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STUDIES ON FORMATION OF COMPLEXES BETWEEN POLY(VINYL PYRROLIDONE) AND IRON (II) SALTS AND ITS ANTIMICROBIAL PROPERTIES

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Abstract: Significance of transition metals in industries and biological systems, in general, and iron, in particular is very well established. But the application of these metals in the form of aqueous solutions in medicinal field is limited as they are highly toxic. In such cases polymer-metal complexes can be thought of better substitutes for introducing the metal ions into a biological system. When a non-toxic, water soluble and biologically compatible polymer like poly(vinyl pyrrolidone) is used as a ligand, the spectrum of applications of such complexes gets broadened. Poly(vinyl pyrrolidone) – Iron (II) complexes were prepared using aqueous solutions of PVP (30K) and ferrous sulphate heptahydrate at room temperature with varied molar compositions. Solid polymer-metal complexes were obtained by evaporating the solvent. The prepared complexes were characterized by FTIR, 1H-NMR with DMSO as solvent and 13C-NMR. The extent of complex formation was predicted by comparing the spectral data of the complexes with those of pure PVP. Crystalline property of the complex was studied by Differential Scanning Calorimetry (DSC) and for magnetic property by Vibrating Sample Magnetometry (VSM). Antimicrobial activity of the complex was also studied by Agar Well Diffusion method.

***Index Terms* – Polymer-metal complexes, poly(vinyl pyrrolidone), transition metals.**

I. INTRODUCTION

Polymer-metal complexes are metal complexes containing a polymer ligand. Metal ions can bind to neutral or weakly charged water soluble polymers. These complexes serve as the best models for metallo-enzymes. They form the basis for the synthesis of wide range of biomedical preparations and drugs. Variations in the properties of complexes of the polymer, poly(vinyl pyrrolidone), abbreviated as (PVP) with different concentrations of iron (II) sulphate heptahydrate solutions were studied and optimum conditions under which the desired properties are exhibited are analyzed. PVP is non-toxic, water soluble, biologically compatible and hence it is eco-friendly. Its capacity to form complexes is also very high. Studies on the formation of complexes of bivalent iron are of utmost importance because of their nutritional properties. Use of iron as catalyst is well established and its deficiency causes multiple health issues including anemia.

II. EXPERIMENTAL

2.1 Materials

AR grade Poly(vinyl pyrrolidone) (PVP) sample of molecular mass 30K, ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) of molecular mass = 278.01 and double distilled water were used for the preparation of the complexes. Chemicals were of SD Fine Chemicals Company. All the chemicals were used directly as they were supplied without any further purification.

2.2 **Synthesis of Poly (vinylpyrrolidone) – Iron (II) Complex**

Reactants taken were 50 ml of aqueous solution of PVP (30K) having the concentration 25% (w/v %) and 10 ml of 0.5 M aqueous solution ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) of molecular mass = 278.01. The mixture is stirred constantly at 25ºC, on a magnetic stirrer, approximately for about 10-12 hours. The volume of the solution was reduced to half of the initial volume. Thickened gum like semisolid was poured into Petri plates and dried in hot air oven at slightly above room temperature i.e., at 35-40 ºC for 15-16 hours. Dull yellow coloured solid was obtained. Once the product attained constant weight, crystals were collected in air tight bottles.

To optimize the relative molar ratio of the two reactants for the synthesis, few other samples of poly (vinyl pyrrolidone) – iron (II) complexes were prepared by taking 50 ml each of 10%, 25% and 40% (w/v %) aqueous solutions PVP – 30K and 10 ml each of 0.1 M, 0.5 M and 1.0 M aqueous solutions of ferrous (II) sulphate heptahydrate (Table 3.1.1.).

One more sample, named as PF-5A, was also prepared by mixing 25% aqueous solution of PVP (30K) and 0.5 M solution of ferrous sulphate heptahydrate in absolute alcohol, by taking the same volumes of reactants as in the previous case, to study the effect of solvent used for dissolving the salt, on complex formation.

The aqueous solution of PVP was colourless and that of ferrous (II) sulphate was very pale green. But the crystals obtained had dull yellow colour. The crystals obtained were hygroscopic hence stored in airtight bottles. Crystals obtained were characterized by solubility tests, FTIR, 1H-NMR, 13C-NMR, DSC and VSM studies. Antimicrobial activities were studied by Agar Well Diffusion method.

III. RESULTS AND DISCUSSION

3.1. Synthesis

The complexes were prepared by following the procedure given in paragraph 2.2 and are tabulated in **Table 1**.

Table 1: Different molar compositions of aqueous solutions of PVP and ferrous sulphate heptahydrate for the synthesis of PVP – Fe (II) complexes

PVP↓ / Salt Solution→	0.1M	0.5M	1M
10% (w/v)	PF-1	PF-4	PF-7
25% (w/v)	PF-2	PF-5	PF-8
40% (w/v)	PF-3	PF-6	PF-9

3.1.1. Solubility

Solubilities of the prepared samples of PVP – Fe (II) complexes were tested in both polar and non-polar solvents including water. It was found that the complexes were soluble in polar solvents like water, methanol, ethanol, 2-propanol, DMF and DMSO. But insoluble in THF and chlorobenzene, which are also polar solvents. In chloroform slight turbidity was observed.

Complexes were insoluble in non-polar solvents like acetone, diethyl ether, n-hexane, n-heptane, toluene, carbon tetrachloride and 1, 4 – dioxane. The solubility of the reactant, PVP was very similar in the solvents listed above.

3.2 Spectral Analysis

3.2.1 FTIR Spectral Studies

Structure and structural transformations can be studied effectively by FTIR and NMR spectroscopy. IR spectra help in the location of the coordination sites in the polymer – metal complexes. The absorption peaks observed in the FTIR spectrum of pure PVP sample used for the synthesis of the complexes clearly indicate that they correspond to the characteristic bonds present in PVP molecule (Fig. 1).

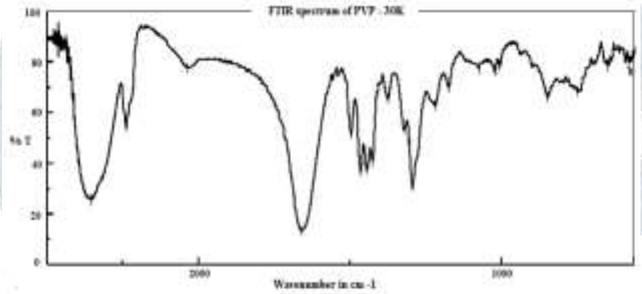


Fig. 1. FTIR spectrum of PVP-30

The modifications in polymer due to the formation of complex were studied by recording FTIR spectrum of PVP – Fe (II) complex shown in the Fig. 2.

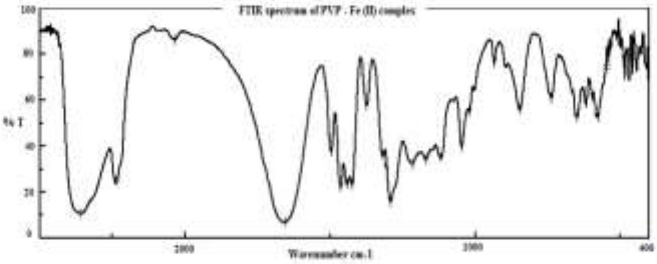


Fig. 2. FTIR spectrum of PVP – Fe (II) complex

Fig. 3 shows the overlay spectra of pure PVP – 30K, PVP – Fe (II) complex, ferrous sulphate heptahydrate and sample PF-5A.

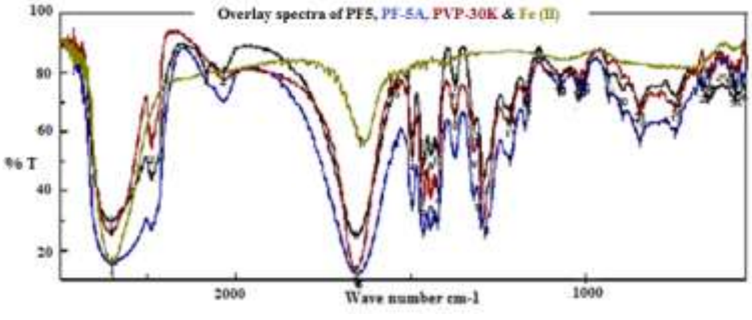


Fig 3. Overlay spectra of PVP – Fe (II) complexes (PF5 & PF-5A), pure PVP and pure ferrous sulphate heptahydrate salt

Polymer – metal complexes are formed due to the interaction between macromolecular functional groups and metal ions. Here metal ion acts as acceptor and groups such as $–NH_2$, heterocyclic N, -CO-, etc., of polymer chain act as donors. The stretching frequencies relating to the donor atoms present in PVP are noted to investigate the bond formation in the complex.

The ketone (C=O) group of pure PVP shows a prominent peak at 1663.4 cm^{-1} in FTIR spectrum which is characteristic of C=O bond in PVP (i.e., amide C=O bond). Oxygen being one of the potential donor atoms in PVP, this peak can be studied to explore the polymer – metal interactions in polymer – metal complexes.

The stretching frequencies of C–N–C, –N–C and C=O groups in pure PVP sample and in PVP – Fe (II) complexes that are prepared, are given in the Table 2.

Table 2. Comparison of stretching frequencies of C-N-C, N-C and - C=O bonds in PVP – Fe (II) Complexes

Sample	CNC Stretching	N-C Stretching	C=O Stretching
PVP – 30K	**1443.5**	**1292.1**	**1663.4**
PF-1	1441.5	1292.1	1659.4
PF-2	1440.6	1291.1	1659.4
PF-3	1440.6	1292.1	1653.7
PF-4	1440.6	1292.1	1653.7
PF-5	1440.6	1292.1	1653.7
PF-5A	1440.6	1291.1	1653.7
PF-6	1440.6	1292.1	1653.7
PF-7	1440.6	1292.1	1653.7
PF-8	1440.6	1292.1	1653.7
PF-9	1440.6	1292.1	1653.7

In PVP molecule, both O-atom of C=O group and N-atom of heterocyclic ring can form coordinate bonds with M^{n+} ions. But from the table it is evident that there is no observable change in C-N-C and N-C stretching frequencies in any of the samples. However there is a variation in stretching frequency of carbonyl (-C=O) group. In pure PVP, peak for –C=O group appears at 1663.4 cm^{-1} and in the PVP – Fe (II) complex it appears at 1653.7 cm^{-1}. The shift in the peaks towards lower wave number region indicates that C=O bond is getting weakened and there exists an interaction between ferrous ions and PVP through oxygen of C=O group of the polymer.

Moreover, in both PF-5 and PF-5A, the magnitude of the shift in the stretching frequency of C=O towards the low wave number direction is same. This indicates that the extent of interaction between PVP and ferrous ions is same with both aqueous solution and with alcoholic solution of ferrous salt i.e., the change in the solvent used, for dissolving the metal salt, from water to alcohol doesn't affect the complex formation.

3.2.2 ^{1}H-NMR Spectral Studies

^{1}H-NMR spectrum of the PVP – Fe (II) complex is shown in Fig. 4. Appearance of five peaks shows five different types of hydrogen in PVP.

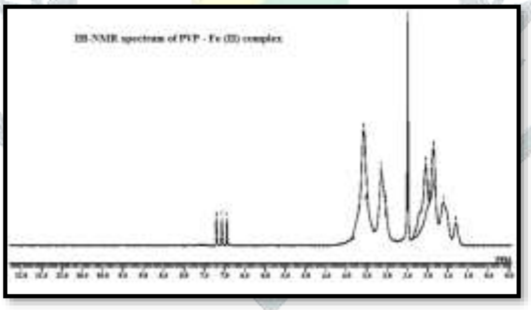


Fig. 4. ^{1}H-NMR spectrum of PVP – Fe (II) complex

The spectrum indicates that,

- Main chain methylene proton ($–CH_2–$) of PVP resonate at $\delta = 3.15$ ppm
- Methine proton (– CH –) of PVP resonate at $\delta = 3.34$ ppm
- Methylene protons of the side chain (i.e., pyrrolidone ring) in PVP signal at δ values = 1.86 ($–^4CH_2$) ppm, $\delta = 1.61$ ($–^2CH_2$) ppm and $\delta = 1.31$ ($–^3CH_2$) ppm respectively.

3.2.3 ^{13}C-NMR Spectral Studies

^{13}C NMR (100 MHz DMSO-d6) spectrum of PVP – Fe (II) complex indicates that the methylene carbons ($^2CH_2$, $^3CH_2$, $^4CH_2$) of side chain resonate and produce peaks in the range of 17.9 ppm to 30.88 ppm. The carbonyl carbon ($^1C=O$) produces peak at $\delta = 173.7$ ppm

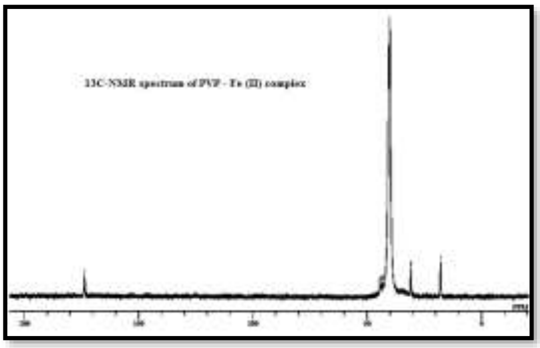
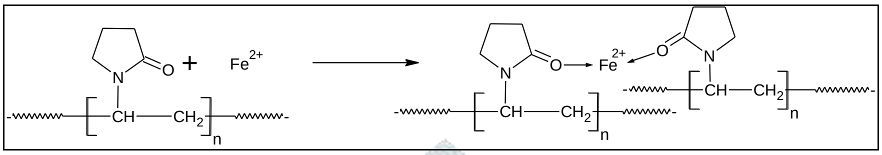


Fig. 5. 13C-NMR spectrum of PVP – Fe (II) complex

Based on all the above spectral data, the possible structure of the complex may be given as shown in the scheme 1.

Scheme 1: General reaction for the formation of PVP – Fe (II) complexes



3.2.4 Optimization of the Conditions

The metal complexes of PVP – Fe (II) were prepared in different molar compositions. FTIR spectra of all the complexes were taken and studied for the optimization of the conditions for better complexation of PVP with ferrous ions. The variation in the stretching frequency of C=O reveals that the formation of complex is through oxygen of ketone group of PVP. The ^{1}H- NMR and ^{13}C-NMR spectral studies are complementary to FTIR data.

Based on the stretching frequencies of C=O in the samples, we can conclude that interaction between ferrous ions and PVP is same at all molar compositions except in the lower concentration of PVP and very low concentration of salt solution (PF-1 and PF-2). Except in these two compositions, in all others the magnitude of the shift is same indicating that the change in molar composition has little effect on the extent of interaction between ferrous ions and PVP.

3.2.5 Thermal Analysis – Differential Scanning Calorimetric (DSC) Studies

DSC thermogram of PVP – Fe (II) complex is shown in Fig. 6.

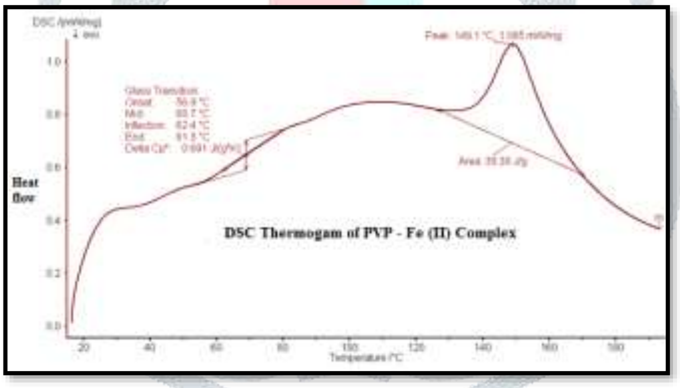


Fig. 6. DSC thermogram of PVP – Fe (II) complex

There will be change in Tg of a polymer when different degrees of polymerization are observed or when the additives are inserted. Tg of PVP-30K from literature is 163ºC. Thermogram of PVP – Fe (II) complex shows that its Tg is 68.7ºC. The deviation in the Tg value of the PVP – Fe (II) complex indicates that there is interaction between PVP and ferrous ions.

The complex melts (Tm) at 149ºC. DSC study facilitates us to evaluate the heat capacity of the given polymeric compound. The heat capacity of the complex is given by the area under the peak which is equal to 38.38 J/g for this complex.

AS there is no crystallization dip in the thermogram, it can be concluded that the complex is amorphous.

3.3.6 Magnetic Properties – Vibrating Sample Magnetometric (VSM) Studies

The magnetization curve of PVP – Fe (II) complex obtained by VSM studies is shown in the Fig. 7.

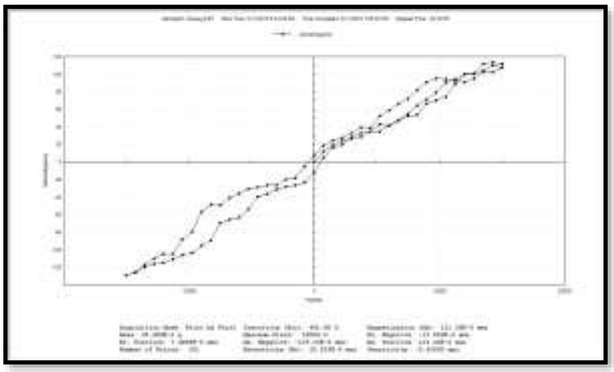


Fig. 7. Magnetization Curve of PVP – Fe (II) complex

- VSM curve of the PVP – Fe (II) complex shows curvilinear magnetization of the sample.

- As the applied field (H) varies between -20000G and +20000G, the dipole moments align randomly, showing the complex to be anisotropic.
- For a zero external field, there is small trace of residual magnetization. Hence the complex is ferromagnetic for low dipole moments.
- For all higher fields the sample exhibits paramagnetic behaviour.

3.2.6 Antimicrobial Studies

Antimicrobial studies are screened by 'Agar well diffusion'. The standard antibacterial used was Streptomycin sulphate. The standard antifungal used was Fluconazole. The inhibition zone (in mm) for the polymer – metal complex is shown in the Table 3.

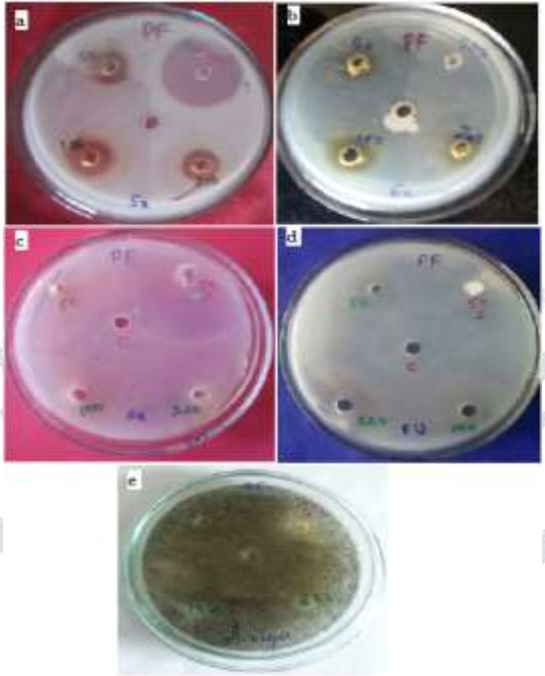
Table 3. Inhibition zones (in mm) of PVP – Fe (II) complex on pathogenic organisms

Test Sample	**Volumes of the sample (µl)**	**Bacterial Strains**				**Fungal Strains**		
		Bc	**Sa**	**Ec**	**Ea**	**Fu**	**An**	**Pe**
PF	50	20	14	10	20	-	-	-
	100	18	16	13	20	-	-	-
	200	25	20	12	20	-	-	-

Bc*: Bacillus pumillus,* ***Sa****: Staphylococcus aureus,* ***Ec****: Escherichia coli,* ***Ea****: Enterobacter aerogenes,* ***Fu****: Fusarium oxysporum,* ***An****: Aspergillus niger,* ***Pe****: Penicillium sp,* '-': - inactive.

The table shows that the PVP – Fe (II) complex exhibits good inhibition for all the bacteria selected at all the dosages administered but it is inactive towards selected fungi at any dosage.

Photographic images of the antimicrobial activity of the PVP – Fe (II) complex on the selected pathogens are shown in the Fig. 8.



Photographic representation of antimicrobial test
a. *Staphyllococcus aureus*, b. *Escherichia coli*,
c. *Enterobacter aerogenes*, d. *Fusarium oxysporum*,
e. *Aspergillus niger*

Fig. 8. Photographic image of antimicrobial activity of PVP – Fe (II) complex

IV. CONCLUSIONS

The metal complexes of PVP – Fe (II) were prepared in different molar compositions. FTIR spectra of all the complexes were taken and studied for the optimization of the conditions for better complexation of PVP with ferrous ions. The shift in the stretching frequency of ketone (C=O) group in PVP – Fe (II) complexes from that in pure PVP reveals that the formation of complex may be through oxygen of the –C=O group of PVP. The ^{1}H- NMR and ^{13}C-NMR spectral studies also supplement the same.

Based on the stretching frequencies of –C=O group in the samples, we can conclude that lower concentration of ferrous salt and PVP are not so favourable conditions for the formation complex between them. Further, the solvents water and absolute alcohol used for the dissolution of ferrous salt have no effect on the complex formation.

DSC thermogram of the complex shows that PVP – Fe (II) complex is amorphous. Magnetization curve by VSM studies shows that the complex exhibits curvilinear magnetization and ferromagnetism and the complex is anisotropic.

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