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Synthesis and Characterisation of Poly(Vinyl Pyrrolidon)-Cobalt(II) Complexes

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ABSTRACT:
The biological and industrial importance of many transition metals like iron, cobalt, copper etc., has been well studied. However, the attempts to employ inorganic salts of these metals in medical practice were not successful as most of them are highly toxic. In such cases Polymer-Metal Complexes can be used as substitutes both for addition and removal of metal ions into and out of a system. The use of water soluble polymer like poly (vinyl pyrrolidone), as a ligand, broadens the applications of these complexes. Polymer-metal complexes of poly (vinyl pyrrolidone) and cobalt were prepared by using aqueous solution of PVP (30K) and alcoholic solution of cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) 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 FTIR, ^1H -NMR with DMSO as solvent and ^{13}C - NMR. Procedure was repeated with aqueous solution of the salt also. The extent of complex formation was predicted by comparing the spectral data of the complexes with that of pure poly (vinyl pyrrolidone). The conditions for better complexation were optimized.

Key words: *Poly (vinyl pyrrolidone), Cobalt chloride hexahydrate, FTIR, ^1H-NMR, ^{13}C-NMR.*

1. INTRODUCTION

Metal ions can bind to neutral or weakly charged water soluble polymers. 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 have interesting and important characteristics, especially catalytic activities, which are different from that of the corresponding ordinary metal complexes of low molecular weight.

Metal complexes are generally of two types - Werner type and non-Werner type. Non-Werner type complexes are also called organometallic 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. In recent years the study of polymer-metal complexes has been of great interest to chemists [1-10] as they serve as excellent models for metalloenzymes [4,5]. They also lead to the development of highly efficient catalysts. These complexes are 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 metal ions were studied and the optimum conditions, under which the desired properties are exhibited, are analyzed. PVP is non-toxic, water soluble, biologically compatible [11, 12] and hence it is eco-friendly [13, 14]. It is also resistant to thermal degradation in solution and relatively inert towards action of acids and bases. With poly (vinyl pyrrolidone) (PVP) as ligand, it is easy to achieve the desired success as it exhibits unique combination properties and high capacity for complex formation. Hence it can be used either to introduce or to remove metal ions into or out of a system because of its complex forming ability [15,16].

2. EXPERIMENTAL

2.1. Materials

Poly (vinyl pyrrolidone) sample of molecular mass 30K with molecular formula $(C_6H_9NO)_n$ and cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Molecular

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mass=238) were used for the synthesis of complexes. Double distilled water is used for the synthesis. The reactants and other solvent (i.e., absolute alcohol) used were of AR grade and of SD Fine Chemicals. The chemicals were used directly without further purification.

2.2. Method

PVP-cobalt complexes were prepared in aqueous medium in the following manner: 50 mL of aqueous solution of PVP was mixed with 10mL of alcoholic solution of cobalt (II) chloride hexahydrate in different molar compositions as given in the Table 1. The aqueous solution of PVP was colourless and alcoholic solution of cobalt salt was ink blue 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 ºC for 9-10 hours. Shining crystals having ink blue colour, whose intensities increased with increase in PVP-cobalt composition, were obtained. The crystals showed hygroscopic properties. They were soluble in water as well as in ethanol producing pink and blue colours respectively.

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

PVP / Salt Solution	**0.1M**	**0.5M**	**1M**
10%	C1	C4	C7
25%	C2	C5	C8
40%	C3	C6	C9

A complex (C5A) with 25% aqueous solution of PVP (30K) and 0.5 molar **aqueous** solution of cobalt (II) chloride was also prepared, by taking the same volumes of reactants as in the previous case, to study the effect of solvent on the complex formation.

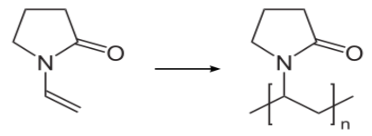


Figure1: Formation and Structure of Poly (vinylpyrrolodone)

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

Fourier Transform Infra Red (FTIR) spectra of the prepared samples, pure samples of PVP and cobalt (II) chloride hexahydrate were recorded on a Jasco model FTIR – 4100 spectrophotometer in 400-4000 cm^{-1} range in the form of KBr pellets. The signals corresponding to different groups are tabulated in the Table 2.

^{1}H-NMR and ^{13}C-NMR of the sample, C5 were recorded on a JNM-400 model, Jeol 400-MHz spectrophotometer.

FTIR spectroscopy and NMR spectroscopy are very useful techniques to examine the structure and structural transformation of materials.

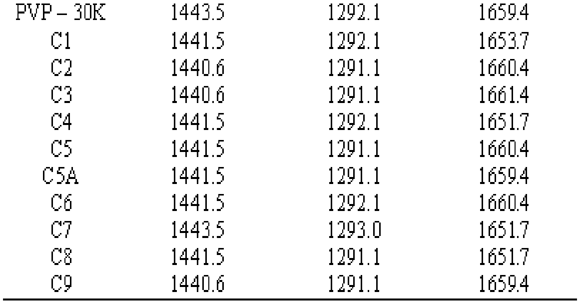
3. RESULTS AND DISCUSSION

3.1. FTIR Spectra

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 clearly indicates that the observed absorption peaks correspond to the characteristic chemical bonds present in PVP.

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 [17, 18]. The FTIR peaks of C=O groups in the PVP-cobalt complexes 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(vinylpyrrolidone) - Cobalt Complexes



Sample	CNC Stretching	N-C Stretching	C=O Stetching
PVP – 30K	1443.5	1292.1	1659.4
C1	1441.5	1292.1	1653.7
C2	1440.6	1291.1	1660.4
C3	1440.6	1291.1	1661.4
C4	1441.5	1292.1	1651.7
C5	1441.5	1291.1	1660.4
C5A	1441.5	1291.1	1659.4
C6	1441.5	1292.1	1660.4
C7	1443.5	1293.0	1651.7
C8	1441.5	1291.1	1651.7
C9	1440.6	1291.1	1659.4

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. But there is a variation in stretching frequency of carbonyl C=O.

The shifts in the peaks towards lower wave number region indicate that C=O bond is getting weakened and there exists an interaction between cobalt ions and PVP through oxygen. Further it is observed that the order of interaction between PVP and cobalt ions from weak to strong is: (i) C1, C4, C7 (ii) C2, C5, C8 (iii) C3, C6, C9. In other words there is decrease in the stretching frequency of C=O with increase in the Co ion concentration keeping amount of PVP constant. This implies that there is increase in the interaction between PVP and metal ion with increase in the concentration of metal ion.

Stretching frequency of C=O increases with increase in PVP concentration keeping Co^{+2} ion concentration constant. This implies that the interaction between PVP and metal ions is not much favoured by the increase of only PVP concentration keeping metal ion concentration same.

Moreover, between C5 and C5A, in C5A the shift in the stretching frequency of C=O towards the low wave number direction is more, indicating more interaction between PVP and cobalt ions when aqueous solution of cobalt chloride is used instead of alcoholic solution during preparation.

3.2. ^{1}H NMR

^{1}H 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. ^{1}H NMR data: (400 MHz, DMSO): 1.316 (2H, t, J=123.535Hz, Me), 1.865 (1H, t, J=67.99Hz, CNMe), 2.05 (2H, t, J=71.28Hz, NMe), 3.155(2H, J=159.42Hz, Me), 3.554 (2H, t, J= 77.88Hz, COMe).

3.3 ^{13}C NMR

Carbon atoms form the skeleton of an organic molecule. Hence information about the carbon atoms of a molecule is very useful in the identification of the structure of the unknown compound. ^{13}C NMR spectrum of PVP-cobalt complex shows five peaks indicating five types of carbons. Spectral data: ^{13}C NMR (100 MHz DMSO-d_6): 17.9 (CH_2), 30.9 ($2CH_2$), 33.8 (CH_2), 174.3 (C=O).

4. CONCLUSION

The metal complexes of PVP-Co 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 Cobalt. The variation in the stretching frequency of C=O reveals that the formation of complex may be through Oxygen of PVP. The ^{1}H- NMR and ^{13}C-NMR spectral studies also supplement the same.

Based on the stretching frequencies of C=O in the samples, we can decide in which case the bond between cobalt and PVP is strong and in which it is weak. Hence this comparative study helps us in optimizing the conditions for the preparation of PVP-metal complexes depending on whether we want to introduce metal ions into a system (as in the case of essential elements) or to remove metal ions out of a system (as in the case of heavy metal ions).

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5. REFERENCES

[1]. E. Diaz, R. Valenciano, P. Landa, J. L. Arana, Gonzalez, (2002), Study of complexes of Poly (vinyl pyrrolidone) with Co^{2+}, ***Journal of Polymer Test,*** **21**, 247.

[2]. E. Diaz, R. Valenciano I.. Katime, (2004), Study of complexes of poly (vinyl pyrrolidone) with copper and cobalt on solid state, ***Journal of Applied Polymer Science,*** **93**, 1512-1518.

[3]. I. Katime, J. R. Ochoa, (1987), Study of complexes of poly (vinyl pyrrolidone) with Cobalt and Copper, ***Journal of Applied Polymer Science,*** **34**, 1953.

[4]. E. T.Tsuchida, H. Nishide (1977), Preparation of Polymer-Bound Dinitrogen Complexes by Direct Reactions of Polymer–Metal Complexes with Molecular Nitrogen ***Advanced Polymer Science***, **24**,1.

[5]. N. Giri, R. K. Natarajan, S. Gunasekaran, S. Shreemathi, (2011), 13C NMR and FTIR spectroscopic study of blend behavior of PVP and nano silver particles, ***Archives of Applied Science Research,*** **3 (5),** 624-630

[6]. IARC Monographs Supplement, (1987) N-vinyl-2-pyrrolidone and polyvinyl pyrrolidone, ***IARC Monographs Supplement,*** **7**, 1181-1187

[7]. Md. Saleem Khan, K Gul, N Ur Rehman, (2004), Interaction of polyvinylpyrrolidone with metal chloride aqueous solutions, ***Chinese Journal of Polymer Science,*** **22**, 581-584.

[8]. I. A. Katime, J. R. Ochoa, Bilbao, C. S. D. Nido, (1987), Synthesis and characterization of poly (vinyl carbazole) complexes with copper (II) chloride in THF Solution, ***Journal of Applied Polymer Science,*** **34**, 1953-1958.

[9]. B.M. Kanth, K. Kalishwaralal, M. Sriram, Suresh Babu, P. Ram Kumar, H.Youn, S. Eom, S. Gurunathan, (2010) Anti-oxidant effect of gold nanoparticles restrains hyperglycemic conditions in diabetic mice, ***Journal of nanobio technology*, 8**: 1-16.

[10]. Z. J. Jiang, C. Y. Liu, and L. W. Sun, (2005) Catalytic properties of silver nanoparticles supported on silica spheres, ***Journal of Physical Chemistry B*, 109 (5),** 1730–1735,

[11]. B. L. Rivas, G V. Seguel, C. Ancatripal (2000), Polymer metal complexes; Synthesis, characterization and properties of poly(maleic acid) metal complexes with Cu(II), C0(II), Ni(II) and Zn(II), ***Polymer Bulletin*, 44**, 5-6.

[12]. P. Jain, T. Pradeep, (2004), Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter, ***Biotechnology Bioengineering*. 90,** 59**.**

[13]. H Hossienkhani, M Hosseinkhani, (2009), Biodegradable polymer-metal complexes for gene and drug delivery, ***Current Drug Safety***, **4**, 79-83.

[14]. M Adharvana Chari, D Shobha, T Kiran Kumar and K Syamasundar, (2007), Polymer (PVP) supported ferric chloride as a heterogeneous catalyst for selective deprotection of aldoximes and hydrazone, ***Trends in Applied Sciences Research*, 2(1)**, 80-84.

[15]. ***A. Pınar, O. Kavaklı, Gü*** (2004), Removal of concentrated heavy metal ions from aqueous solutions using polymers with enriched amidoxime groups, ***, Journal of Applied Polymer Science*, 93**:1705-1710..

[16]. K. E. Geckeler, (2001) Polymer-metal complexes for environmental protection. Chemoremediation in the aqueous homogeneous phase, ***Pure and Applied Chemistry*, 73**, 1, 129-136.

[17]. W-X Tu, X-B Zuo, H-F Liu (2008), Study on the interaction between polyvinylpyrrolidone and platinum metals during the formation of the colloidal metal nanoparticles, ***Chinese Jouranl of Polymer Science*,** 26, 1, 23-29.Text Book of Organic Spectroscopy by William Kemp (3rd Edition).