

Synthesis and Characterisation of Poly (Vinylpyrrolidone) – Nickel (II) Complexes

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Abstract: Main use of polymer – metal complexes lies in their ability to act as catalysts. In the proposed work we have selected poly (vinyl pyrrolidone) as ligand for complexing with nickel. Poly (vinyl pyrrolidone) is a water soluble polymer having a large number of consumer and environment friendly uses which are the consequences of its unique properties like biological compatibility, low toxicity, film forming ability, complexing ability, resistance to thermal degradation in solution and relatively inert behavior towards salts and acids. Nickel, being a transition metal, shows very good catalytic properties. Nickel based catalysts meet the criteria required for the catalysis of a wide range of chemical reactions. Polymer-metal complexes of poly (vinylpyrrolidone) and nickel were prepared by using aqueous solution of PVP (30K) and alcoholic solution of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) at room temperature with different molar compositions. The polymer-metal complexes were obtained in crystalline form by evaporation of the solvent. They were characterized by solubility studies, FTIR, ¹H - NMR and ¹³C - NMR. Procedure was repeated with aqueous solution of the salt also. The spectral analysis of the reactants and the polymer-metal complexes confirmed the formation of expected complexes. The conditions for better complexation were optimized.

Keywords: ¹³C-NMR, FTIR, ¹H-NMR, Nickel chloride hexahydrate, Poly (vinyl pyrrolidone).

I. Introduction

Organic polymers like poly (vinyl pyrrolidone), poly (vinyl alcohol), etc can act as ligands and form complexes with transition metal ions through co-ordinate bonds. A polymer-metal complex is a metal complex containing a polymer ligand. Such complexes show a specific structure in which central metal ions are surrounded by a gigantic polymer chain. Polymer-metal complexes exhibit many interesting characteristics such as improved thermal stability [1], hardness and especially catalytic activities, which are different from that of the corresponding ordinary metal complexes of low molecular weight [1-3].

Metal complexes are generally of two types - Werner type and non-Werner type. Non-Werner type complexes are also called organo-metallic compounds which contain carbon-metal (C-M) bonding. Most of the polymer-metal complexes studied so far belong to Werner type. But those of non-Werner type are more attractive to chemists because of their specific catalytic activities [2-4]. In recent years the study of polymer – metal complexes has been of great interest to chemists as they serve as excellent models for metallo-enzymes [4, 5]. They also lead to the development of highly efficient catalysts [5]. These complexes are the basis for the synthesis of wide range of biomedical preparations and drugs also [6-8].

Poly (vinyl pyrrolidone), henceforth abbreviated as PVP, is non-toxic, water soluble, biologically compatible [9-11] and hence it is eco-friendly [12]. It is resistant to thermal degradation in solution and relatively inert towards action of acids and salts. With poly (vinyl pyrrolidone), as ligand, it is easy to achieve the desired success as it exhibits unusual strong tendency towards complex formation [13, 14].

Nickel is a transition metal of 3d series which exhibits variable oxidation states from 0 to +2 in its compounds. As a consequence of this variable oxidation state it is known for its catalytic activity [15, 16]. Further nickel and its compounds are more economical compared to other competing material of the platinum group [17].

Nickel based catalysts meet wide range of requirements of most of chemical reactions and therefore often the preferred choice [18].

II. Experimental

2.1 Materials

Poly (vinyl pyrrolidone) sample of molecular mass 30K with molecular formula $(C_6H_9NO)_n$ and nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) of molecular mass = 237.7 were used for the synthesis of complexes. Double distilled water was used for the synthesis. The reactants and other solvents used were of AR grade from SD Fine Chemicals, India. The chemicals were used directly without any further purification.

2.2 Synthesis of PVP-Nickel Complexes

PVP - Nickel complexes were prepared in aqueous medium. Aqueous solution of PVP was mixed with alcoholic solution of nickel (II) chloride hexahydrate in different molar compositions. The aqueous solution of PVP was colourless and alcoholic solution of nickel salt was pale green in colour. The resulting mixtures were stirred on magnetic stirrer at room temperature till the volume was reduced to about half of the initial volume. The thickened masses were evaporated to dryness in oven at 70-80°C for 9-10 hours. Shining crystals having green colour, whose intensities increased with increase in PVP-nickel composition, were obtained.

One more complex namely N5A with 25% aqueous solution of PVP (30K) and 0.5 molar aqueous solution (instead of alcoholic solution) of nickel (II) chloride was also prepared, by taking the same volumes of reactants as in the case of N5, to study the effect of solvent on the complex formation.

Crystals thus obtained were characterized by solubility studies, FTIR, 1H -NMR and ^{13}C -NMR.

2.3 Solubility Studies

Solubility of PVP-Nickel complexes were tested in water and various polar and non-polar organic solvents. To 5 mL each of different solvents in standard test tubes, about 8-10 mg of PVP-Ni complexes were added and kept overnight. The solubility of the complexes in these solvents was observed after 24 hours.

2.4 FTIR Spectral Analysis

Fourier Transform Infra Red (FTIR) spectra of the prepared samples, pure samples of PVP and nickel (II) chloride hexahydrate were recorded on a Jasco model FTIR – 4100 spectrophotometer in 400-4000 cm^{-1} range in the form of KBr pellets.

2.5 NMR spectral Analysis

1H -NMR and ^{13}C -NMR spectra of the samples, were recorded on a JNM-400 model, Jeol 400-MHz spectro-photometer respectively.

III. Results And Discussion

3.1 Synthesis

50 mL of aqueous solution of PVP was mixed with 10mL of alcoholic solution of nickel (II) chloride hexahydrate in different molar compositions as given in the Table 1. The complexes were synthesized as per the procedure given in Para 2.2. The green coloured crystals obtained showed deliquescent properties.

Table 1 : Different molar compositions of aqueous solution of PVP and alcoholic solution hexahydrate nickel chloride

PVP↓ / Salt Solution→	0.1M	0.5M	1.0M
10%	N1	N4	N7
25%	N2	N5	N8
40%	N3	N6	N9

3.2 Solubility

The complexes obtained were soluble in polar solvents like water, methanol, ethanol, 2-propanol, DMF and DMSO. But the complexes did not show solubility in THF and chlorobenzene, which are also polar solvents. The complexes were soluble in chloroform with slight turbidity. They were insoluble in non-polar solvents like acetone, diethyl ether, n-hexane, n-heptane, toluene, carbon tetrachloride and 1, 4 -dioxane. The reactant, PVP also showed exactly similar behavior with the solvents listed above.

3.3 FTIR Spectra

FTIR spectroscopy and NMR spectroscopy are very useful techniques to examine the structure and structural transformation of materials. The most useful and simple physical method for determining the functional groups on polymers and the formation of complexes with metal ions is the IR spectroscopy. It helps in the location of coordination sites in the metal complexes with polymeric ligands.

The FTIR spectrum of pure PVP sample used for the synthesis of the complexes clearly indicates that the observed absorption peaks correspond to the characteristic chemical bonds present in PVP (Fig.1).

The C=O groups of pure PVP show a prominent peak at 1659.4 cm⁻¹ in FTIR spectrum which is characteristic of C=O bond in PVP (i.e., amide C=O bond). This characteristic peak can be investigated to explore the interaction between PVP and metal ions.

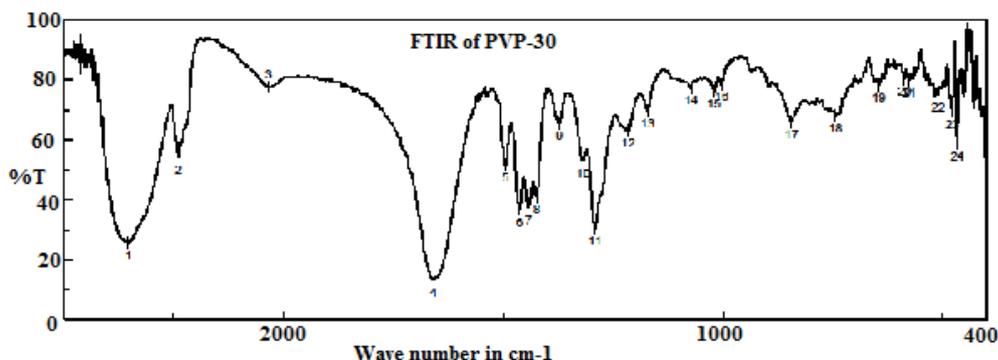
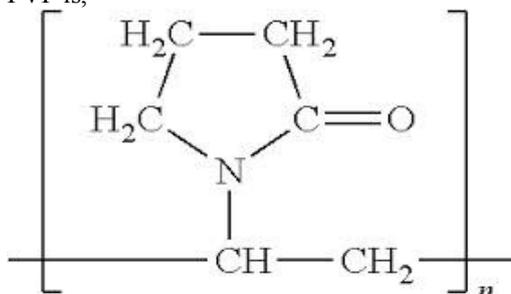


Fig. 1. FTIR spectrum of PVP-30

Polymer– metal complexes are formed due to the interaction between macromolecular functional groups and Mⁿ⁺ ions. Here Mⁿ⁺ ion acts as acceptor and groups such as –NH₂, heterocyclic N, –CO–, etc, of polymer chain act as donors.

Partial Structure of the polymer, PVP is,



The stretching frequencies of C–N–C, –N–C and C=O groups in pure PVP sample and in PVP-nickel 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 Poly (vinyl pyrrolidone)-Nickel Complexes

Sample	CNC Stretching	N-C Stretching	C=O Stretching
PVP – 30K	1443.5	1292.1	1659.4
N1	1442.5	1292.1	1651.7
N2	1443.5	1293.0	1648.8
N3	1441.5	1292.1	1652.7
N4	1444.4	1293.0	1651.7
N5	1443.5	1292.1	1651.7
N5A	1444.4	1293.0	1651.7
N6	1443.5	1292.1	1653.7
N7	1445.4	1294.0	1650.8
N8	1443.5	1293.0	1651.7
N9	1444.4	1293.0	1655.6

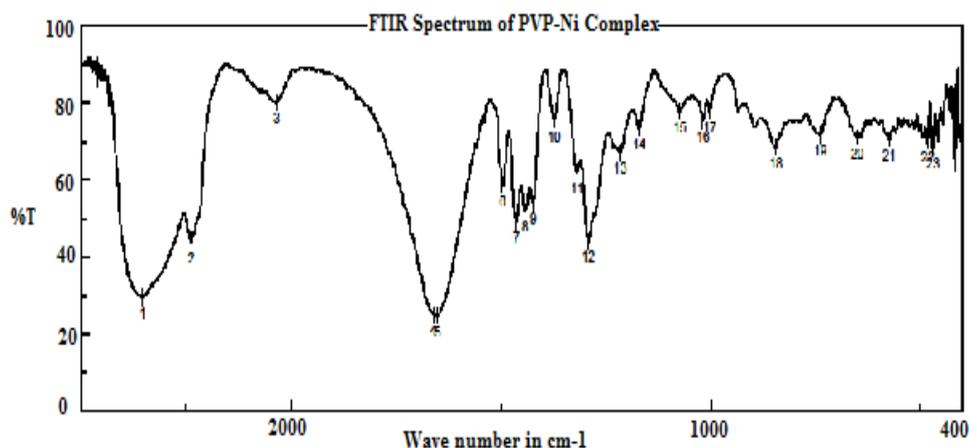


Fig. 2. FTIR spectrum of PVP-Nickel complex

Even though both O-atom of C=O group and N-atom of heterocyclic ring can form coordinate bonds with M^{n+} ions, from the table it is evident that there is no observable change in C-N-C and N-C stretching frequencies in all 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 1659.4 cm^{-1} and in the PVP-Nickel complex it appears at 1648.8 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 nickel ions and PVP through oxygen of C=O group of the polymer.

Moreover, in both N5 and N5A, 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 nickel ions is same with both aqueous solution and with alcoholic solution of nickel salt. In other words the change in the solvent used, for dissolving the metal salt, from water to alcohol has little effect on the complex formation.

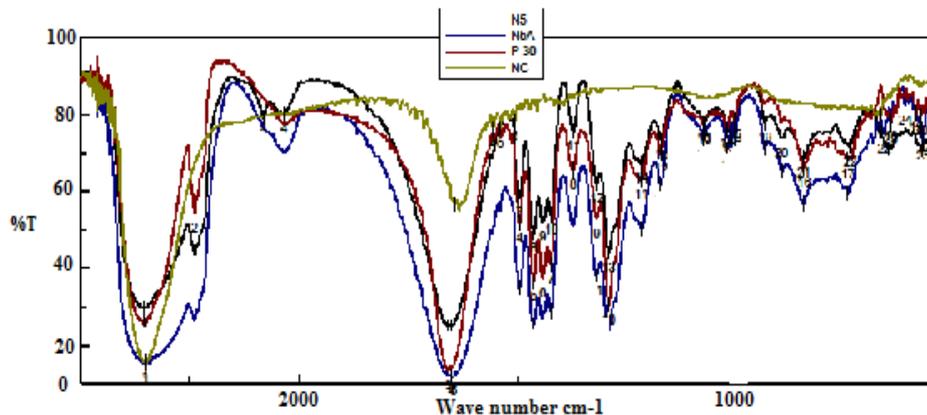


Fig.3. Overly spectra of PVP –Nickel complex, pure PVP and pure nickel salt

3.4 ^1H NMR

^1H NMR gives the information about the types of protons, number of each type of proton and their environments. Thereby it helps in arriving at important conclusions about the structure of the polymer-metal complex.

^1H NMR spectrum of the polymer-metal complex shown in Fig. 4, has the main chain methylene proton signals that resonate at chemical shift (δ) of 2.05 ppm. The methine proton (-CH) of PVP appeared at $\delta = 3.55$ ppm. The ring methylene protons in PVP signals are at $\delta = 1.87$ ($^4\text{CH}_2$) ppm, $\delta = 1.63$ ($^2\text{CH}_2$) ppm and $\delta = 1.32$ ($^3\text{CH}_2$) ppm.

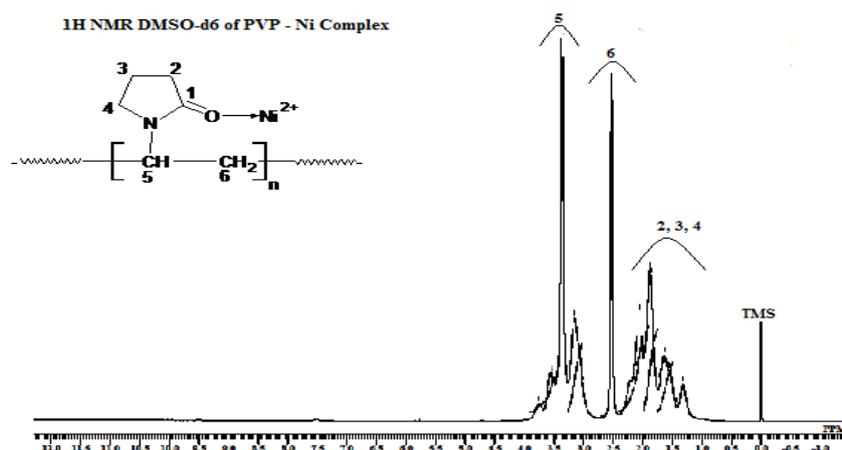


Fig. 4. ¹H-NMR spectrum of PVP-Nickel complex

3.5 ¹³C NMR

Carbon atoms form the skeleton of an organic molecule. Hence information about these carbon atoms of a molecule is very useful in the identification of the structure of a newly synthesized compound. ¹³C NMR spectrum of PVP-nickel complex is shown in Fig. 5.

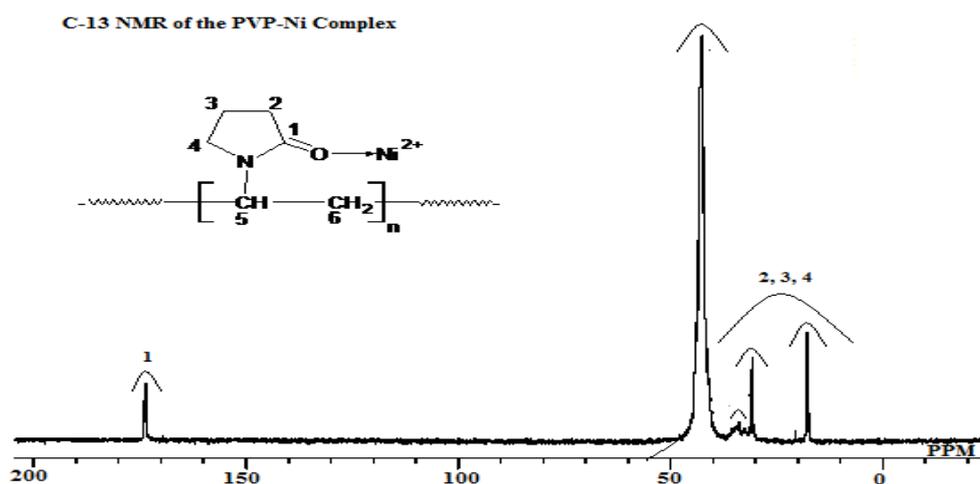
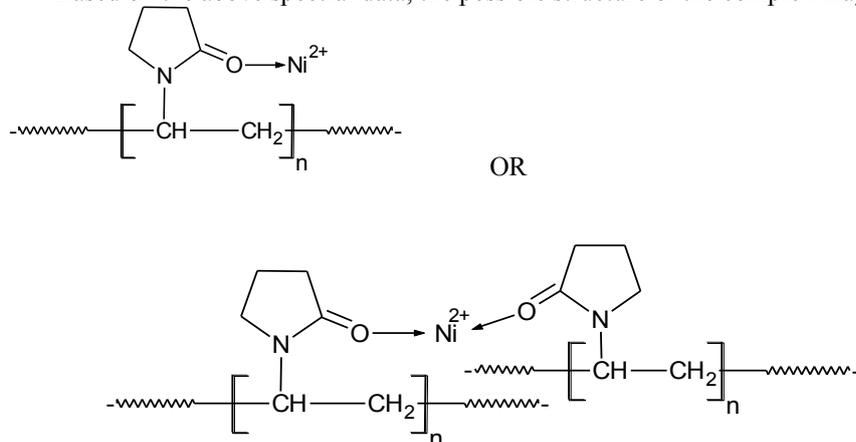


Fig. 5. ¹³C-NMR spectrum of PVP-Nickel complex

The peaks in the range of 17.8 ppm to 33.7 ppm are due to side chain methylene carbons (²CH₂, ³CH₂, ⁴CH₂). The peak at $\delta = 173.6$ ppm is due to carbonyl carbon (¹C=O).

Based on the above spectral data, the possible structure of the complex may be given as:



IV. Conclusion

The metal complexes of PVP-Nickel 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 nickel. The shift in the stretching frequency of C=O in PVP-Ni complexes from that in pure PVP reveals that the formation of complex may be through Oxygen of PVP. The ¹H-NMR and ¹³C-NMR spectral studies also supplement the same.

Based on the stretching frequencies of C=O group in the samples, we can decide in which case the bond between nickel and PVP is strong (N2) and in which it is weak (N9). Hence this comparative study may help to study and optimizing the conditions for the preparation of PVP-metal complexes. Further, the solvents water and absolute alcohol used for the dissolution of nickel salt showed very little effect on the complex formation.

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References

- [1]. Diaz, E, Valenciano, R, Landa P.; Arana, J. L.; Gonzalez, Viscometric study of complexes of poly(vinyl pyrrolidone) with Co²⁺, Polymer Testing, 21, 2002, 247-251
- [2]. Diaz E, Valenciano R, Katime I.A. Study of complexes of poly (vinyl pyrrolidone) with copper and cobalt on solid state J Applied Polymer Science, 93, 2004,1512-1518.
- [3]. R I Musin, V A Li, et-al, Synthesis and biological activity of cobalt-containing polyvinylpyrrolidone complexes, Pharmaceutical Chemistry Journal, 23 (5), 1989, 375-378
- [4]. David C Sherrington, Polymer-supported metal complex oxidation catalysts, Pure and Applied Chemistry, 60 (3), 1988, 401-414
- [5]. Kurt E Geckeler, Polymer-metal complexes for environmental protection. Chemoremediation in the aqueous homogeneous phase, Pure and Applied Chemistry, 73 (1), 2001, 129-136.
- [6]. N-vinyl-2-pyrrolidone and polyvinyl pyrrolidone, IARC Monographs Supplement, 7, 1987, 1181-1187
- [7]. Mohammad Saleem Khan, Khaista Gul and Najeeb Ur Rehman, Interaction of polyvinylpyrrolidone with metal chloride aqueous solutions, Chinese Journal of Polymer Science, 22 (6), 2004, 581-584
- [8]. Issa A Katime and Jose. R. Ochoa, Bilbao, Carlos Sieiro Del Nido, Synthesis and characterization of poly (vinyl carbazole) complexes with copper (II) chloride in THF Solution, J of Appl Pol Sci, 34 (5), 2003, 1953-1958.
- [9]. B. L. Rivas, G V. Seguel and C. Ancatripal, Polymer metal complexes: Synthesis, characterization and properties of poly(maleic acid) metal complexes with Cu(II), Co(II), Ni(II) and Zn(II), Polymer Bulletin, 44 (5-6), 2000, 445-452.
- [10]. Clear.B.M. Kanth, K. Kalishwaralal, M. Sriram, Suresh Babu, P. Ram kumar, H.Youn, S. Eom, S. Gurunathan, Anti-oxidant effect of gold nanoparticles restrains hyperglycemic conditions in diabetic mice, Journal of nanobiotechnology, 8, 2010, 1-16.
- [11]. Ashraf Malik, Shadma Parveen, et-al, Coordination Polymer: Synthesis, Spectral Characterization and Thermal Behaviour of Starch-Urea Based Biodegradable Polymer and its Polymer Metal Complexes, Bioinorganic Chemistry and Applications, 2010, Article ID 848130, 8 pages
- [12]. N. Giri, R. K. Natarajan, S. Gunasekaran, S. Shreemathi, 13C NMR and FTIR spectroscopic study of blend behavior of PVP and nano silver particles, Archives of Applied Science Research, 3 (5), (2011), 624-630
- [13]. S. Vijaya Kumar, S Prasanna Kumar, B. S. Sherigara, Boreddy S.R. Reddy, T M Aminabhavi, N-Vinylpyrrolidone and 4-vinyl benzylchloride Copolymers: Synthesis, Characterization and Reactivity Ratios, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 45 (10), 2008, 821-827
- [14]. Didier Astruc, Transition-metal nanoparticles in catalysis, Nanoparticles and Catalysis, (Wiley-VCH Verlag GmbH & Co.) 2008, ISBN: 978-3-527-31572-7
- [15]. Final Report on The Importance of Nickel Compounds: Catalysts, prepared for European Nickel Institute, 05th October 2007
- [16]. Wei-xiaTu, Xiao-bin Zuo and Han-fan Liu Study on the interaction between polyvinylpyrrolidone and platinum metals during the formation of the colloidal metal nanoparticles, Chinese J of PolymSci, 26 (1), 2008, 23-29
- [17]. F A Carey R J Sundberg, Advanced Organic Chemistry, 2nd Edition, ISBN 0-306-41199-7
- [18]. Robert Crabtree, Comprehensive Organometallic Chemistry III, (Mike Mingos) 2006 ISBN 0-08-044590-X.