Microwave Synthesis of tris-(1,10-phenanthroline)vanadium(III) complex and their electrocatalytic activity towards uric acid

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Abstract— Vanadium is most important biological element which play a vital role in diabetic treatment to the human. In 1899, a report shows the decreasing level of glucose in urine with the aid of sodium vanadate. It is the first report of vanadium used for diabetic patients to know the level of glucose. The insulin mimetic activity of vanadium is the most important area for the research, recent interest has been shown to synthesis of stable vanadium complex with minimum toxicity to the biological system. The vanadium has different oxidation states which exhibit better electrocatalytic activity and sensing ability. The vanadium complex with phenanthroline ligand shows batter stable complex due to planar nature and presence of sp^2 hetero nitrogen atoms. Many metal complexes of 1,10-phenanthroline (1,10-phen) and its derivatives often show fascinating chemical and physical properties because of their fine π-conjugated character and strong chelating abilities. It gives a rigid planar metal complexes with different metal ions. The vanadium phenanthroline complex was synthesized by microwave irradiation method. The microwave method gives more yield at short reaction time with minimum solvents. Hence, the microwave method is one of the green chemical process for synthesis of different chemicals. The synthesized tris-(1,10-phenanthroline)vanadium(III) complex shows good electrocatalytic activity, it used for the detection of uric acid (UA). UA is the end product of catabolism of the purine nucleosides. UA levels in physiological fluids such as plasma and urine serve as valuable indicators for certain clinical conditions. For example, an elevated level of UA in blood is associated with gout, renal failure, leukemia, and lymphoma as well as other pathological conditions. Therefore, a simple, sensitive, and accurate analytical method for the quantitation of UA would be useful for physiological investigations as well as disease diagnosis. Thus, a simple, fast, sensitive, and accurate analytical method for determining uric acid in human is needed. Electrochemical method is one of the best method for sensing of UA with high selectivity. It has simple procedure, inexpensive, time consuming and low limit of detection. The modified electrodes exhibit better electrocatalytic activity than the bare glassy carbon electrode (GCE). Vanadium complex was electrochemically polymerized on the surface of GCE, the modified GCE was used for the electrocatalytic sensing of UA. Due to good electrochemical redox activity of vanadium complexes, it can be utilized as an electrochemical sensor for uric acid. The vanadium complex is better electrochemical sensor for UA.

Index Terms— tris-(1,10-phenanthroline)vanadium complex, uric acid, electropolymerization, electrochemical sensor, microwave synthesis.

1 INTRODUCTION

1,10-Phenanthroline(phen) is most commonly used bidentate chelating ligand. It forms more stable metal complexes due to its rigid planarity, hydrophobicity and presence of heteroaromaticity. Due the presence of nitrogen atoms in juxtaposition the phen ligand forms more stable complexes. The rigid planarity of phen ligand makes it an entropically better chelating molecule than the other chelating ligands. This entropic advantage for phen makes complexes with metal ions more rapidly [1]. Vanadium is most important biological element living organisms, which play a vital role in metabolic activity and diabetic treatment to the human [2]. The effects of vanadium in diabetic treatment was found in 1899 with the use of sodium vanadate, it decrease the glucose level in the urine of patients. The insulin-mimetic activity mechanism of vanadium is not clearly studied, but it involves inhibit the protein tyrosine phosphatase and activate protein tyrosine kinase [3]. The different oxidation states in vanadium play major role in active center of different enzymes. The rich chemistry of vanadium is due to its ability to adopt in different oxidation states which can be easily inter convertible.

Based on these factors tris-(1,10-pheanthroline)vanadium(III) complex was synthesized with the aid of microwave irradiation. The microwave irradiation method gives high yield at very short time. It is one of the best method in synthetic chemistry, it need minimum quantity of solvent and energy. The vanadium complex shows better electrochemical activity due to the presence of different oxidation states. This vanadium complex was utilized for the sensing of uric acid (UA). UA is the end product of catabolism of the purine nucleosides. UA levels in physiological fluids such as plasma and urine serve as valuable indicators for certain clinical conditions. For example, an elevated level of UA in blood is associated with

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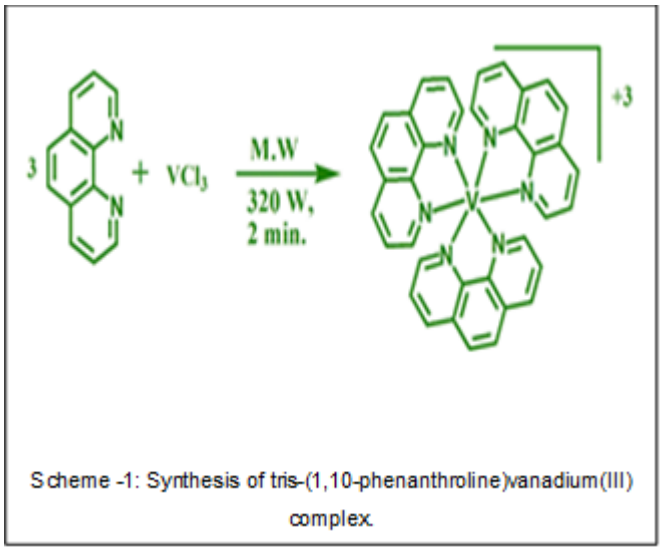
gout, renal failure, leukemia, and lymphoma as well as other pathological conditions [4]. Therefore, a simple, sensitive, and accurate analytical method for the quantitation of UA would be useful for physiological investigations as well as disease diagnosis. Electrochemical method is one of the best method for sensing of UA with high selectivity. It has simple procedure, inexpensive, time consuming and low limit of detection. The modified electrodes exhibit better electrocatalytic activity than the bare glassy carbon electrode (GCE). Vanadium complex was electrochemically polymerized on the surface of GCE, the modified GCE was used for the electrocatalytic sensing of UA. Due to good electrochemical redox activity of vanadium complexes, it can be utilized as an electrochemical sensor for uric acid.

2 Synthesis of tris-(1,10-phenanthroline) vanadium(III) complex.

An absolute methanolic solution of 3 mmol, 1,10-phenanthroline (0.540 g) was taken in a beaker and it was stirred by using magnetic stirrer. To the stirred phenanthroline solution, 1 mmol methanolic solution of Vanadium(III) chloride (0.157 g) was added by drop wise. After the complete addition of vanadium(III) chloride solution, it was continuously stirred about 2 hr. Then it was employed for the microwave irradiation at 320 W, for 2 mins. A green colour precipitate was obtained, it was collected and washed with methanol at several times. The systematic procedure for the synthesis of tris-(1,10-phenanthroline)vanadium(III) complex was given in Scheme -1.



Scheme -1: Synthesis of tris-(1,10-phenanthroline)vanadium(III) complex.

3 RESULTS AND DISCUSSION

3.1 Characetrization OF tris-(1,10-phenanthroline) vanadium(III) complex.

The FT-IR spectrum of vanadium complex shows the C=N stretching frequencies at 1640 cm-1 but the C=N band appeared in the region of 1700 - 1650 cm-1 for the free phen ligand. The shift in lower frequency, indicates that bond order of C=N is decreasing due to the coordination of vanadium metal with the nitrogen lone pair electron. Another important characteristic band at 538 cm-1, exhibit the stretching vibration of metal nitrogen bond, it conforms the complex formation between phen ligand and vanadium(III) metal ion (N••••V+3). The C=C stretching bands are appeared at 1479 cm-1, it normally exhibit at 1550 – 1600 cm-1 after the coordination of metal with phen ligand the C=C stretching get shift. A band at 829 cm-1 conforms the presence of phenyl ring in the metal complex. The electronic spectrum of vanadium complex in methanol solution shows four absorption peak at 267, 335, 380 and 590 nm. The first absorption peak at 267 is due to π→π* transition, a peak at 335 is due to n→π* transition, the peak at 378 is due ligand-to-metal charge transfer transition and 590 shows the d-d transition of vanadium metal [5]. Tris-(1,10-phenanthroline) vanadium(III) complex shows the emission at 770 nm for the irradiation of 590 nm wave length. The emission arises due to electron transition in d-orbitals. Electrochemical activity of vanadium complex was examined by cyclic voltammetry (CV) at the potential range of 0 V to 1.8 V, it shows a anodic peak at 1.3 V due to the oxidation of V(III) to V(IV) with one electron transfer. It shows that vanadium complex has electrochemical activity.

3.2 Electrocatalytic sensing of Uric Acid by vanadium complex

Electrochemical polymerization method was utilized for the modification of glassy carbon electrode at 0.1 M tris-(1,10-phenanthroline)vanadium(III) complex in acetonitrile solution. The vanadium complex deposited on the surface of GCE as a polymer flim (poly-V-phen/GCE), it was used for the electrocatalytic sensing of UA. The electrocatalytic behaviors of Uric acid (UA) at GCE and poly-V-phen/GCE were investigated by CV in phosphate buffer as background electrolyte. The UA shows only an anodic peak at 0.626 V (vs SCE) for bare GCE at pH 7 as shown in Fig. 2, the modified GCE exhibit the anodic peak at 0.461 V, which is about 165 mV more negative than that of GCE. The peak current in modified GCE is double the time greater than that of Bare GCE. The electrocatalytic results indicated that poly-V-phen/GCE has an excellent electrocatalytic activity towards UA, and the fabricated modified electrode might be used for the determine UA in real samples [6, 7].

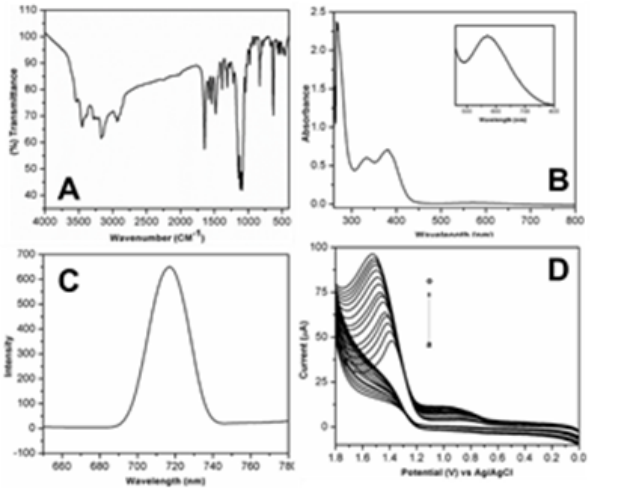


Fig.1: A) FT-IR, B) UV-Vis., C) Emission spectra of vanadium vomplex and D) Cyclic voltammogram of phen V(III) complexes in 0.1 M TBAP at different scan rate from 50-500 mVs^{-1}.

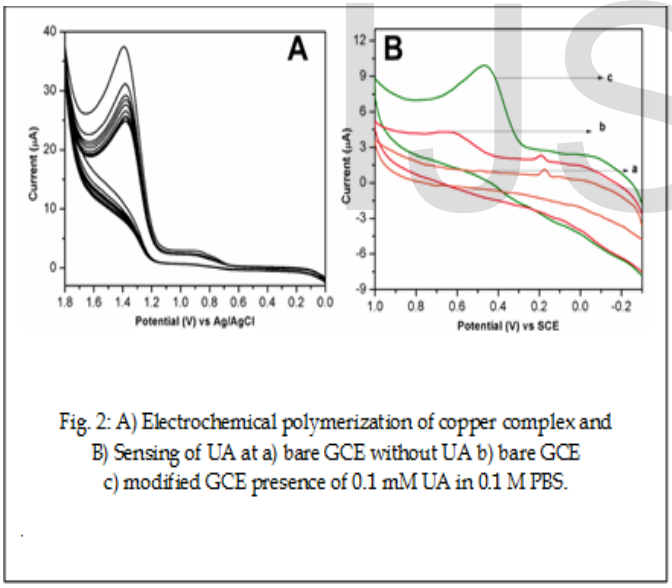


Fig. 2: A) Electrochemical polymerization of copper complex and B) Sensing of UA at a) bare GCE without UA b) bare GCE c) modified GCE presence of 0.1 mM UA in 0.1 M PBS.

4. Conclusion

The tris-(1,10-phenanthroline)vanadium(III) complex was synthesized by microwave irradiation method. The synthesized vanadiun(III) complex was characterized by different spectral techniques such as FT-IR, UV-Vis and emission. Further, the electrocatalytic activity of poly-V-phen/GCE tested for UA sensing. The electrochemical polymerization method used for modification of GCE. The results shows that fabricated poly-V-phen/GCE exhibit high electrocatalytic activity towards the sensing of UA.

ACKNOWLEDGMENT

One of the authors (S.P.K) wish to thank Department of Science and Technology (DST), Government of India for the financial assistance in the form of INSPIRE fellowship (Inspire Fellow no: 130032) under the AORC scheme.

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