities of the bands for reacted and unreacted ligand units but a figure of about 75% reacted units seems probable. Here in the absence of water it is unlikely that other complicating peaks occur at 1632 cm^{-1}.

The nitrate salts of Cu(II), Ni(II), Co(II) and Manganese gave the bis P4VP complexes as previously reported and the I.R. spectra of these complexes in the 1600 region was very similar to those of the related chloride species. Table 7 shows the comparison of absorption frequencies confirming the formation of coordinate bonds between the polymer and the T.M. cations with full reaction of all units.

Vanadyl sulphate like the chloride gave a solid complex having an I.R. showing two peaks in the 1600 region of the spectrum due to C = C, C = N vibrations. As previously these were due to reacted and unreacted ligand units. Once again an approximate idea of the ratio of the two units is possible from peak height measurement. This showed a value of 65% reacted groups.

The infra-red spectrum of the reaction product of P4VP with Iron (II) sulphate also showed two peaks near 1600 cm^{-1}, one at

1635 cm^{-1} with the second at 1607 cm^{-1}. This peak at the lower frequency was too high for unreacted units and it is thought to be due to units complexed to Iron (II) cations whilst that at 1635 cm^{-1} is assigned to units forming bonds to Iron (III) cations. This shows then that although oxidation of the Iron (II)/P4VP complex occurs in the atmosphere the process is not fully completed at normal temperatures, possibly 15% Iron remains in the divalent state. The Fe(III) - N bond is stronger than the Fe(II) - N bond and as for other complexes the stronger the bond the greater the shift in the C = C, C = N stretching vibrations. It seems then that the Fe(II) - N bonds can be inserted into the bond strength order slightly above that of Mn(II) - N and Zn(II) - N.

Coordinated Water 3200 - 3600 cm^{-1}

Generally for those complexes produced from hydrated salts there appears a rather broad band in this region of the spectrum and this has generally been taken to be a confirmation of the presence of water in the complexes; where there is no other absorption above 1620 cm^{-1} it is possible to observe a band which is of medium strength at 1640 cm^{-1} and it may be that this vibration also is due to C - C stretching which appeared in the unreacted monomer ligand and its complexes, in the polymers this peak is considered to include an element of the vibration of the MO - H bond of coordinated water. In some cases presence of water contradicts other results as will be seen later (for the $COCl_2 6H_2O$/P4VP reaction product for example). Cu(II), Co(II) and Ni(II) can thus form octahedral complexes even when only two P4VP ligand units form co-ordinate bonds to each cation, the remaining co-ordination sites being filled either by counterion or water,

this contrasts with the complexes of the monomer where water is often absent..

Far Infra-Red Spectra of Complexes of P4VP

This region of the spectrum can provide information on metal - ligand coordinate bonds and by comparison with previously published work vibrations can be assigned to ν(M - N) or ν(M - Cl) in some cases. Table 8 gives a list of peaks. Resolution in this region of the spectrum was dramatically reduced thus detail available in spectra of the monomer complexes has to be inferred for related complexes of P4VP.

Complexes of P4VP with sulphates of Cobalt (II), Copper (II) and Vanadyl showed poor resolution generally and no peaks appeared in this area of spectra of those complexes.

The Counterions

A single peak at ~ 1385 (broad) for nitrate showed that this ion was generally un-coordinated (P4VP/$Cu(NO_3)_2 6H_2O$, $Co(NO_3)_2 6H_2O$, $Ni(NO_3)_2 6H_2O$). Sulphate in the complex of P4VP with Copper (II) sulphate showed four peaks (1040, 1070, 1120 and 1170 cm^{-1}) and this points as for the complex of 4VP monomer to bidentate sulphate ligand. Similarly for the complex of P4VP with Vanadyl sulphate.

Vanadyl V = O vibration

Though there is little precedent for far infra-red study of vanadyl complexes a considerable amount of work concerning the (V = O) vibration has been published.[105] In complexes studied here this vibration occurs at 990 cm^{-1} with a shoulder at 978 cm^{-1} suggesting a second (minor) environment for the cation. Selbin however has suggested that this vibration is rather insensitive to changing environment.

Magnetic Susceptibility Measurements

Magnetochemistry has provided a further tool for study of the T.M. complexes prepared in this project. Of prime interest were studies of products from two phase reactions. Results for those products are discussed in the next section. Studies of the model complexes involving the 4VP monomer and P4VP ligands were also made, values for gram and molar susceptibilities are listed in Table 12.

Calculation of μ effective for complexes prepared can allow determination of the number of unpaired electrons in the d orbitals of the cations involved and indicate the stereo chemistry of the complex.

Copper (II) Complexes

Values of μ_e for the Copper (II) complexes of both monomer and polymer fall in the range usually associated with Copper (II), near but slightly above the spin only value for a single unpaired electron. Orbital contribution as a first order effect cannot be expected for a d^9 octahedral or square planar system where d_{z^2} and $d_{x^2-y^2}$ do not commutate (oct.) or where the $d_{x^2-y^2}$ and d_{xy} are of dissimilar energy (tet.). In the former the ground term, ^2E_g, does contain an orbital contribution however, this comes from a remnant mixing of higher T terms of the same multiplicity occurring in the free ion.

Cobalt (II) Complexes

Cobalt (II) complexes of the monomers and polymers prepared from solution show usual values for μ_e. Table 12 shows that all are well above the spin only formula and that some division can be made on the basis of differing stereochemistries:-

For Cobalt (II) (d^7) ions in a regular octahedral field commutation of the t_{2g} electrons is possible with one orbital

Table 12

Magnetic Susceptibility for Complexes of 4VP Derivatives with First Row Transition Metal Ions

Effective Complex formula (1) or Overall empirical formula (2)		$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_M' \times 10^{-6}$	μ_e(B.M.)
$(VOCl_2)(4VP)_{1.25}$	(1)	3.4473	931	977	1.51
$*(VOCl_2 3H_2O)(P4VP)_{1.5}$	(1)	0.9912	299.6	390.6	0.96
$(VOSO_4 H_2O)(P4VPNO)_3$	(1) (2)	2.37	1417.26	1450	1.84
Polymerised $Mn(4VP)_2Cl_2$		23.417	7868.2	7914.1	4.30
$Fe(4VP)Cl_3$	(1) (2)	9.945	2659.8	2731.8	2.53
$Fe(P4VP)Cl_3$	(1) (2)	26.37	7053.9	7126	4.09
$Fe(P4VPNO)Cl_3.3H_2O$	(1) (2)	20.21	6820.9	6934.9	4.03
$Co(4VP)_2Cl_2$	(1)	26.75	9093.9	9139.9	4.62
$Co(4VP)_4Cl_2$	(1)	18.61	10235.3	10281.3	4.90

Table 12 (Cont'd)

Effective Complex formula (1) or Overall empirical formula (2)		$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_M' \times 10^{-6}$	μ_e(B.M.)
$Co(P4VP)_2Cl_2 2H_2O$	(1) (2)	24.1141	9836.11	9905.5	4.80
$Co(P4VP)_2(NO_3)_2 4H_2O$	(1) (2)	20.7826 21.70	9767.0 10779.6	9851 10168.8	4.79 4.87
† $Co(P4VP)_2SO_4 2H_2O$	(1)	21.62	11188.0		5.15
† $Co(P4VP)_2(ACO)_2 2H_2O$	(1)	23.31	11300.0	11390.0	5.16
Polymerised $Co(4VP)_4Cl_2$ $Co(4VP)_2Cl_2$	(1) (2)	26.98	9173.2	9219.2	4.64
Polymerised $Co(4VP)_2Cl_2$	(1) (2)	26.75	9094.0	9139.9	4.62
Polymerised $Co(4VP)_2(NO_3)_2 4H_2O$		19.92	9260.8	9344.8	4.67
$Cu(4VP)_2Cl_2$	(1) (2)	3.89	1341.4	1387.4	1.80
† $Cu(P4VP)_2Cl_2 2H_2O$	(1) (2)	3.90	1486.16	1562.16	1.91
$Cu(P4VP)_{1.8}Cl_2 2H_2O$	(1) (2)	4.18	1372.4	1418.4	1.82

Table 12(Cont'd)

Effective Complex formula (1) or Overall empirical formula (2)		$X_g \times 10^{-6}$	$X_M \times 10^{-6}$	$X_M' \times 10^{-6}$	μ_e(B.M.)
$Cu(P4VP)_2(NO_3)_2 2H_2O$	(1) (2)	3.80	1646	1730	2.01
† $Cu(P4VP)_2SO_4 2H_2O$	(1)	3.76	1525.0	1595.0	1.93
$Co(P4VPNO)_4(NO_3)_2 2H_2O$	(1)	14.930 14.5462	10496.8 10224.5	10604.0 10300	4.97 4.89
$Co(P4VPNO)_3Cl_2 3H_2O$		16.5326 17.5495	9043 9597.8	9435 9681.8	4.64 4.75

* Based on I.R. Data

† Two Phase Reactions

only partly filled. An orbital contribution to the spin moment is therefore expected, the spin orbit coupling constant (λ) is negative for d^7 ions and so μ_e (oct.) is expected to be greater than the equivalent value (μ_e tet.) for the tetrahedral arrangement where transformation of orbitals is not possible for d^7 systems. Ranges of values for tetrahedral (μ_e = 4.4 - 4.8) and octahedral (μ_e = 4.8 - 5.2) have previously been quoted.[101,115]

From the above and with observation of the colour of the complexes as confirmation some comment on the stereochemistries of the complexes can be made:-

The monomers $Co(4VP)_4Cl_2$ and $Co(4VP)_2Cl_2$ are clearly octahedral and tetrahedral respectively, $Co(P4VP)_2Cl_2\ 2H_2O$ is also tetrahedral but the rather high value of μ_e suggests that some distortion towards octahedral with associated coupling occurs. $Co(P4VP)_2(NO_3)_2\ 4H_2O$ is pink indicating octahedral arrangement, here the low μ_e suggests that some distortion towards tetrahedral arrangement with resulting lowering of the orbital contribution to μ_e

Table 12 shows that μ_e values for these products have similar values to those from two phase reaction (all near 4.8) suggesting that the polymeric ligand may be restricting the environment of the Co(II) ion to an intermediate distorted octahedral arrangement.

$Co(P4VPNO)_4(NO_3)_2\ 2H_2O$ is pink and clearly has a regular octahedral arrangement with considerable spin-orbit coupling. Lower μ_e values for $Co(P4VPNO)_3Cl_2 3H_2O$ show that this grey complex, which was previously shown to have a largely octahedral arrangement (visible spectrophotometry), maybe experiencing considerable distortion with reduction of the orbital contribution.

Iron (III) and Vanadyl Complexes

μ_e values for complexes of Iron (III) and Vanadyl have proved difficult to interpret, the values calculated are generally lower than spin only values.

Vanadyl (d^1) usually shows μ_e values close to the spin only value reflecting the high distrotion present in the system. Similarly Iron (III) high spin usually gives spin only values. Table 12 shows the results of this work. Values for Iron (III) below the high spin value are usually attributed to spin pairing but this is improbable for complexes of 4VP and P4VP. No alternative explanation is at present available.

The complex of VO^{2+} with 4VP also has an unusually low and though this not totally unprecedented[105] it is surprising for such an apparently simple system. The related complex of P4VP is still more unusual with its very low μ_e (1.1 BM). It may be that here some element of spin coupling occurs.

Table 12 shows that for complexes involving P4VPNO as ligand values approach that of the spin only value.

Electron Spin Resonance Studies

epr spectra were obtained for complexes of VO^{2+}, Mn (II) and Cu (II) produced from solution reactions. The samples were studied as powders at room temperature.

The Copper Complexes

The product $Cu(P4VP)_{1.76}Cl_2\ 2H_2O$ gave a spectrum showing less detail than had that of $Cu(4VP)_2Cl_2$ with only a single broad line, comparison of $g_\perp$ and $g_{||}$ values then was not possible and rather little information can be obtained from the average g value of 2.09. The spectrum is typical of high Copper (II) content powders at room temperature and shows the result of interaction with

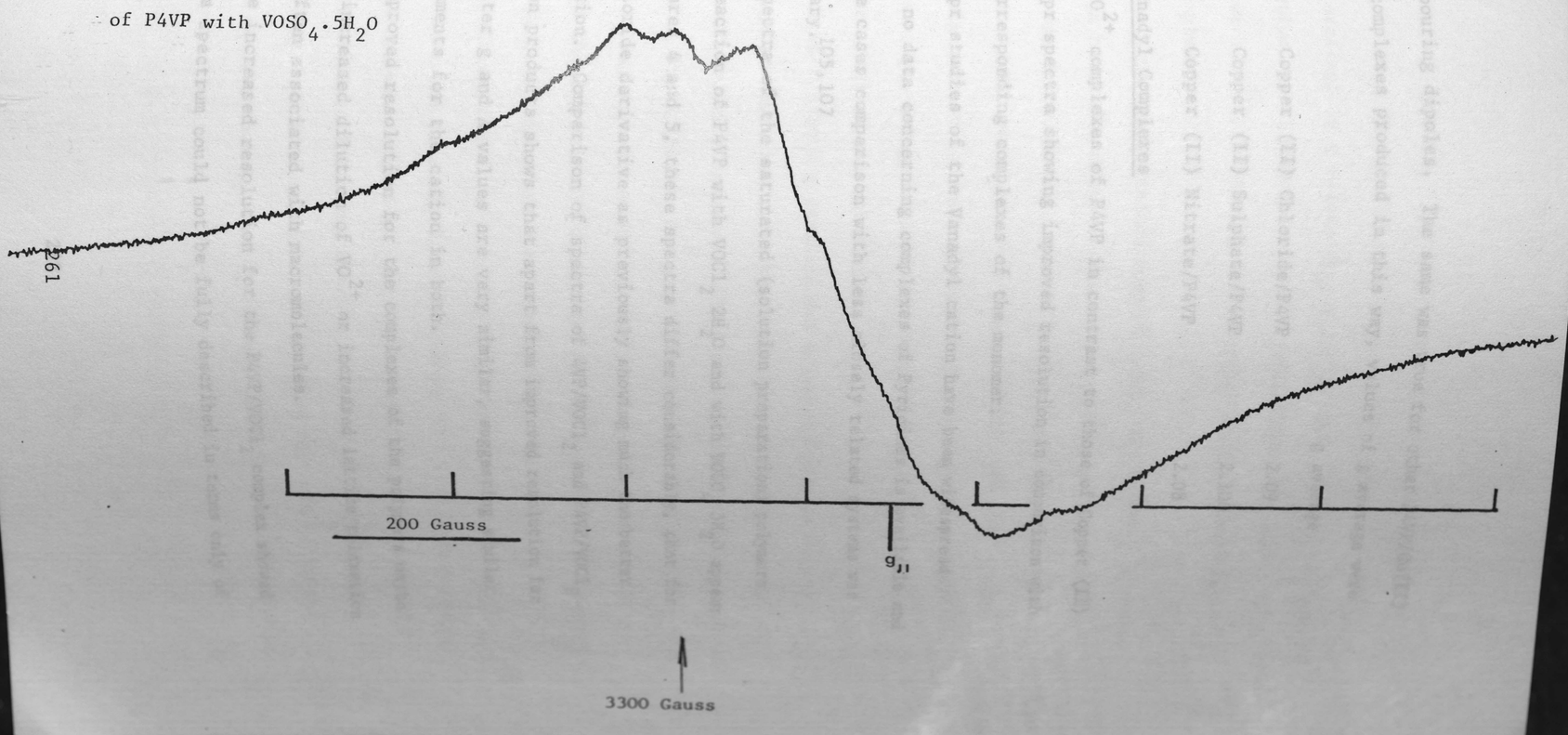
Figure 4
Electron Spin Resonance Spectrum
of 'Solution' Reaction Product of
P4VP with $VOCl_2 \cdot 2H_2O$

Figure 5

Electron Spin Resonance Spectrum

of Product from 'Solution' Reaction

of P4VP with $VOSO_4 \cdot 5H_2O$



neighbouring dipoles. The same was true for other P4VP/Cu(II) salt complexes produced in this way, values of g average were

	g average
Copper (II) Chloride/P4VP	2.09
Copper (II) Sulphate/P4VP	2.108
Copper (II) Nitrate/P4VP	2.08

The Vanadyl Complexes

VO^{2+} complexes of P4VP in contrast to those of Copper (II) gave epr spectra showing improved resolution in comparison with the corresponding complexes of the monomer.

Epr studies of the Vanadyl cation have been widespread though no data concerning complexes of Pyridines is available and in some cases comparison with less closely related systems was necessary.[105,107]

Spectra of the saturated (solution preparation) polymers from reaction of P4VP with $VOCl_2$ $2H_2O$ and with $VOSO_4$ $5H_2O$ appear in figures 4 and 5, these spectra differ considerably, that for the chloride derivative as previously showing much the better resolution. Comparison of spectra of $4VP/VOCl_2$ and $P4VP/VOCl_2$ reaction products shows that apart from improved resolution for the latter g and A values are very similar, suggesting similar environments for the cation in both.

Improved resolution for the complexes of the polymers maybe due to increased dilution of VO^{2+} or increased lattice relaxation times often associated with macromolecules.

The increased resolution for the $P4VP/VOCl_2$ complex showed that the spectrum could not be fully described in terms only of

two g values ($g_{\parallel}$, $g_{\perp}$) it was necessary to invoke a third set of eight lines (I = 7/2) and to describe the spectrum in terms of three overlapping g values (g_x, g_y, g_z). This suggests rhombic distortion rather than merely tetragonal distortion usually associated with VO^{2+}, indicating unsymmetrical ligand arrangement in the xy plane.

The high concentration complex $(VOSO_4\ 4H_2O)_3(P4VP)_4$ in common with the related complex of the monomer shows poor resolution in the epr spectrum, it was possible to identify individual lines and confirm overall resemblance to spectra of the $VOCl_2$/P4VP product but assignment of separate g values for parallel and perpendicular directions was not possible. An average g value close to that of the free electron was calculated.

Values for both g parallel and g perpendicular as well as g average are expected to be below the free electron value (positive spin orbit coupling constant). This was the case for these complexes. For $(VOCl_2\ 3H_2O)_2(P4VP)_5$ the g values are nearly isotropic (figure 4) whilst $A_{\perp}$ and $A_{\parallel}$ values differ widely. These calculated values resemble those previously determined for VO^{2+} complexes[107] confirming the presence of the short V = O bond.

An alternative interpretation of the epr spectrum of this complex in terms of a mixed complex having VO^{2+} ions in two distinct environments with common $g_{\parallel}$ and $A_{\parallel}$ but with differing values for $g_{\perp}$ was considered following the I.R. data which indicated this possibility. No firm rejection was possible but in this latter case it is felt that $g_{\perp}$ and $A_{\perp}$ values might then be more dissimilar.

3.3.1.1 Complexes From Solution Reactions of Poly(4-Vinylpyridine-N-Oxide)

We have described the macromolecular ligand poly(vinylpyridine-N-oxide) (P4VPNO), reported its preparation and given explanations for the failure to isolate the related monomer 4VPNO. That failure meant that reactions of the linear polymer with T.M. ion solutions was the only approach possible which might give complexes having regular stoichiometry which could serve as models for the products (having irregular stoichiometry) from two phase reactions of the cross-linked P4VPNO's mentioned in the next section and Chapter III.

As with the solution reactions of P4VP excess of the reacting T.M. cations in solution and the polymer solution added slowly with stirring. Water was the only suitable solvent for these reactions.

The product complexes do not always precipitate from solution during polymer addition or upon standing, this would generally be accepted as evidence either that

i) If the bis (P4VPNO) complex forms it does so in a manner which does not involve cross-linking of the macromolecules.

or ii) that only species of the type M(P4VPNO)X

where a single ligand coordinates to each cation with no

O - M (II) - O cross-links occurring.

This is because though P4VPNO is very hydrophilic we cannot expcet products involving high levels of cross-linking by metal cations to have similar properties, certainly we observed a dramatic reduction in the affinity for water when an organic cross-linking agent was incorporated in the matrix at low levels (1% DVB) and would expect an effect similar to that seen for P4VP upon forming such cross-links in alcohol solvents to occur

for P4VPNO in water.

The water solubility of the complexes did present problems in their isolation, the only successful method involved a fractional precipitation procedure where methanol was gradually added (dropwise) with stirring to the solution until an initial precipitate formed after which the mixture was chilled for twelve hours and the solid product filtered off. Clearly using this method can involve difficulties in itself, the reacting homo polymer is quite insoluble in Methanol and will precipitate at some stage even if no complex formation has occurred, so too might partially reacted chains if the factionation process is unsuccessful.

Some complexes do precipitate immediately however, including those of Fe(III), Cu(II) and VO^{2+} and here it was expected that preparative reactions involving 1% solutions of P4VPNO would give the fully saturated complexes just as for P4VP. The immediate precipitation maybe an indication that for these three ions cross-linking does occur to some degree.

A summary of elemental analysis results for the complex products is shown in Table 13. This shows clearly that the P4VPNO ligand does form coordinate bonds to T.M. ions. Equally clearly it shows that we have not necessarily been successful in preparing products having regular stoichiometry and must consider the possibility that some of the N-oxide units on the polymer chains are not coordinated in the complex product. This would be surprising as we know that the metal cation was present in large excess in the solution and from comparison with the P4VP reactions we might have expected the bis complex $M(P4VPNO)_2Cl_2\ 2H_2O$ or the mono complex $M(P4VPNO)Cl_2\ 3H_2O$. It is improbable in this case that the rate of precipitation encourages

Table 13

Elemental Analysis of Some N-Oxide Complexes - A Summary

	%					
	M (II)	C	H	N	Fully * Reacted ?	
Vanadyl						
Found	8.5	41.6	5.0	6.9		
Calculated	8.5	42.1	4.85	7.0	?	$VO(P4VPNO)_3SO_4 4H_2O$
Found	14.7	38.1	4.3	6.1		
Calculated	15.1	37.4	3.1	6.2	yes	$((VOCl_2)H_2O)_2(P4VPNO)$
Iron (III)						
Found		26.3	3.4	4.4		
Calculated		24.9	3.85	4.1	yes	$Fe(P4VPNO)Cl_3 3H_2O$
Cobalt (II)						
Found	9.72	42.7	4.6	6.8		
Calculated	9.8	41.9	5.3	6.9	yes	$Co(P4VPNO)_3Cl_2 6H_2O$
Found	8.7	45.2	5.0	9.2		
Calculated	8.4	47.0	4.84	11.7		$Co(P4VPNO)_4(NO_3)_2 2H_2$
Nickel (II)						
Found	14.5	27.5	4.27	4.6		
Calculated	14.9	27.4	4.8	4.6	yes	$Ni(P4VPNO)_{1.28}Cl_2 6H_2$
Copper (II)						
Found	11.7	42.8	4.1	7.1		
Calculated	11.9	42.6	5.0	7.1		$Cu(P4VPNO)_{2.7}Cl_2 2H_2O$
Found	9.97	42.2	4.5	9.1		
Calculated	10.8	43.0	4.26	11.9		$Cu(P4VPNO)_3(NO_3)_2 2H_2$

* From IR Study

production of the copolymer having irregular stoichiometry, as complex formation should have already occurred with the required product actually present in solution (Ni, Co, Mn). There is some possibility that the equilibrium

$$M(H_2O)_6^{2+} + P4VPNO \longrightarrow M(H_2O)_5(P4VPNO)^{2+} + H_2O$$

might lie sufficiently far to the left that the T.M./P4VPNO never actually forms in solution but then we might expect the T.M. ion to remain in solution rather than precipitate with the polymer.

Infra-Red Studies Of Complexes Of P4VPNO

I.R. can show that reaction of P4VPNO does form complexes with T.M. salts involving donation of an electron pair from the Oxygen atom as ligand. It can also confirm that some ligand units do not form coordinate bonds to cation. Metal oxygen bonds are of similar strength to metal - Nitrogen bonds and were also expected to absorb in the far infra-red (below 400 cm^{-1}). Previous work involving P4VPNO as ligand has not described this region of the I.R. spectrum but Quagliano et al describe M - O bond vibrations for complexes of Pyridine-N-oxide (PyNO) as appearing above 300 cm^{-1}. [84] Spectra of complexes of P4VPNO prepared in this project showed peaks in this region and by direct analogy these were assigned to M - O stretching vibrations (Table 14).

N - O stretching vibrations occur at 1265 cm^{-1} for PyNO and a similar strong peak appears in the I.R. spectrum of P4VPNO, here however a considerable reduction in the frequency occurs (1235 - 1237 cm^{-1}). Upon complex formation the N - O band at 1265 cm^{-1} (PyNO) drops to lower frequency and similarly a drop in frequency can be expected for P4VPNO. Here however

if full coordination of the monomer units from the chains does not occur (that is a copolymer forms) there should be two peaks due to N - O stretch one due to reacted ($\leq$ 1235 cm^{-1}) and one to unreacted ($\backsim$ 1235 - 1237 cm^{-1})

The reduction in frequency observed for the N - O vibration occurs because of the effective redistribution of electrons as the partial positive charge gained by oxygen influences and weakens the N - O bond. It is expected then that the stronger the M - O bond the greater the reduction in strength (and I.R. frequency) of the N - O bond.

Several of the M(II) - P4VPNO complex products prepared did show two peaks in the region under consideration thus confirming the incomplete reaction indicated by elemental analysis. From the relative intensities of the two bands it was possible to gain an approximate idea of the ratio of reacted to unreacted units when the latter are present. Generally the ratio of T.M. ions to reacted ligand units is $\backsim$ 1/2 suggesting that the bis complex is usually formed.

Holt et al describe preparation of complexes with P4VPNO which are said to be of regular stochiometry[71] these were prepared in a manner similar to that used in this project, two series of complexes were reported $M(P4VPNO)Cl_2$ and $M(P4VPNO)_2Cl_2$, (M = divalent T.M. ion including Cu(II), Co(II), Ni(II)) these were both thought to have cross-linked structures (see Chapter I).

Table 14

N - O Stretch and Metal Ligand Bond Vibrations in the Infra-Red for P4VPNO Complexes

N - O stretch cm^{-1}		M - L Stretch*	Reacting Salt
Reacted	Unreacted		
1212	none	326 broad	$VO(II)Cl_2.2H_2O$
1212	1235	-	$VOSO_4.5H_2O$
1228	none	-	$Mn(ClO_4)_2.6H_2O$
1210	none	310 broad, strong	$FeCl_3.6H_2O$
1210	none	305 medium*	$CoCl_2.6H_2O$
1210	none	363 weak*	$Co(NO_3)_2.6H_2O$
1210	none	310 medium*	$NiCl_2.6H_2O$
1211	1235sh	310 medium*	$Ni(NO_3)_2.6H_2O$
1210	none	318 medium	$CuCl_2.2H_2O$
1210	1235sh	-	$Cu(NO_3)_2.6H_2O$

* M - O bond vibration?

both were water soluble and as previously noted, cross-linking on a scale such as envisaged by Holt et al would be expected to give insoluble products.

That the bis (P4VPNO) complexes form under conditions involving excess T.M. ion suggests that preparation of the mono (P4VPNO) complex might be more difficult than had originally been expected and it is unfortunate that Holt et al do not report analyses for their proposed $M(P4VPNO)Cl_2$, M = Co(II), Ni(II), Cu(II) complexes.

We have expanded the work on reactions of P4VPNO with T.M. cations a little by considering P4VPNO/$M(NO_3)_2$ hydrate reactions in water. Here we found very much the similar picture as for the chlorides, N-O bonds appeared at exactly the same frequencies in both series but M-O vibrations were less easily observed, Tables 13, and 14 give analyses and I.R. spectral data. Clearly products from the two series are similar.

Resolution generally in I.R. spectra of the P4VPNO complexes was ectremely poor and this has prevented detailed study of other I.R. bands.

One point of particular interest concerns the apparent change of stereochemistry about the Co (II) ion in $Co(P4VPNO)_3Cl_2 6H_2O$, this solid is bright blue after drying at 50°C and visible spectrophotometry confirms a tetrahedral structure (complex envelope at about 640 n.m.) on standing however, the complex turns grey (days), visible spectroscopy confirms that this product consists largely of octagedral species (octahedral/tetrahedral 15/1) an increase in weight suggests that absorption of atmospheric moisture is the cause of this change.

Although I.R. shows a drop in the N-O stretching frequency upon complex formation we did not observe the differences in resulting N-O stretching frequencies we had expected. It had been anticipated that the change would increase with increasing bond strength between the P4VPNO ligand and T.M. ion, clearly this was not the case for Cu (II), Co (II) and Ni (II) chlorides and nitrates, (Table 14) or for Fe (III) and VO (II) chlorides as a shift to a nearly constant frequency occurs. (1210 cm^{-1}).

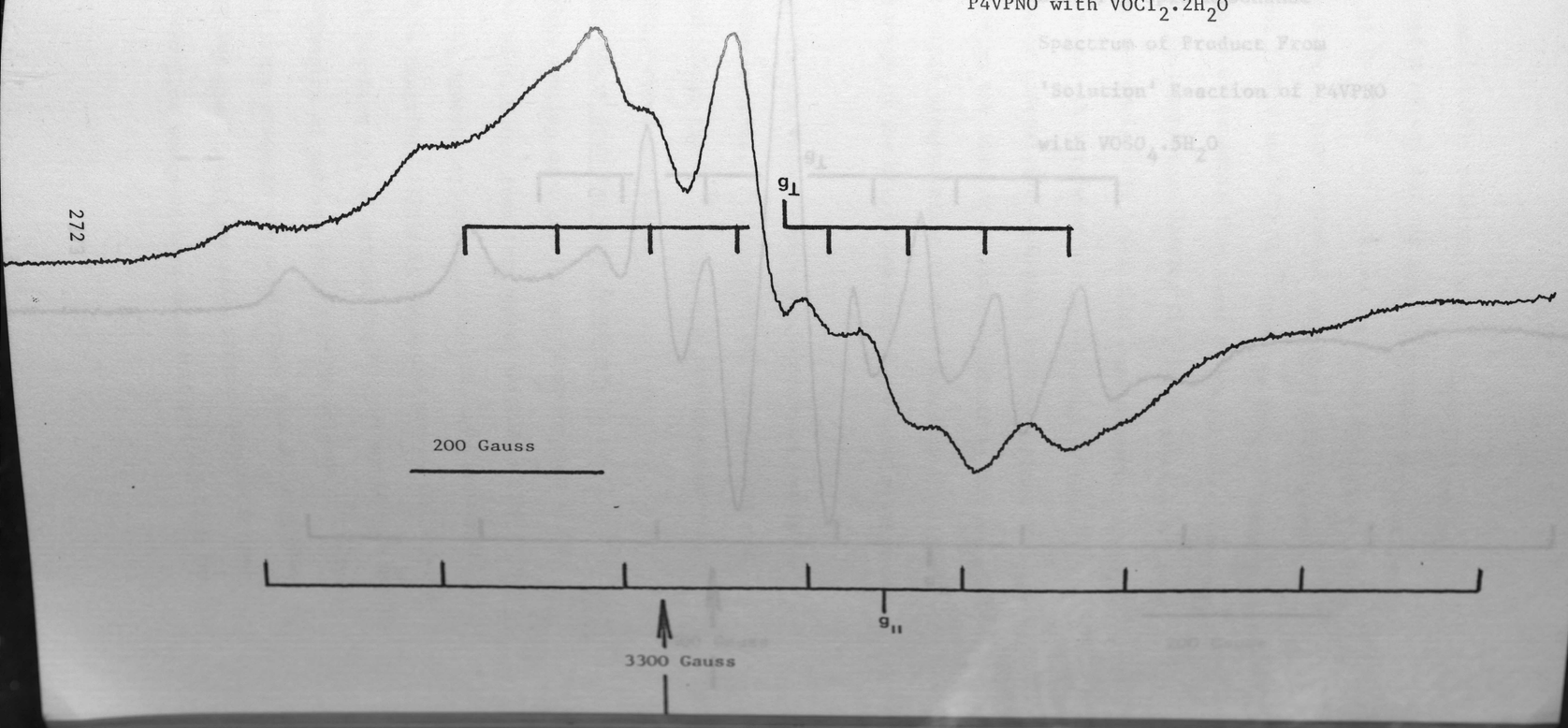
Previous workers have considered M-O stretching frequencies in related complexes,[84] in their studies however they have used perchlorate as counterion thus simplifying the study by ensuring no confusing metal - ligand bonds occur. The situation is less simple in this study where those other metal-ligand bonds are present and may confuse. Assignments for M-O coordinate bonds formed by P4VPNO are only given where there is some evidence to support them.

E.S.R. Studies of P4VPNO/Transition Metal Complexes.

Just as we could obtain e.p.r. spectra for the powdered P4VP complexes so we could for high Cu (II), VO^{2+} or Mn (II) content P4VPNO complexes. Those of Cu (II) gave little information once again and g average values for the broad lines are given in Table 10. Vanadyl complexes once again provide detailed spectra:- Whereas three g values could be identified for the complexes with P4VP the spectra of the related P4VPNO complexes could be described in terms of just two sets of eight lines, effectively $g_{\perp}$ and $g_{\parallel}$. The spectra of the $VOSO_4.5H_2O$ and $VOCl_2.2H_2O$ products are shown in figures 6 and 7 and from these spectra we obtain the values shown in Table 10. Resolution for the $VOSO_4.5H_2O$/P4VPNO complex is

Figure 6

Electron Spin Resonance Spectrum of Product from 'Solution' Reaction of P4VPNO with $VOCl_2.2H_2O$



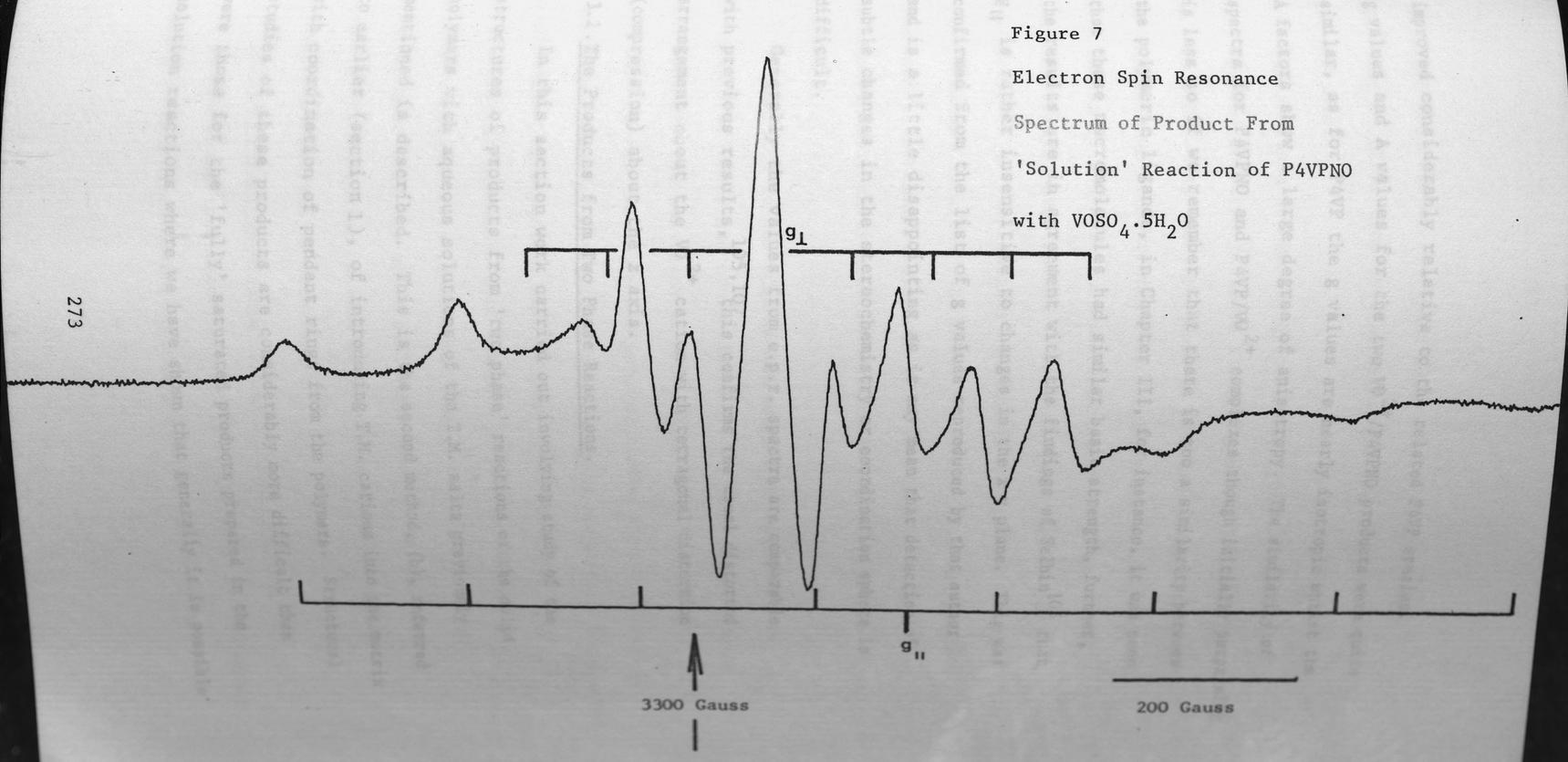


Figure 7

Electron Spin Resonance

Spectrum of Product From

'Solution' Reaction of P4VPNO

with $VOSO_4.5H_2O$

improved considerably relative to the related P4VP species. g values and A values for the two VO^{2+}/P4VPNO products were quite similar, as for P4VP the g values are nearly isotropic whilst the A factors show a large degree of anisotropy. The similarity of spectra for P4VPNO and P4VP/VO^{2+} complexes though initially surprising is less so if we remember that there is too a similarity between the polymeric ligands, in Chapter III, for instance, it was seen that these macromolecules had similar basic strength, further, the results are in agreement with the findings of Selbin[105] that $g_{||}$ is rather insensitive to changes in the x y plane. This was confirmed from the list of g values reproduced by that author and is a little disappointing as it may mean that detection of subtle changes in the stereochemistry or coordination sphere is difficult.

Generally the values from e.p.r. spectra are comparable with previous results,[105,107] this confirms the usual distorted arrangement about the VO^{2+} cation with tetragonal distortion (compression) about the z axis.

3.3.2. The Products from Two Phase Reactions.

In this section work carried out involving study of the structures of products from 'two phase' reactions of the solid polymers with aqueous solutions of the T.M. salts previously mentioned is described. This is the second method, (b), referred to earlier (section 1), of introducing T.M. cations into the matrix with coordination of pendant rings from the polymers. Structural studies of these products are considerably more difficult than were those for the 'fully' saturated products prepared in the solution reactions where we have shown that generally it is possible

to ensure that few or no ligand units remain uncoordinated (VO^{2+} and Fe (III) complexes excepted) provided reaction conditions are suitable.

It was shown in Chapter III that absorption of T.M. cations from aqueous solution followed a definite order, VO^{2+} > Cu(II) > Ni > Co > Zn > Mn, and experience in that work showed that even in reactions of concentrated (0.5 - 1.0M) solutions of the cations with the solid polymers full coordination of the ligand units does not always occur though it was found that much greater concentration of T.M. cations appeared in the products in some cases, than had occurred with 0.1 M solutions. It is the products from such concentrated solutions which will largely be considered in this section, under headings related to those used for the model complexes.

In addition to the high cation content polymers mentioned in Chapter III, P4VP and cross-linked (2% DVB) P4VPNO were reacted with concentrated solutions of $VOCl_2.2H_2O$, $VOSO_4.5H_2O$ and $CuCl_2.2H_2O$. A summary of all the two phase products studied appears in Table 15. Generally elemental analysis of these products can offer rather limited confirmation of structure save in these cases where near fully stoichiometric products occur having a large proportion of the available ligand units reacted and usually values for T.M. ion absorbed have been the major analytical value of interest with analysis of counterion in some cases in order to determine the extent of hydrolysis if occurring.

Poly(4-Vinylpyridine) Ligand In Absorption Complexes.

It was found that reaction with Copper (II) salts to equilibrium could give complexes having empirical formulae which were very

Table 15

Products from Absorption Reactions Considered

Cation	Ligand		Anions
	P4VP	P4VPNO	
VO^{2+}	High content Low content	High and Low content	Cl^-, SO_4^{2-}
Mn (II)	Low content	Low content	Cl^-, NO_3^-, ClO_4^-
Co (II)	High content	High content	Cl^-, NO_3^-
Cu (II)	High and Low content	High and Low content	Cl^-, NO_3^- $SO_4^=$, ClO_4^-

closely similar to those from the equivalent solution reactions. The elemental analysis results show that in some cases absorption can give a product having a ratio of P4VP/Cu (II) less than 2 with chloride counterion whilst the sulphate gives the bis complex.

Attempts to absorb VO^{2+} onto P4VP from concentrated (0.5M) aqueous solution caused partial dissolution of the linear polymer. This points to lack of cross-linking in the product. A gel could be isolated, careful washing and drying gave a green water soluble product which analyses as $VOCl_2(P4VP).2H_2O$. Reaction of the 2% DVB cross-linked P4VP gave a similar green product which analysed as $VOCl_2(P4VP)_{4.2}6H_2O$. Other cations gave products having a lower ratio of metal ion to ligand in the final product, the data are reproduced in Table 16. Nickel (II) did not show the improved absorption from concentrated solutions observed for some other cations and it has not been possible to examine two phase products of this ion, the same is true of Zinc (II) and Manganese (II). Attempts to prepare Iron (III) complexes by two phase reaction failed when precipitation of a hydrated oxide occurred presumably under near neutral pH associated with the presence of the basic solid polymer. Previous workers have not reported this.[61]

Only Copper (II), Vanadyl and Cobalt (II) complexes with P4VP having high cation content could be prepared by absorption of the cation from aqueous solution.

Infra-Red Studies Of Complexes From Two Phase Reactions.

Studies of the T.M. containing polymers by I.R. spectrophotometry were carried out as previously. Products from solution reactions could give very fine powders, those from the two phase

reactions sometimes caused problems, generally grinding of the solid became more difficult as the T.M. content dropped. Polymers containing Cu(II) or VO^{2+} thus gave the best resolution in I.R. spectra. Attempts to press films suitable for I.R. study from the polymer complexes using a steam press (130 - 170°C:30 tes) were unsuccessful.

The Copper Complexes

The I.R. Spectrum of $Cu(P4VP)_2Cl_2.2H_2O$ produced by absorption of Copper (II) chloride resembles closely that of the 'solution' product, in particular showing a similar shift of the C = N, C = C band from 1596 cm^{-1} to 1618 cm^{-1} after reaction. Water possibly in the co-ordination sphere, is indicated by a broad band at 3200 - 3600 cm^{-1} together with appearance of a stronger band than previously at 1640 cm^{-1}. No unreacted units in the polymer chain could be detected. The slight difference in stoichiometry of the 'two phase' and'solution' products may be due to limiting of a secondary reaction possibly chloride bridging, in the former because of the inflexibility of the absorbing matrix.

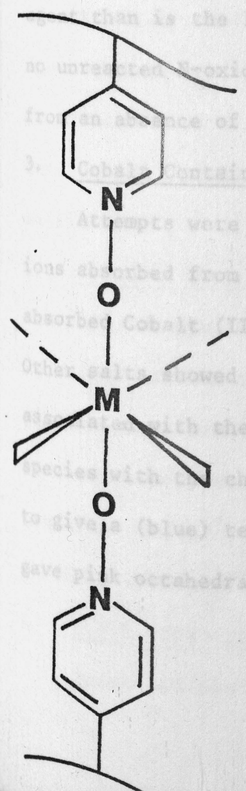
Absorption of Copper (II) sulphate by P4VP was shown in Chapter III to give a limiting stoichiometry of Cu/P4VP = 1/2. Products from reaction of more concentrated solutions of $CuSO_4.5H_2O$ with the P4VP's quickly gave the bis P4VP complex even with cross-linked or very dense polymer samples. Infra-red confirmed the coordination of the P4VP ligand to Cu(II) ions (1596 - 1617 cm^{-1} shift). The sulphate ligand shows for I.R. active bands (1158, 1115 1050 and 970 cm^{-1}) suggesting that it acts as a bidentate ligand.

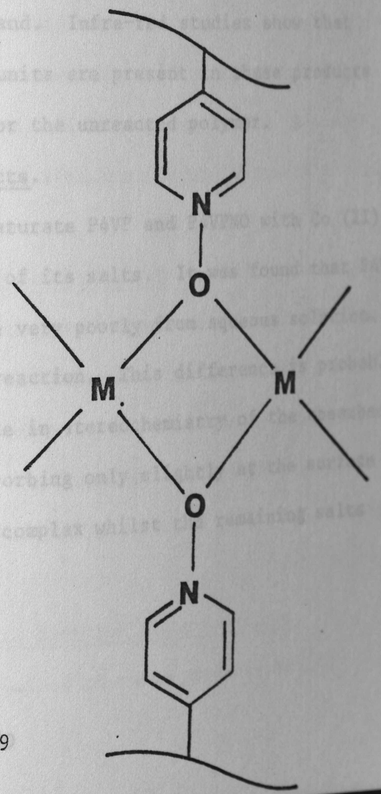
I.R. bands which can be assigned to Cu - Ligand bond vibrations

appear at 305cm^{-1} for the product with chloride counterion and 285cm^{-1} for the sulphate containing products. Presence of water is confirmed in all cases (3200 - 3600cm^{-1}).

Cross-Linked P4VPNO In Absorption Of Transition Metal Ions.

Table 16 shows that absorption by 2% and 8% DVB cross-linked P4VPNO's of Copper (II) from concentrated (~1.0M) solutions does occur. The formulae differ from that of the complex from the linear polymer. I.R. study shows that in both cases N-oxide units are fully reacted and Cu (II) analysis shows that on average 1.5 ligand units coordinate to each cation in the 8% DVB polymer and 1.3 units in the 2% resin. This compares with values of between two and three N-oxide units per Cu (II) in the solution product. This difference is probably due to lower flexibility in the cross-linked N-oxide restricting the number of monomer units from the chain coordinating to each cation:-





N-O stretching vibrations appear in the I.R. spectrum at 1210cm^{-1} as previously together with a Copper-ligand bond vibration at 318cm^{-1}.

2. Vanadyl Containing Products.

The gel-like reaction product VO(P4VP)$Cl_2 2H_2O$ had higher VO^{2+} content than did the equivalent product from solution reaction perhaps reflecting the ease of access of VO^{2+} ions. Infra-red spectra showed however that coordination remains incomplete with peaks at 1640 and 1600cm^{-1} due to reacted and unreacted units in the chain. Peaks due to V = O stretch vibrations as usual occurs at 990cm^{-1}, a shoulder here indicates that there may be more than one site.

The N-oxide complex $VO(P4VPNO)_{4.8}Cl_2 2H_2O$ from the two phase reaction of $VOCl_2.2H_2O$ with a 2% DVB cross-linked P4VPNO shows that the cross-linked macromolecule is a less powerful complexing agent than is the linear ligand. Infra-red studies show that no unreacted N-oxide ligand units are present in these products from an absence of ν(N-O) for the unreacted polymer.

3. Cobalt Containing Products.

Attempts were made to saturate P4VP and P4VPNO with Co (II) ions absorbed from solutions of its salts. It was found that P4VP absorbed Cobalt (II) chloride very poorly from aqueous solution. Other salts showed improved reaction. This difference is probably associated with the difference in stereochemistry of the absorbed species with the chloride absorbing only slightly at the surface to give a (blue) tetrahedral complex whilst the remaining salts gave pink octahedral species.

Table 11 of Chapter III shows the composition of these 'saturated' polymers.

Infra-red spectra of these products showed poor resolution because of difficulty in preparing fine powders from these solids, they do however clearly show the limited reaction with Cobalt (II) ions with broad peaks centered at 1610 - 1611cm^{-1} and 1598cm^{-1}. No detail was evident in the far infra-red.

P4VPNO (2% DVB cross-linked) absorbed Co (II) more strongly than did P4VP (Table 11 Chapter III). It is noteworthy that the Cobalt (II) chloride reaction product was red at all stages in contrast with the blue or grey colouration observed for the dry product from the corresponding solution reaction of the linear P4VPNO. Visible spectrophotometry confirms the octahedral arrangement.

4. Nickel Containing Polymers.

Though P4VP did not absorb Nickel (II) ions from solution the 2% DVB cross-linked P4VPNO did so quite strongly. Table 16 shows the empirical formula at equilibrium. Shift of the peak at 1235cm^{-1} in the I.R. spectrum is incomplete and it is clear that as for the Co (II) product free N-oxide units remain in the matrix.

5. Products from Absorption at Optimum pH

I.R. studies of samples isolated from reactions of P4VP with T.M. cations at optimum pH (described in Chapter III) showed that complex formation could generally be detected by presence of a small peak above 1600cm^{-1} as for the products from solution reactions:- (VO^{2+}, 1638cm^{-1} ; Cu (II), 1617cm^{-1} ; Ni (II), 1613cm^{-1} ; Co (II), 1610cm^{-1}).

6. E.S.R. Spectra of Products from Two Phase Reactions.

Infra-red studies were limited to those products having

relatively high cation content, that is to products of those cations best absorbed, in contrast e.s.r. can allow detailed study of even powdered samples having low T.M. ion concentration. Indeed it is often best to have low ion content for powder studies. Unfortunately it was possible to apply the technique successfully only to Copper (II), Vanadyl and Manganese (II) complexes.

Our initial studies of e.s.r. in two phase products having high T.M. content gave results very much as for the equivalent products from solution reactions, the lines were again broad and gave little detail.

The products from two phase reactions with Cu (II) and VO^{2+} do have one distinct advantage over those from solution reactions:- we are able to obtain them containing T.M. cations distributed throughout the solid matrix as equilibrium with dilute solution occurs. Apparently they are not concentrated merely at surface sites (as occurs for $CoCl_2 6H_2O$). Solution reactions must automatically lead to high localisation of the Cu (II), VO^{2+} or other T.M. ion as, in addition of the ligand to the T.M. solution, it quickly reacts to give cross-linked high cation content product with excess polymer remaining unreacted in solution. Our initial attempts to dilute the Cu (II) (or VO^{2+}) cations in the solution products by reaction with a Zn (II)/Cu (II) mixed solution to give a product more easily studied by e.s.r. techniques failed with all available Cu (II) being absorbed immediately to give a high copper content complex. This is understandable as we have already shown the great preference of the polymer for Cu (II) over Zn (II) ions. Indeed reference to Biedermann's work [52] shows that the order of preference

shown in two phase absorption is generally reflected in products from reaction with mixed cation solutions and it was shown earlier in this work that Cu (II) ions could displace even Cobalt (II) easily from its complexes.

Copper (II) Complexes from Two Phase Reactions.

As the concentration of Copper (II) in the reacting aqueous solutions was reduced more detail could be observed in e.s.r. spectra of the washed dried products. Reaction of P4VP with 10^{-3} Molar Copper (II) salts gave spectra showing at least two g values. These values were very similar for products containing different salts (chloride, nitrate, sulphate, perchlorate). In each case g_{II} has a value above that of $g_{\perp}$, Table 17 shows the results. Clearly we are dealing with systems in which there is tetragonal distortion along the z axis, an extension as is usual for Copper (II). The $g_{\perp}$ region of the spectrum has fine structure from interaction of the electron in the $d_{x^2-y^2}$ orbital with the Cu (II) nuclei (I = 3/2), there is however insufficient detail to allow determination of A_{II}, this is because a second g_{II} value causes complications.

That salts gave products having nearly identical spectra is taken as an indication that at such low Cu (II) concentration the structure of the complex is the same in all cases, with the counterion not participating in the inner coordination sphere possibly species such as $Cu(P4VP)_4(H_2O)_2^{2+}$ are major components. The presence of at least two g_{II} values suggests that there may be a range of species:-

$Cu(P4VP)_4(H_2O)_2^{2+}$, $Cu(P4VP)_3(H_2O)_3^{2+}$

etc., whose composition may depend on the conformations of the

Table 17

Data from Electron Paramagnetic Resonances Spectra of Reaction Products from Reaction of Dilute Copper (II) Solutions with Linear P4VP.

Copper Solution	$g_{\perp}$	A	$g_{\parallel}$	A
$Cu(ClO_4)_2$ Aq.	1) 2.006 2) 2.000	76 G	1) 2.27 2) 2.18	112 127
$Cu(NO_3)_2$ Aq.	1) 2.008 2) 2.000	76 G	1) 2.26 2) 2.18	115 122
$Cu\ SO_4$ Aq.	1) 2.003 2) 2.000	71.5G	1) 2.27 2) 2.19	107 125
$Cu\ Cl_2$ Aq.	1) 2.005 2) 2.000	74 G	1) 2.28 2) 2.18	102 117

polymer. A square planar arrangement for instance of $Cu(P4VP)_4^{2+}$ is probably unlikely, we might then expect g values closer to the free electron value.

Vanadyl Complexes from Two Phase Reactions.

Reaction products of cross-linked P4VP and P4VPNO with concentrated Vanadyl solutions gave e.s.r. spectra which showed a remarkable resemblance to those of the solution reaction products, values are reported in Table 18. Some resemblance was also apparent for products from reaction with much more dilute solutions of this T.M. cation. Figure 8 shows the spectrum for the product from two grams of P4VP with 50ml of 10^{-2} Molar $VOSO_4$. (5×10^{-4} Moles $VOSO_4$, 2×10^{-2} moles P4VP) and that for a similar reaction with $VOCl_2 2H_2O$ appears in figure 9. Table 19 shows a full data table.

A related product from reaction of Vanadyl sulphate with an 8% DVB cross-linked P4VPNO again gave a spectrum we have come to associate with the Vanadyl complexes (Table 19). Clearly in several cases we have found g values for the x y plane close to the free electron value. Generally the g and A values for monomer, solution reaction and two phase polymer complexes are all very similar with the large anisotropy in $A_{||}$ and $A_{\perp}$ but nearly isotropic values for the g tensor. It is of some interest to note that as VO^{2+} content was reduced in the polymer matrix, especially those with the sulphate, resolution in the e.s.r. spectrum improved. Once again it is with some difficulty that we obtain structural information from the g and A values in Tables 18 and 19. In these cases where two g values are obtained for the x and y axes it is difficult to state definitely that both originate in a

Table 18

E.s.r. Data for Product
From Two Phase Reactions

Ligand	T.M. Salt	$g_{\|\|}$	$A_{\|\|}$	$g_{\perp}$	$A_{\perp}$
P4VP 2%DVB	$VOCl_2.2H_2O$ (1.0M)	1.94	184	1.996	78
P4VPNO 2%DVB	$VOCl_2.2H_2O$ (1.0M)	1.934	192	1.971	75
P4VPNO 2%DVB	$VOSO_4.5H_2O$ (1.0M)	1.93	188	1.99	80
P4VP 2%DVB	$CuCl_2.4H_2O$ (1.0M)	g average 2.09			

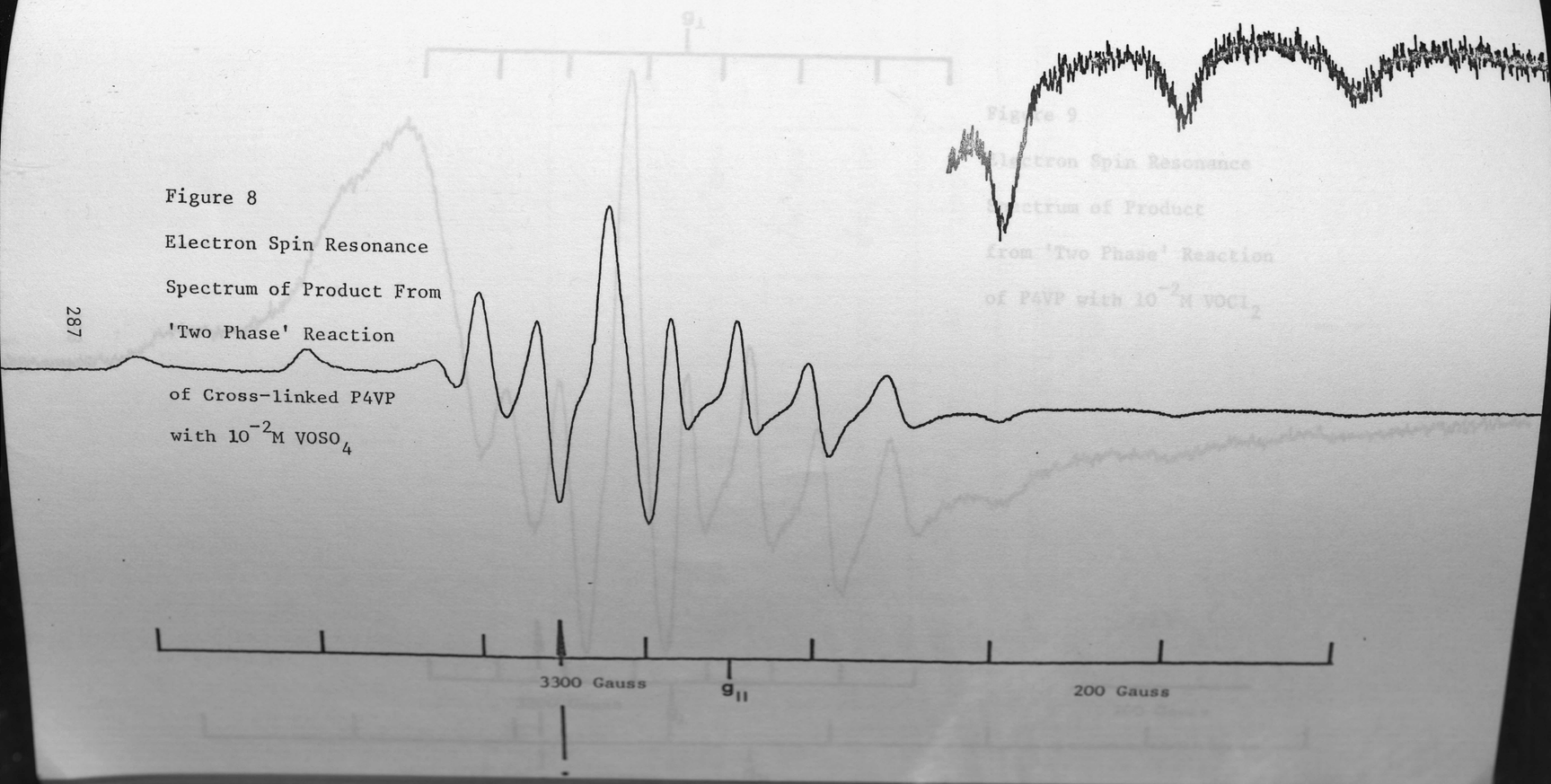


Figure 8

Electron Spin Resonance

Spectrum of Product From

'Two Phase' Reaction

of Cross-linked P4VP

with 10^{-2}M $VOSO_4$

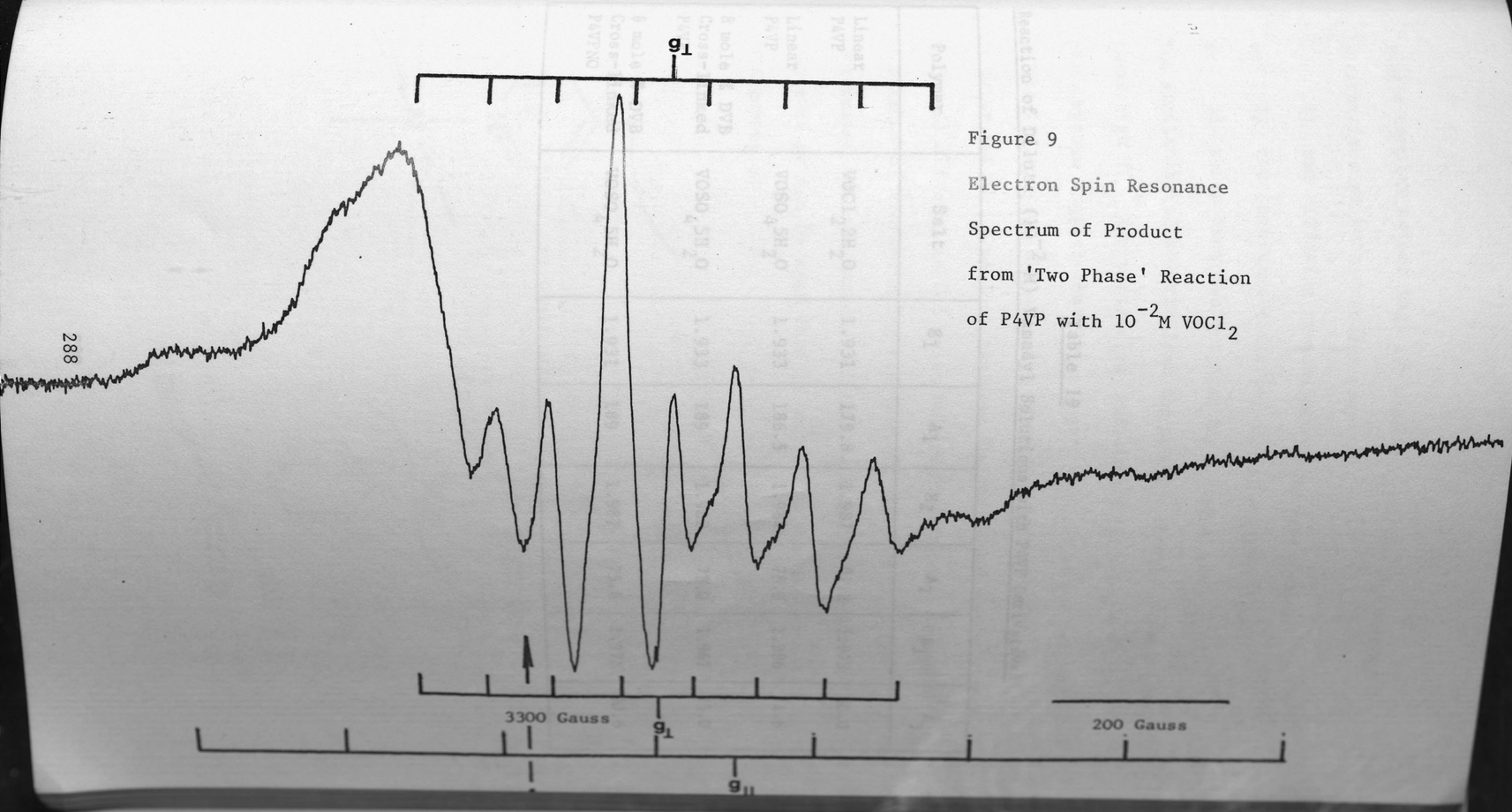


Figure 9

Electron Spin Resonance Spectrum of Product from 'Two Phase' Reaction of P4VP with 10^{-2}M $VOCl_2$

Table 19

Reaction of Dilute (10^{-2} M) Vanadyl Solutions with P4VP Derivatives

Polymer	Salt	g_1	A_1	g_2	A_2	g_3	A_3
Linear P4VP	$VOCl_2 2H_2O$	1.931	179.8	1.987	81.2	1.973	80.0
Linear P4VP	$VOSO_4 5H_2O$	1.933	186.5	1.984	75.6	1.986	74.6
8 mole % DVB Cross-linked P4VP	$VOSO_4 5H_2O$	1.933	189	1.987	73.0	1.967	75.0
8 mole % DVB Cross-linked P4VPNO	$VOSO_4 5H_2O$	1.931	189	1.987	75.6	1.978	80.6

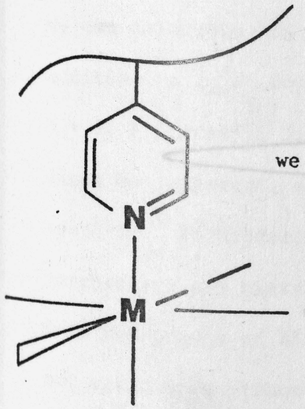
single complex rather than two distinct species. The possible alternatives we must consider are:-

1) two differing stoichiometry complexes present

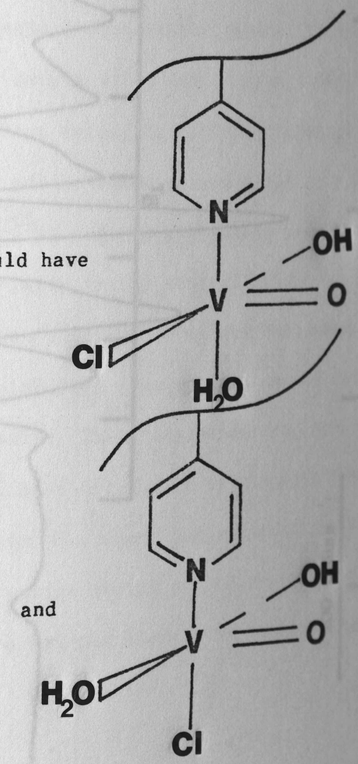
or 2) two complexes differing only in stereochemistry

or 3) three inequivalent axes for a single species.

The similarity of spectra from the solution reaction products, two phase high VO^{2+} ion containing products and the dilute VO^{2+} two phase system suggest that 1) is improbable. We have already commented on the tendancy of the solution product of P4VP with $VOCl_2$ to dissolve in water and for a similar tendancy for the solid linear polymer to (gel and) dissolve in 0.5 Molar $VOCl_2 2H_2O$ solutions, this suggests an absence of cross-linking and with only one P4VP ligand unit coordinated to each cation. If this were generally so for VO^{2+}/P4VP complexes it can be seen that in contrast to the usual symmetrical arrangement of



we could have



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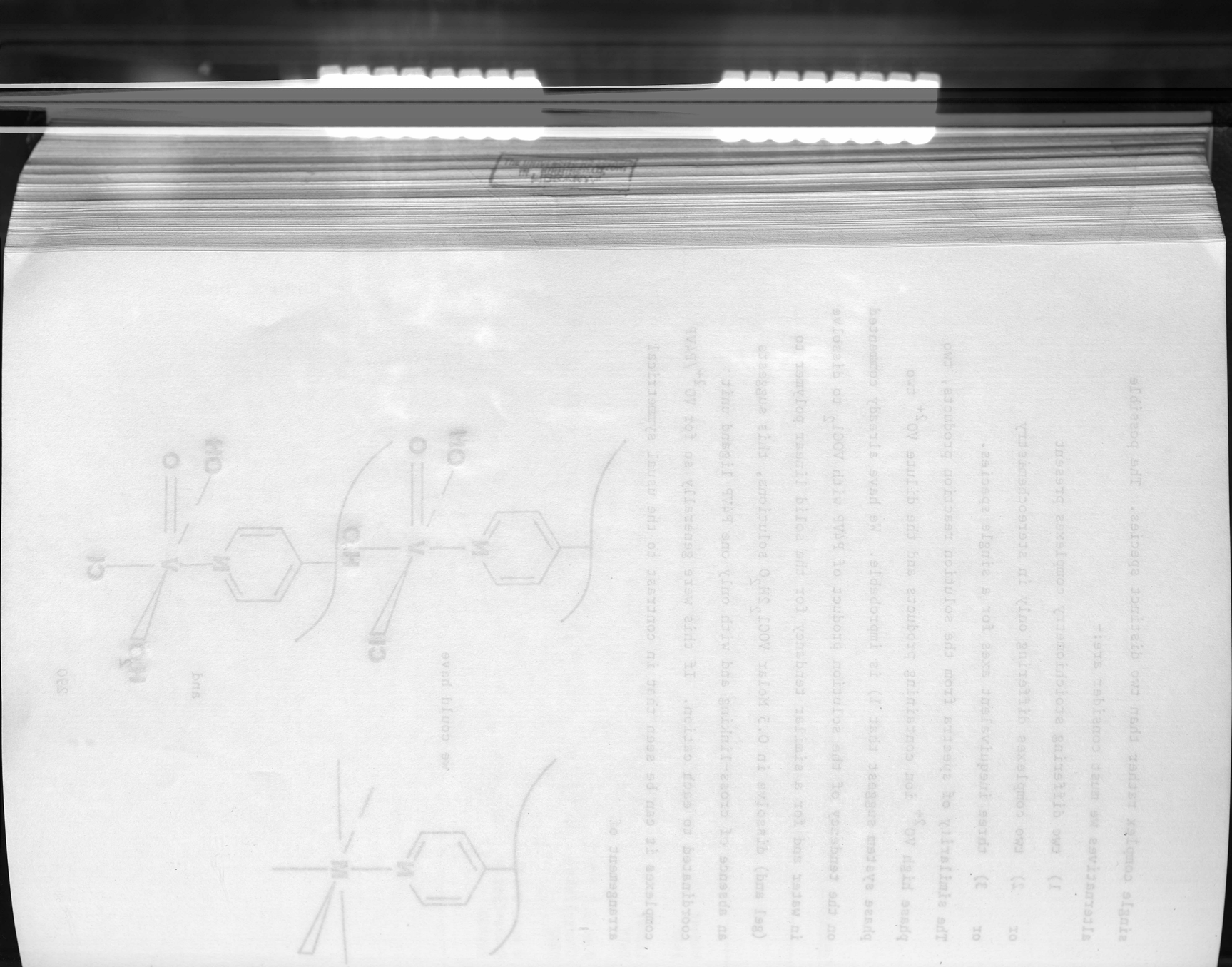


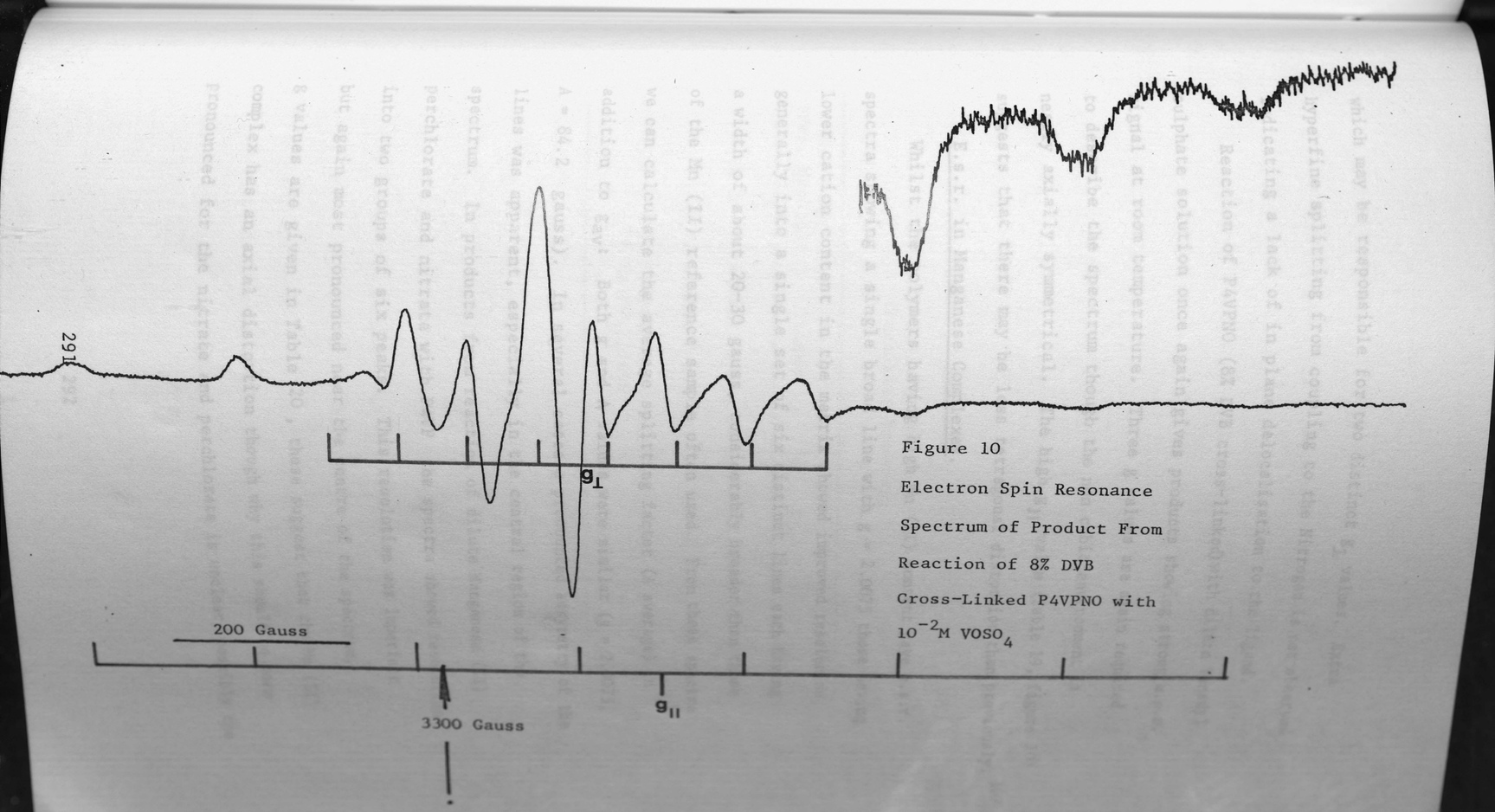


Figure 10

Electron Spin Resonance Spectrum of Product From Reaction of 8% DVB Cross-Linked P4VPNO with 10^{-2}M $VOSO_4$

which may be responsible for two distinct $g_{\perp}$ values. Extra hyperfine splitting from coupling to the Nitrogen is not observed indicating a lack of in plane delocalisation to the ligand.

Reaction of P4VPNO (8% DVB cross-linked) with dilute Vanadyl sulphate solution once again gives products showing strong e.s.r. signal at room temperature. Three g values are again required to describe the spectrum though the non cubic environment is nearly axially symmetrical. The high $g_{\parallel}$ value (Table 19, figure 10) suggests that there may be less tetragonal distortion than previously. [107]

E.s.r. in Manganese Complexes.

Whilst the polymers having high Mn (II) content gave e.s.r. spectra showing a single broad line with g = 2.0075 those having lower cation content in the matrix showed improved resolution, generally into a single set of six distinct lines each having a width of about 20-30 gauss, considerably broader than those of the Mn (II) reference sample often used. From these spectra we can calculate the average splitting factor (A average) in addition to g_{av}: Both g and A values were similar (g = 2.0075, A = 84.2 gauss). In several cases a pronounced assymetry of the lines was apparent, especially in the central region of the spectrum. In products from reaction of dilute Manganese (II) perchlorate and nitrate with P4VP the spectra showed resolution into two groups of six peaks. This resolution was imperfect but again most pronounced near the centre of the spectrum. g values are given in Table 20 , these suggest that the Mn (II) complex has an axial distortion though why this should be more pronounced for the nitrate and perchlorate is unclear, possibly the

Table 20

E.s.r. Data for Manganese (II) Containing Products

Prep. Method	Ligand	g_{av}	A_{av}
1	Linear Pol.	2.02, 2.025	84.5, 97.1
1	Linear Pol.	2.02, 2.03	84.2, 97.1
3	Polymerised $Mn(NO_3)_2$/4VP	2.025	94.2

low degree of coordination for these ions is responsible. Comparison with previous work confirms that a distorted octahedral arrangement has been examined and shows two very similar g values.[107] Distortion of the preferred regular hexa co-ordinate arrangement may in part explain the very poor absorption of Mn (II) ions from solution.

8. Magnetic Susceptibility Measurements for Polymers Containing Absorbed Transition Metal Ions.

Determination of the magnetic moments were limited by availability of suitable samples from the two phase reactions, effectively to Vanadyl, Cobalt (II) and Copper (II) containing complexes. The results were generally very much as for the products from solution reaction of the polymer (Table 12). Values of μ_e (Table 12) for the absorbed Copper (II) products were slightly above those of the 'solution' products, and the second order orbital contribution is therefore increased to give values above $\mu_e = 5.0$. (λ is positive).

Table 12 shows that μ_e values for Cobalt (II) containing products fall within the range normally associated with the octahedral arrangement (4.8 - 5.2 B.M.). Study of the Cobalt (II) chloride reaction product was not possible because of limited ion content for the product, visible spectrophotometry however showed this to be a tetrahedral complex. The values suggest that there is less distortion in the regular octahedral stereochemistry in these products than was present in corresponding 'solution' reaction products.

3.4. Cation Exchange By The Poly(4-Vinylpyridinium) Polycation.

Previous workers examined reaction of parially protonated or partially quaternized cross-linked P4VP with Cu (II) using e.s.r.

spectroscopy. We considered that some confusion may have arisen with the possibility that cation or anion exchange may be occurring in these products

$$P4VPH^{+} \quad + \quad Cu\ (II) \longrightarrow P4VP - Cu^{2+} \quad + \quad H^{+}$$

$$CuCl_2 + 2Cl^{-} \longrightarrow CuCl_4^{2-}$$

$$CuCl_4^{2-} + P4VPH^{+}\ X^{-} \longrightarrow 2P4VPH^{+} / CuCl_4^{2-}$$

as well as or instead of mere coordination. Poly(4-Vinylpyridinium) salts ($P4VPH^{+}$) can be expected to be excellent anion exchangers but very poor cation exchangers because of the difference in energy between the N^{+} - H and Cu^{2+} - N bonds. Indeed Russian workers Kopylova et al[57] have suggested that cation exchange should not occur. This was not found to be the case, reaction of the $P4VPH^{+}$ nitrate form (2% DVB) with excess 1.0 Molar Copper (II) salts did indeed result in full anion exchange but the products were highly coloured after washing and drying (sulphate, nitrate, perchlorate-blue; chloride;- bright green) indicating cation coordination, exact degree of Cu (II) retention was not determined because of solvent absorption by the matrix but less than 5% exchange occurred.

E.s.r. studies of the products did not fully agree with results of previous workers dealing with related species.

A typical spectra for the Cu (II) complex is shown in figure 11 and the data is reported in Table 21. The spectra shows resolution into $g_{\parallel}$ and $g_{\perp}$, hyperfine splitting of $g_{\parallel}$ by the Cu (II) nucleus (I = 3/2) occurs but splitting of the major $g_{\perp}$ is not apparent.

Extrahyperfine splitting is not detectable, save perhaps

Table 21

Electron Paramagnetic Resonance Data for

Transition Metal Ions Absorbed on Protonated Polymers

Polymer	Anion	Salt	Colour of Complex	g	A G	g	A G
$P4VPH^+$	Cl^-	$CuCl_2.2H_2O$	green	2.33	145	2.04	
$P4VPH^+$	NO_3^-	$Cu(NO_3)6H_2O$	blue	2.27	155	2.01	
$P4VPH^+$	ClO_4^-	$Cu(ClO_4)_26H_2O$	blue	2.30	150	2.03	
$P4VPH^+$	SO_4^{2-}	$CuSO_45H_2O$	blue	2.27	155	2.044	
$P4VPNOH^+$	Cl^-	$CuCl_2.2H_2O$	green	2.31 (2.34	135 1.96)	2.03	
$P4VPNOH^+$	NO_3^-	$Cu(NO_3)_26H_2O$	green	2.32	135	2.04	
$P4VPNOH^+$	SO_4^{2-}	$CuSO_45H_2O$	green	2.30	155	2.03	
$P4VPH^+$	Cl^-	$VOCl_2.2H_2O$	grey	1.94	181	1.99 1.965	86 72.4
$P4VPH^+$	SO_4^{2-}	$VOSO_4.5H_2O$	grey	1.936	188	1.99	79
$P4VPNOH^+$	Cl^-	$VOCl_22H_2O$	grey	1.930	188.5	1.986	87
$P4VPNOH^+$	SO_4^{2-}	$VOSO_45H_2O$	grey	1.929	181	2.01	76.0

Table 21 (Cont'd)

Polymer	Anion	Salt	Colour of Complex	g		A	
$P4VPH^+$	Cl^-	$MnCl_2 4H_2O$	Pale yellow	2.029	(g average)	80.2	(A average)
$P4VPNOH^+$	Cl^-	$MnCl_2 4H_2O$	yellow	2.03	(g average)	86.7	(A average)
$P4VPNOH^+$	NO_3^-	$Mn(NO_3)_2 6H_2O$	yellow	2.03	(g average)	102	(A average)
$P2VPH^+$	Cl^-	$VoCl_2.2H_2O$	grey	1.934	181	1.987	72.4
		esr Data for Cation Exchange Products				1.961	78.0

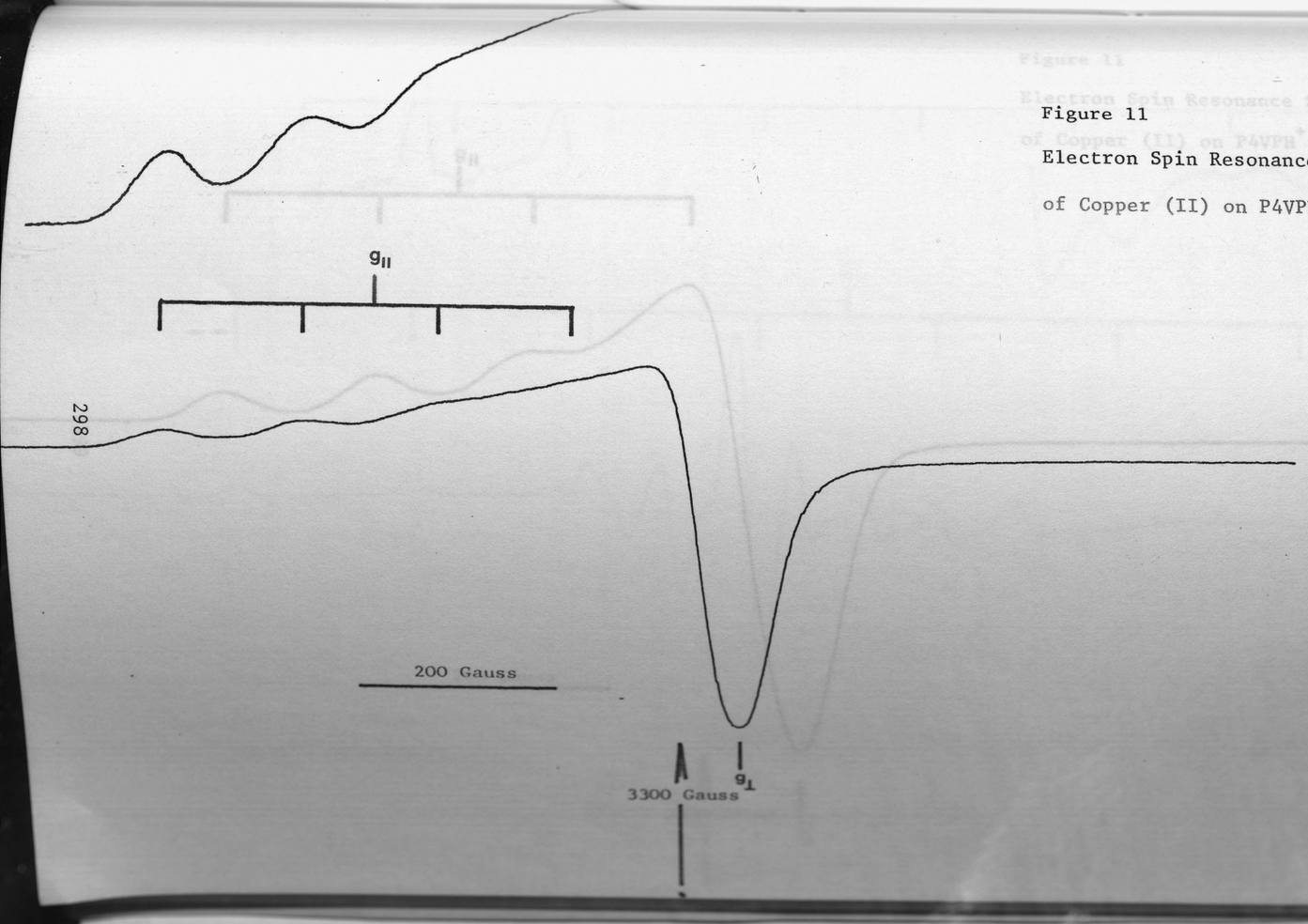


Figure 11

Electron Spin Resonance Spectrum

of Copper (II) on $P4VPNOH^{+}Cl^{-}$

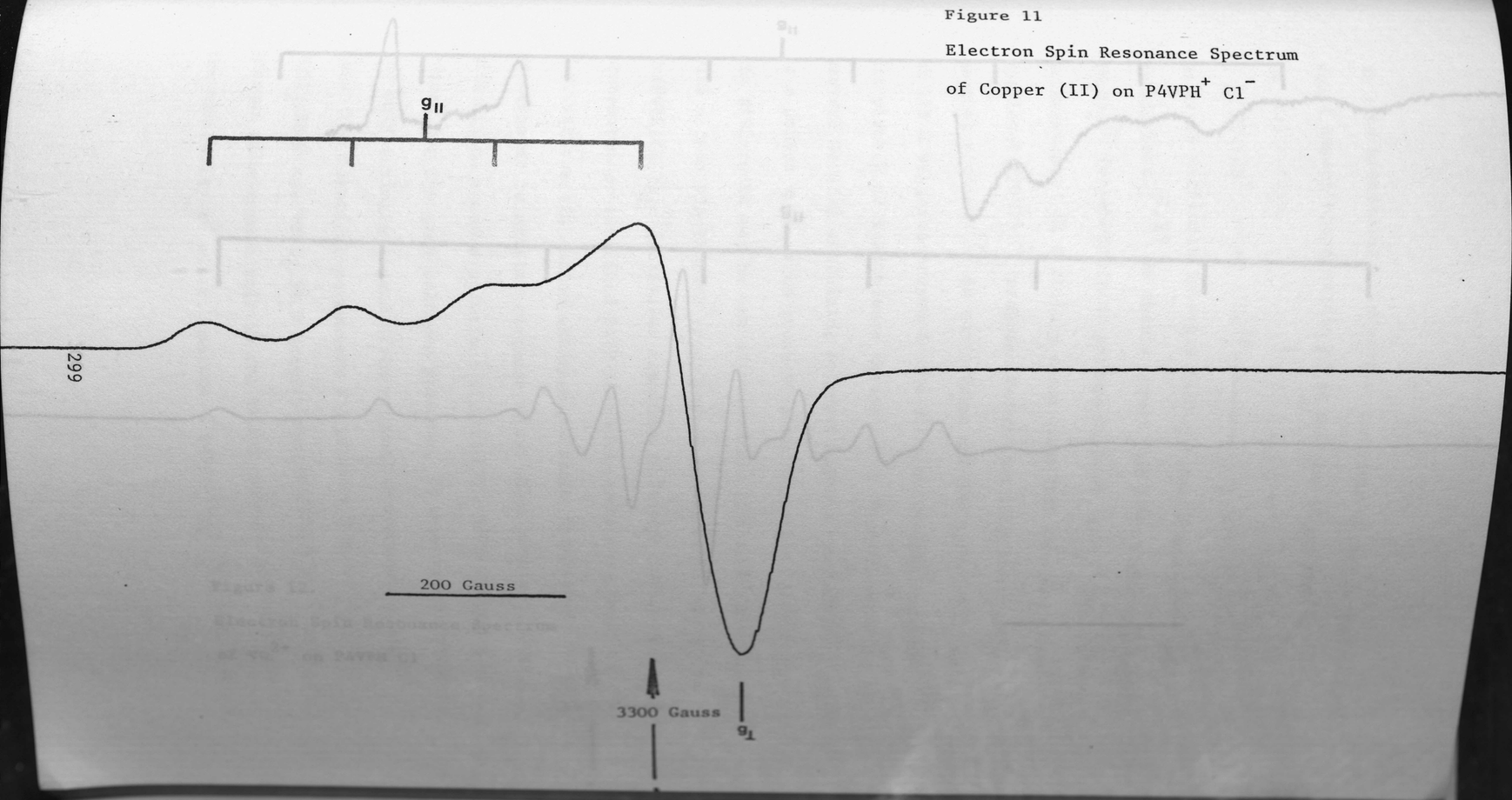
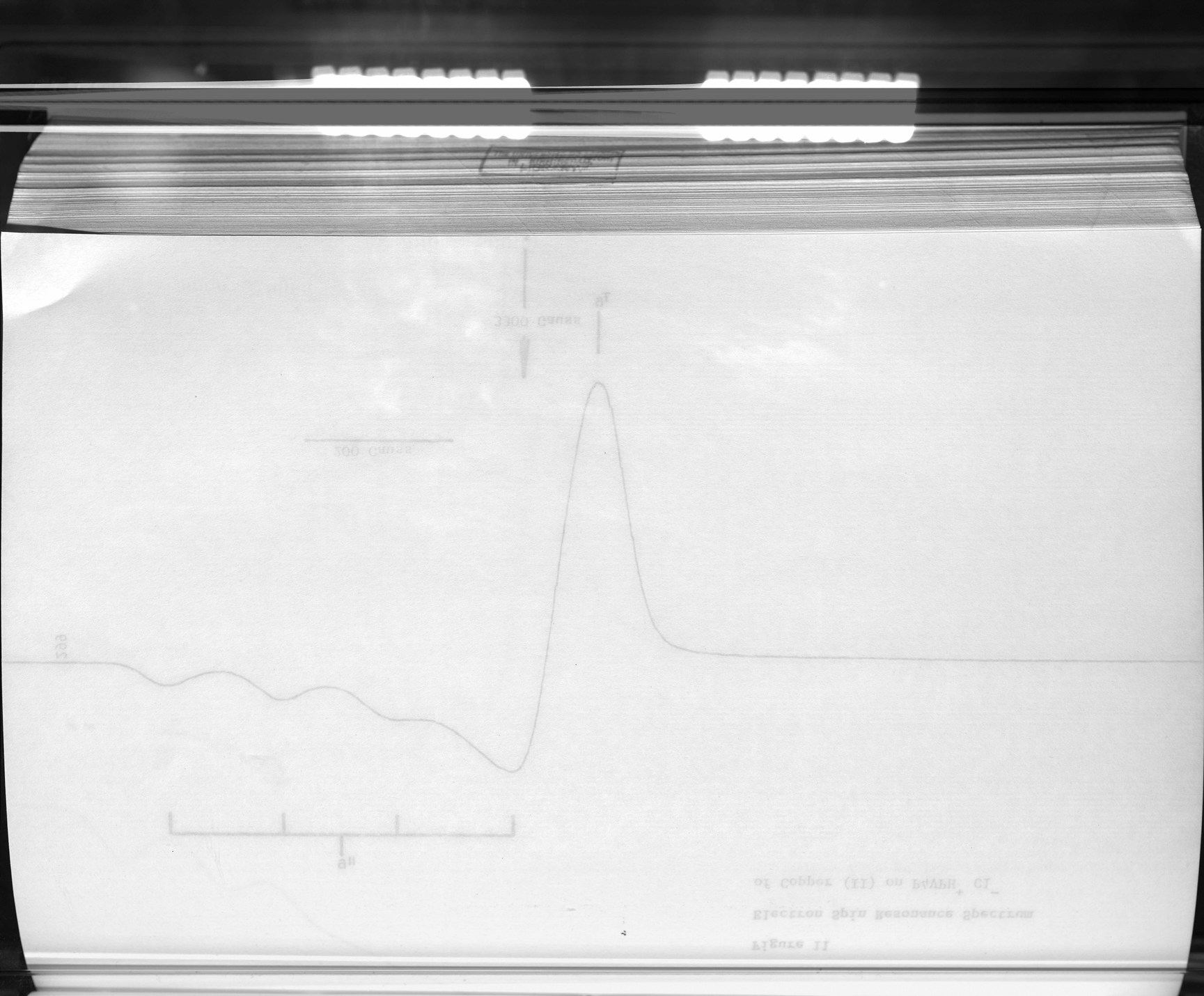


Figure 11

Electron Spin Resonance Spectrum

of Copper (II) on $P4VPH^{+}$ Cl^{-}



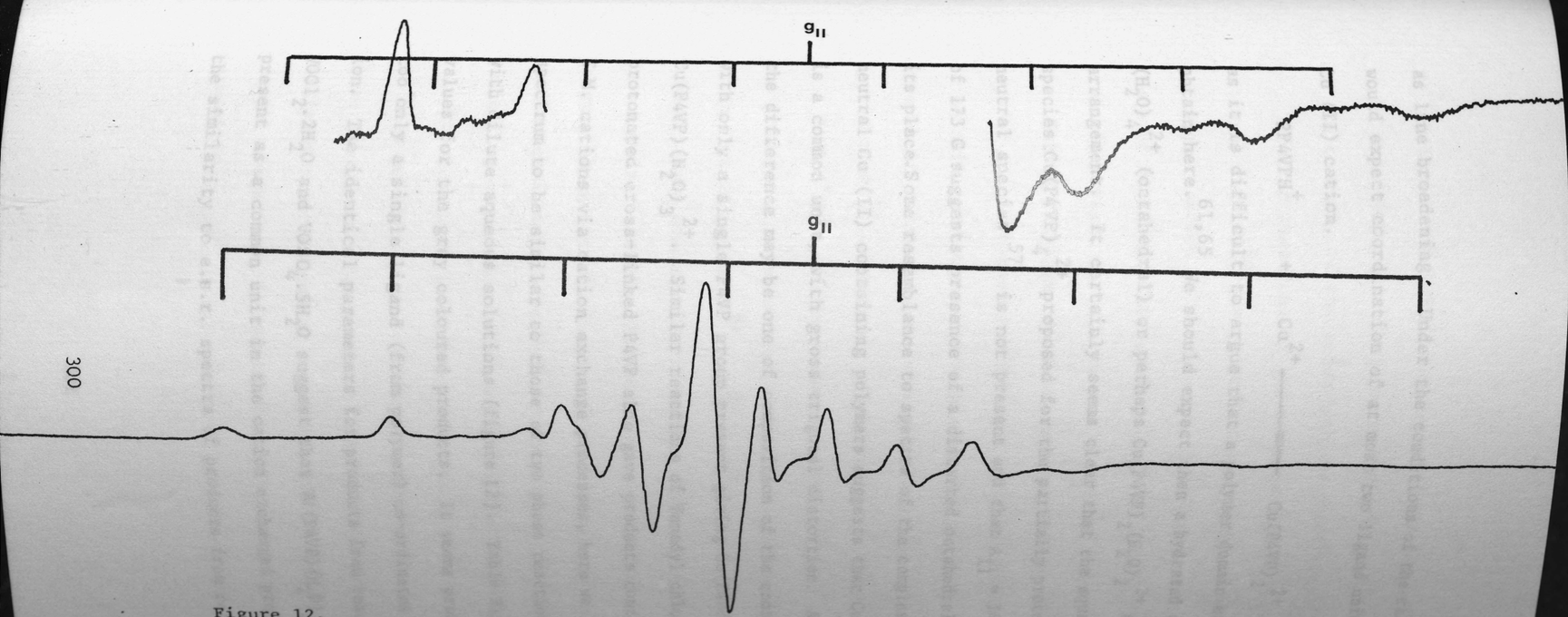


Figure 12.

Electron Spin Resonance Spectrum

of VO^{2+} on $P4VPH^{+}Cl^{-}$

3300 Gauss

as line broadening. Under the conditions of the reactions we would expect coordination of at most two ligand units to each Cu (II) cation.

$$2P4VPH^{+} + Cu^{2+} \longrightarrow Cu(P4VP)_2^{2+} + 2H^{+}$$

as it is difficult to argue that a polymer domain effect would obtain here.[61,65] We should expect then a hydrated species $Cu(P4VP)_2(H_2O)_4^{2+}$ (octahedral) or perhaps $Cu(P4VP)_2(H_2O)_2^{2+}$ square planar arrangement. It certainly seems clear that the square planar species $Cu(P4VP)_4^{2+}$ proposed for the partially protonated or neutral species[57] is not present and that A_{11} = 145-155 G instead of 173 G suggests presence of a distorted octahedral species in its place. Some resemblance to spectra of the complexes of the neutral Cu (II) containing polymers suggests that $Cu(P4VP)_2(H_2O)_4^{2+}$ is a common unit, with gross trigonal distortion. Alternatively the difference may be one of composition of the coordination sphere, with only a single P4VP group present giving $Cu(P4VP)(H_2O)_5^{2+}$ or $Cu(P4VP)(H_2O)_3^{2+}$. Similar reactions of Vanadyl chloride with the protonated cross-linked P4VP also gave products containing the T.M. cations via cation exchange processes, here we found the e.s.r. spectrum to be similar to those of two phase reaction products with dilute aqueous solutions (figure 12). Table 21 shows g and A values for the grey coloured products. It seems probable that here too only a single ligand (from polymer) co-ordinates to each VO^{2+} ion. The identical parameters for products from reaction with $VOCl_2.2H_2O$ and $VOSO_4.5H_2O$ suggest that $VO(P4VP)(H_2O)_4^{2+}$ may be present as a common unit in the cation exchanged product. Further the similarity to e.s.r. spectra of products from reaction of dilute

VO^{2+} solutions with P4VP suggests that the same unit may be present there too, changes in the spectra for solution polymers may then be due to entry of the anion into the coordination sphere.

Similar reactions of the corresponding poly(2-vinylpyridinium nitrate) with VO^{2+} gave a product containing the cation via cation exchange reaction as previously. E.s.r. spectra are similar to those of $P4VPH^{+}$ products. Species such as $VO(PVP)(H_2O)_4^{2+}$ are probably present in both cases.

Cation exchange reactions were carried out in exactly the same way for the exchanger $P4VPNOH^{+}\ X^{-}$. This has previously been considered as an anion exchanger and as a chelating ion exchange polymer, however it seems that the strength of the $N^{+}O$ - H bond was not appreciated.[73] No study of the product of the minor reaction

$$P4VPNO^{+}H + M^{2+} \longrightarrow P4VPNO\text{-}M^{2+} + H^{+}$$

was previously made, however e.s.r. again confirms the occurence of this reaction for $M^{2+} = Cu^{2+}$, VO^{2+} and Mn^{2+} and again the products have characteristic colours (Copper, green; Vanadyl, grey) data appears in Table 21. Here again at most two ligands from the polymer coordinate (probably one) and the e.s.r. suggests a quite similar environment for VO^{2+} occurs with the difference possibly indicating counterion as ligand giving $VO(P4VPNO)(H_2O)_2Cl_2$ (figure 13).

Previous work involving absorption of VO^{2+} on ion exchangers has been published, the conclustions are similar to those reported above though only two g values were reported in that work.[110] The published spectra however contained insufficient detail to allow careful comparison, it may be that a third g value was present but unresolved.

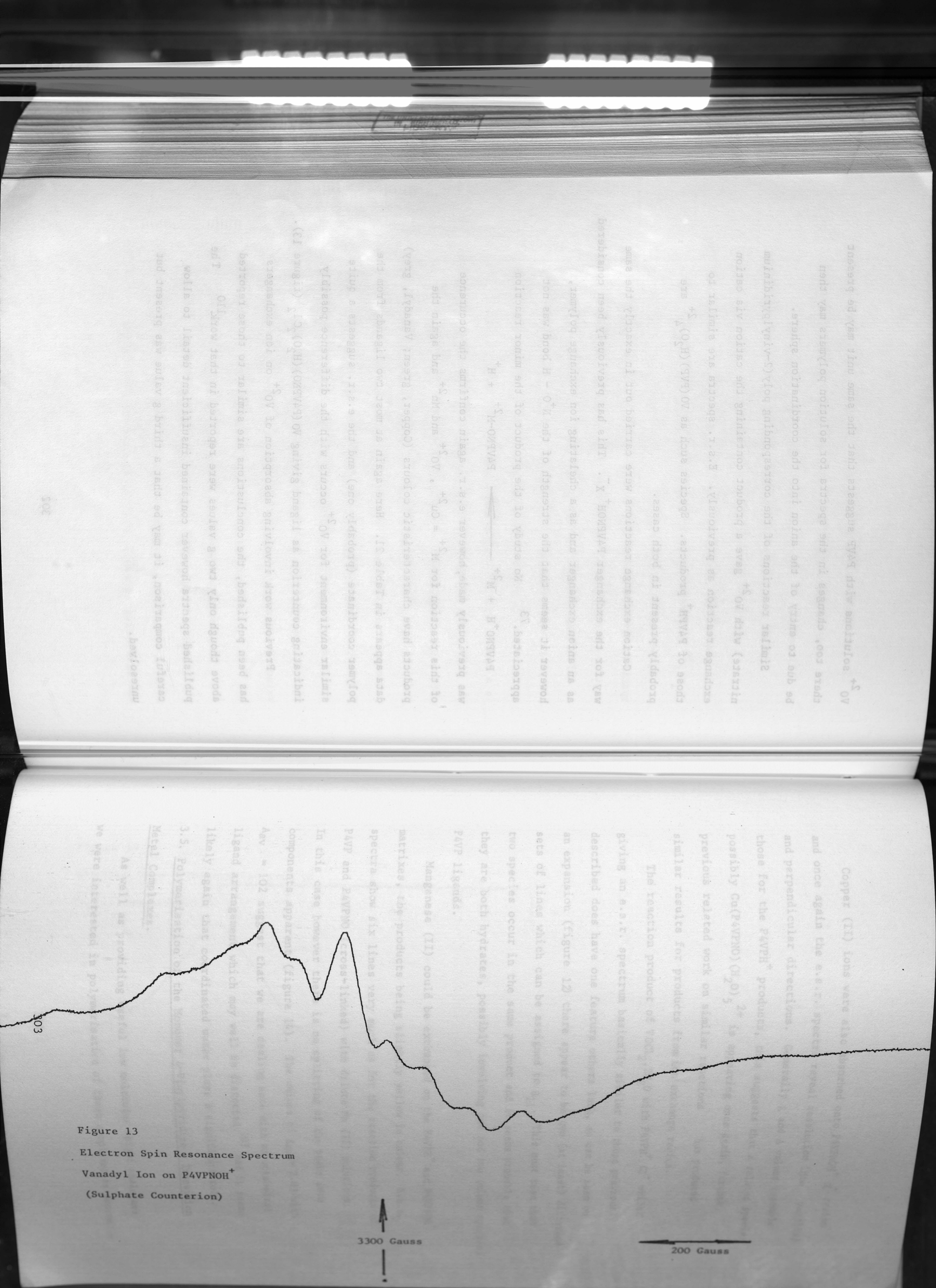


Figure 13

Electron Spin Resonance Spectrum

Vanadyl Ion on $P4VPNOH^+$

(Sulphate Counterion)

Copper (II) ions were also absorbed onto $P4VPNOH^+ X^-$ resins and once again the e.s.r. spectra reveal resolution into parallel and perpendicular directions. Generally g and A values resemble those for the $P4VPH^+$ products, this suggests that a related species possibly $Cu(P4VPNO)(H_2O)_5^{2+}$ is appearing once again, further, previous related work on similar reactions has produced similar results for products from ion exchange resins.

The reaction product of $VOCl_2.2H_2O$ with $P4VPH^+ Cl^-$ whilst giving an e.s.r. spectrum basically similar to those previously described does have one feature others lack, as can be seen on an expansion (figure 12) there appear to be two (at least) different sets of lines which can be assigned to g_{11}. This must mean that two species occur in the same product and it seems probable that they are both hydrates, possibly involving one and two (minor species) P4VP ligands.

Manganese (II) could be exchanged on the $P4VPH^+$ and $P4VPNOH^+$ matrixes, the products being slightly yellow in colour. E.s.r. spectra show six lines very much as for the reaction products of P4VP and P4VPNO (cross-linked) with dilute Mn (II) solutions. In this case however there is no splitting of the peaks into components apparent (figure 14). The values of $g_{av} = 2.03$ with $A_{av} = 102$ suggest that we are dealing here with an octahedral ligand arrangement which may well be distorted [107] and it seems likely again that coordinated water plays a significant role.

3.5. Polymerisation of the Monomer 4-Vinylpyridine - Transition Metal Complexes.

As well as providing useful low molecular weight analogues we were interested in polymerisation of these complexes as monomeric

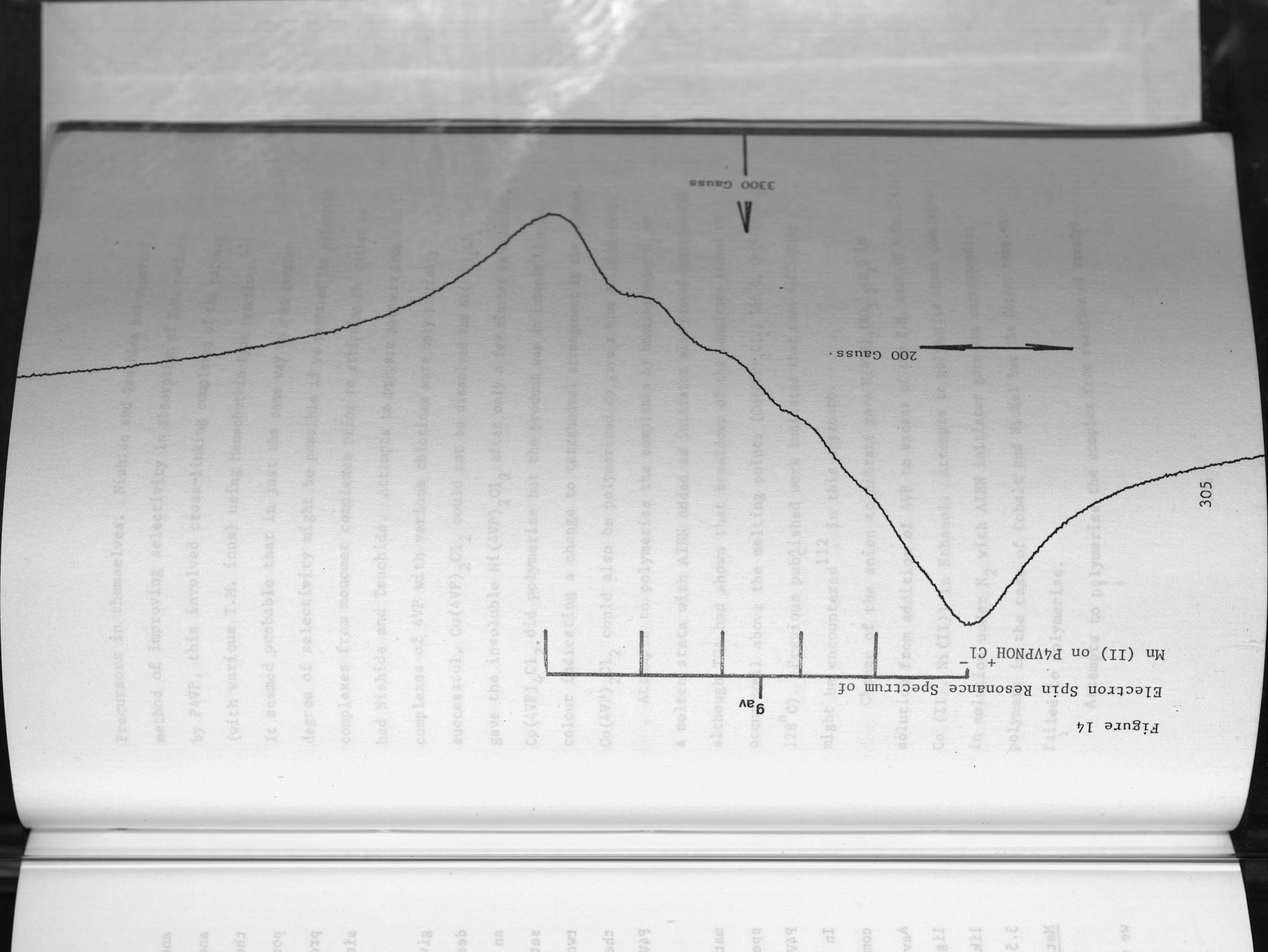


Figure 14

Electron Spin Resonance Spectrum of Mn (II) on P4VPNOH$^+$Cl$^-$

Precursors in themselves. Nishide and Tsuchida had reported a method of improving selectivity in absorption of T.M. cations by P4VP, this involved cross-linking complexes of the polymer (with various T.M. ions) using Menschutkin type reactions.[61] It seemed probable that in just the same way an even greater degree of selectivity might be possible if we prepared the polymeric complexes from monomer complexes prior to stripping the cation as had Nishide and Tsuchida. Attempts to prepare polymers from complexes of 4VP with various chlorides were only partially successful, $Cu(4VP)_2Cl_2$ could not be dissolved and $Ni(4VP)_4Cl_2$ gave the insoluble $Ni(4VP)_2Cl_2$ after only a few minutes in solution, $Co(4VP)_4Cl_2$ did polymerise but the product was an intense blue in colour indicating a change to tetrahedral arrangement in the polymer. $Co(4VP)_2Cl_2$ could also be polymerised to give a blue solid product.

Attempts to polymerise the complexes by heating under N_2 to a molten state with AIBN added as initiator also proved unsuccessful although TGA had shown that breakdown of the complexes seemed to occur well above the melting points ($Cu(4VP)_2Cl_2$, 166°C, $Co(4VP)_2Cl_2$ 128°C). Previous published work indicated that some difficulty might be encountered[112] in this approach.

Change of the anion to nitrate gave $M(4VP)_2(NO_3)_2 4H_2O$ in solution from addition of 4VP to excess of the T.M. salt (M = Cu (II), Co (II), Ni(II)) in Ethanol. Attempts to polymerise these complexes in solution under N_2 with AIBN initiator gave the corresponding polymers in the case of Cobalt and Nickel but the Copper complex failed to polymerise.

Attempts to polymerise the complex from reaction of Vanadyl

chloride with 4VP yielded a solid complex which we were unable to identify with certainty, but which we suspect is not a product from polymerisation of the ligand.

The polymers in most cases were totally insoluble except in acids, which generally caused breakdown. This was not the case for the product from polymerisation of $Mn(4VP)_2(NO_3)4H_2O$, here the product was soluble in alcohols and chloroform but could be precipitated in water. Infra-red of the product deposited as a thin film from chloroform later showed that Mn - N coordinate bonds either do not form or breakdown occurs. The bis 4VP complex of Manganous chloride could however be polymerised to give the corresponding product $Mn(P4VP)_2Cl_22H_2O$ which as for other chlorides proved insoluble. Attempts to prepare the polymers from Iron (III) nitrate and chloride yielded the monomeric complexes as shown by elemental analysis and solubility of the 'stripped' ligand.

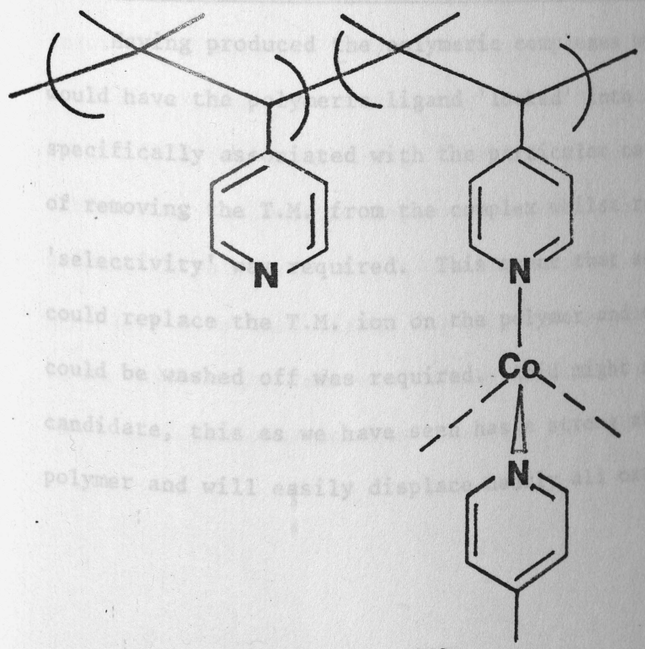
As well as obtaining information from the elemental analysis results we could study these products using techniques previously employed.

Elemental Analysis.

Tables 3-6 show data for the polymer products. As can be seen they generally have rather regular stoichiometry much as for the corresponding products from the solution reactions. One point of particular interest was that in spite of having a tetrahedral arrangement the polymeric product from $Co(4VP)_4Cl_2$ also had an empirical formula of $Co(P4VP)_4Cl_2$.

Infra-Red Spectrophotometry.

Resolution in the I.R. spectra was generally considerably improved over that obtained for solution reaction products and was much better than that of two phase reaction products. Examining the regions of the spectra of particular interest to us, 200-400cm^{-1} and 1500-1650cm^{-1}, we found peaks as shown in Tables 7 and 8. Peaks in the Far I.R. were precisely as for the solution reaction products and, of particular interest, the spectra of polymerised $Co(4VP)_2Cl_2$ and $Co(4VP)_4Cl_2$ were identical in this region. As previously peaks at 307 and 343cm^{-1} are assigned to Co-Cl bond vibrations with that at 248cm^{-1} due to the Co-N coordinate bonds. Peaks appear at 1611cm^{-1} for all the Cobalt complexes confirming the presence of Co-N bonds as previously. The polymer from $Co(4VP)_4Cl_2$ however shows an additional peak at 1600cm^{-1} and this is assigned to unreacted ligand units of the polymer chain, the two peaks are approximately equal and this provides strong evidence on the structure of that product. It must be a copolymer having equal numbers of the units:-



The Nickel complex showed a peak for C = C, C = N vibration at 1613cm^{-1} confirming the coordinate bond formation as for previous related products, whilst the polymer from $Mn(4VP)_2Cl_2 2H_2O$ showed this vibration at 1606cm^{-1}. The product from our attempts to polymerise $Mn(4VP)_2(NO_3)_2 4H_2O$ showed a shift only to 1600cm^{-1} however and Manganese was not present at high concentration in this product. Clearly then polymerisation but no coordinate bond formation occurs here.

The Vanadyl containing product showed the usual peak at 990cm^{-1} in the I.R., characteristic of the complexed cation and there was no detail in the far I.R. region, the appearance of a single peak at 1638-39cm^{-1} suggests that polymerisation has not occurred, attempts to reprecipitate the P4VP ligand (if present) did however yield some evidence of polymerisation. It seems probable that rather limited reaction has occurred. The e.s.r. spectrum (figure 15) bore a strong resemblance to that of the previously isolated monomer complex (figure 2).

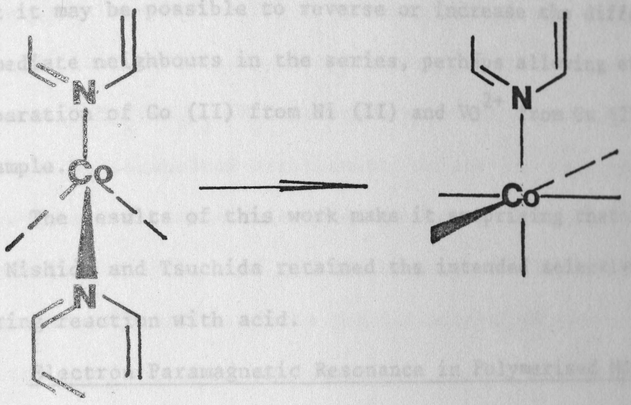
3.6 Isolation of Selective Polymeric Ligand (P4VP)

Having produced the polymeric complexes which we believed would have the polymeric ligand 'locked' into a conformation specifically associated with the particular cation, some means of removing the T.M. from the complex whilst retaining any additional 'selectivity' was required. This meant that some reagent which could replace the T.M. ion on the polymer and which subsequently could be washed off was required. Acid might seem an obvious candidate, this as we have seen has a strong affinity for the polymer and will easily displace nearly all cations from it.

Reaction of the Co (II) containing polymers with dilute Hydrochloric acid followed by precipitation of the polymer ligand from solution in dilute ammonia gave a pure sample after several such cycles. This product however showed no improved absorption of Co (II) from 0.1 M aqueous solutions. This was to be expected perhaps because upon reacting the complex with acid and dissolving it we may be allowing free change of conformation. One method considered to overcome this was to attempt to 'lock' the conformation of the polymer in the 'selective' arrangement about the cation by incorporating a cross-linking agent in the polymerisation stage. This was successfully tried for $Co(P4VP)_4Cl_2$, $Co(4VP)_2Cl_2$, $Ni(4VP)_2(NO)_24H_2O$, $Co(4VP)_2(NO_3)_24H_2O$ and $Mn(4VP)_2Cl_22H_2O$. Stripping these complexes with acid followed by washing with base and water proved much easier than the reprecipitation process required for the linear ligand. Our experiments with Co (II) and Ni (II) solutions however showed that the polymers were not able to absorb these ions from near neutral 0.1 Molar solutions of their salts. It seems that even in the quite highly cross-linked state the protonation reaction involves or allows a permanent change in conformation.

It was decided to study the linear ligand from the polymerised Cobalt (II) complexes using ^{13}C NMR as it seemed probable that differences in conformation would occur in comparison to a reference suspension polymer. It was apparent that acid could not be used to remove that ligand from the cations and so a sequestering agent which might remove that cation without causing change of the ligand conformation was required. The obvious choice was EDTA,

we had already noted that this chelating agent was sufficiently 'powerful' to strip the P4VP ligand. Attempts were made to react the polymerised $Co(4VP)_4Cl_2$ product with a 0.2 Molar aqueous EDTA (disodium salt), the result was total dissolution of the complex for reasons which are uncertain, certainly the resulting pH was sufficiently high to avoid protonation. It is possible that removal of the N-Co-N cross-links in the matrix, with change to octahedral arrangement as shown by the red colouration of the resulting solution was responsible,



X = H_2O or EDTA

where the sequestering agent occupies a number of sites and displaces one of the pendant ligand units of the polymer allowing the product to dissolve. The situation may resemble that for the Co (III); P4VP/ethylenediamine complexes previously reported.

Removal of Co (II) and Ni (II) from the DVB cross-linked complexes has been possible in this manner, the resulting products

however do not show appreciably greater absorption or selectivity in comparison with a standard suspension product. In retrospect we may have reason not to be optimistic, in Chapter III we reported that reaction of the polymerised Cobalt (II) chloride complex with $CuCl_2.2H_2O$ in aqueous solution resulted in total substitution of Cu (II) for Co (II) in the matrix. Thus in these products it seems rather improbable that we shall be able to fully overcome the absorption order established in Chapter III of

$$H^* > VO^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$$

but it may be possible to reverse or increase the difference for immediate neighbours in the series, perhaps allowing effective separation of Co (II) from Ni (II) and VO^{2+} from Cu (II) for example.

The results of this work make it surprising that the complexes of Nishide and Tsuchida retained the intended selectivity even during reaction with acid.

Electron Paramagnetic Resonance in Polymerised Monomer Complexes.

With the failure to polymerise the Copper (II) complexes e.p.r. studies were limited to VO^{2+} and Mn (II) containing polymers. Resolution for Mn (II) was poor as previously for high concentrations of this cation with only a single. broad line (g_{av} = 2.008). Resolution for the VO^{2+} complex product was similar to that for the $4VP/VOCl_2$ product and these spectra were indeed similar (figure15) with some resemblance to the solution $P4VP/VOCl_2$ reaction product. Elemental analysis showed that differences did occur however and it proved impossible to state with certainty that we had obtained

a single complex. Three g values were apparent $g_x = 1.997$, $A_x = 85G$. $g_y = 1.97$, $A_y = 87$. $g_z = 1.927$, $A_z = 186G$. The attempts to prepare the related cross-linked (DVB) product yield an acid soluble product, this provides strong indication that the precipitated solid has not undergone addition polymerisation.

Magnetic Susceptibility Studies in Polymerised Complexes.

Values for the magnetic susceptibilities for polymers successfully prepared from the related monomer complexes are shown in Table 12. Clearly polymers from $Co(4VP)_4Cl_2$ and $Co(4VP)_2Cl_2$ have μ_e values indicating a tetrahedral environment for the Co (II) ion, visible spectrophotometry confirms this. The polymer from $Co(4VP)_2(NO_3)_2.4H_2O$ is shown by visible spectrophotometry to have an octahedral arrangement, values for μ_e contradict this however and resemble values for the corresponding product from 'solution' reactions of the linear polymer. The low value suggests that some distortion of the regular octahedral arrangement occurs as for the 'solution' product.

FURTHER WORK

i) Structural Studies

Application of the isotope substitution technique employed by Nakamoto et al among others may prove rewarding for studies in far infra-red spectroscopy, allowing location of specific metal ligand bond vibrations. Problems may be encountered with reduced resolution, often associated with macromolecules, in this area.

Further clarification of the situation regarding structure of Iron (III) complexes in the polymers may be possible with the aid of Mossbauer spectroscopy, this would provide information on ligand coordination sphere and oxidation state. Further, some examination of the products from reaction of P4VP with Iron (III) in two phase reactions at pH 5.5 is necessary. Nishide et al have implied that basic species are not produced [61] this work has suggested otherwise.

More detailed examination of low T.M. content products from two phase reactions using e.s.r. spectroscopy at low temperature may provide information on different 'sites' available for various ions (Cu (II), VO^{2+}, Mn (II)).

ii) Absorption Studies

Partial N-oxidation of the P4VP chains may provide polymers having rather interesting properties. A greater affinity for water as solvent is expected with only slight drop in selectivity. A comparison may be drawn with the partially protonated polymers of Kopylova. In a similar way incorporation of other water soluble monomers at the polymerisation stage may give copolymers of 4VP having affinity for the solvent with improved access to the

nucleophilic pendant rings. If conformational limitations are reduced by such 'spacer' units selectivity and capacity may be affected with a change in the order previously observed.

2) Modification of the method used in this project for N-oxidation of 4-vinylpyridine is expected to provide a simple route to the 4-vinylpyridine-N-oxide. Previous preparation of this monomer on a large scale has not been possible.

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