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Electrochemical sensing of Pyrocatechol by Schiff base modified GCE

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Abstract— **Salen type Schiff base was synthesized by condensation of 5-methylsalicylaldehyde with the Diethylenetriamine using simple microwave irradiation method. Schiff base was characterized by UV-visible, FT-IR, and NMR spectroscopy techniques. The redox behaviour of the Schiff base was studied by cyclic voltammetry (CV). The synthesized Schiff base was electrochemically polymerized. The polymerized Schiff base was used for electrochemical sensing of Hydroquinone. The electrochemically polymerized Schiff base has high sensitivity towards the determination of phenolic compounds like pyrocatechol. The polymerized Schiff base has ability to form hydrogen bond with phenolic compounds. The formation of hydrogen bond between the polymerized schiff base and pyrocatechol is one of the reasons for sensing of phenolic compounds at low potential. Polymerized acyclic Schiff base modified electrode shows better electrochemical sensing ability when compared to that of bare GCE.**

Keywords- Schiff base, electrochemical polymerization, pyrocatechol, hydrogen bond, electrocatalytic sensing.

I. INTRODUCTION

In recent years, the attention of Schiff bases and their metal complexes are increasing due to their remarkable biological and pharmacological applications. The Schiff base contains the azomethine group, the carbon, nitrogen double bond (C = N) has various chemical and biological application [1]. The Schiff base ligands are having tendency to coordinate with the transition metals to form stable complexes at many oxidation states of the metals. Nowadays the Schiff bases are used for many applications apart from the biological activities, it can be used as sensors [2, 3], electrodes, energy storage devices, solar cells [4] and environmental sensor [5]. The π-systems of the Schiff base ligands develop the structural constriction and affect the electronic structure. The Schiff base complexes get investigation in electrochemical redox reaction. In our present work we design a Schiff base in the salen derivative, derived from the 5-methylsalicylaldehyde and diethyltriamine. The synthetic process of the reaction was carried out by the microwave irradiation method. In this method the reaction has high yield at very short Time. The salen family Schiff base ligands have many good electrocatalytic activities. It can be used for the sensing of variety of compounds. Here we take phenolic compounds as an environmental pollutant. Most of the phenolic compounds are highly toxic. They are used in herbicides and pesticides. The phenolic compounds are mostly spread out through the industries. They are used in many industries such as thermoset plastics, phenolic resins, polymer chemistry, wood industry, aerospace, building industry, automotive industry, abrasives, plasticizers, cleaning products, pesticide manufacturing, detergent applications, etc., [6]. The phenolic compounds are the predominant contaminants in water sources. The phenolic compounds are affecting the living organism, human and animal health. It also has harmful effect on food quality. In view of the toxicity of phenolic compounds in environmental matrices we take as a subject to discuss in this work. The Schiff base modified GCE shows a better sensitivity when compare with the bare GCE for the detection of phenolic compounds.

II. EXPERIMENTAL

A. Chemicals and reagents

5-methylsalicylaldehyde was prepared following the literature method. Analytical grade methanol and acetonitrile were purchased from Qualigens. TBAP, used as supporting electrolyte in electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol. diethyltriamine were purchased from Aldrich.

B. General synthesis of 5-methylsalicylaldehyde

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 0.76 mol) were heated for 30 min at 170 °C to expel the water. Then a mixture of 4-methylphenol (25 g, 0.23 mol) and hexamethylenetetramine (25 g, 0.18 mol) was added. The mixture was stirred for 15 min. The thick brown liquid obtained was allowed to cool to 110 °C. A solution of concentrated sulphuric acid (30 mL) in water (70 mL) was added and the whole mixture was boiled in a current steam. The product was collected by steam distillation. The solid obtained was recrystallized from 75mLof 80% ethanol.Yield: 8.2 g (26%) M.P.: 55 °C.

C. Synthesis of ligands N1,N1-bis((E)-2-(2-hydroxy5-bromobenzylideneamino)ethyl)ethane-1,2-diamine

An absolute methanol solution (10 mL) containing Diethyltriamine. (0.1490 g, 1 mmol) was added drop-wise to a stirred solution of 5-methylsalicylaldehyde (0.2720 g, 2 mmol), an yellow colour solution was obtained. The solution was kept in a microwave oven about 10 min at 160 W, the above reaction shown in Fig. 1. The resulting solution was cooled in room temperature. The yellow precipitate formed was filtered, washed with hexane and dried under vacuum. The crude product on recrystallization from methanol gave yellow crystals.

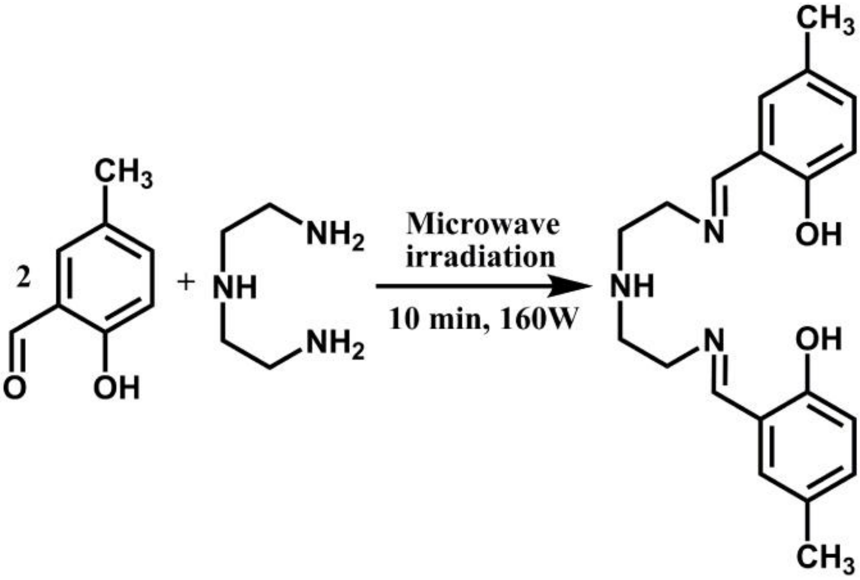

Fig. 1: Synthesis of Schiff base

III. RESULTS AND DISCUSSION

A. FTIR spectral analysis

The FT-IR spectrum of the Schiff base compound was show in Fig-2a. It shows a sharp band at 1641 cm^{-1} due to the presence of imine C=N group. The phenolic hydroxyl group shows a small peak at 3789 cm^{-1}. A band at 2911 cm^{-1} is due to C-H stretching. A band present at 2810 cm^{-1} shows that presence of internal hydrogen bond between the imine nitrogen and hydroxyl hydrogen C=N•••••HO. The band in the region 1250-1070 cm^{-1} in the ligand is due to the presence of aliphatic amine C-N stretching. A sharp band in the region of 1650-1410 cm^{-1} is due to aromatic (C-C) stretching in ring. The complete elimination of aldehydic group C=O in the spectrum shows that the formation of imine CH=N- group in the Schiff base [7].

B. Electronic spectra

The electronic spectrum of the Schiff base was shown in Fig-2b. It was recorded in methanol solution in the region of 200-800 nm. In this electronic spectrum Schiff base exhibit two bands. A band at 240 nm is due to the n→ π * transition in the C=C and C=N chromophores. Second band appears at 290 nm due to π → π * transition. These transitions are shifted to higher wavelength because of the presence of conjugations in the Schiff base.

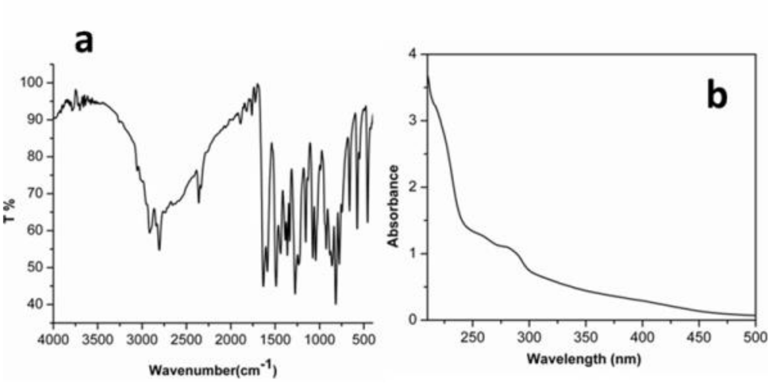

Fig. 2: (a) FT-IR spectrum and (b) Electronic spectrum of Schiff base.

C. NMR spectral analysis

The ^{13}C NMR spectrum of the Schiff base was shown in Fig-3a. It shows various level peaks based on their chemical environmental. The peaks are appeared in the down field when compared with the internal reference. 20.35 ppm is due to the methyl carbon, peaks at 33.01, 49.64, 56.61 ppm is shows the aliphatic carbons which are present in the amine chain. In the range of 116,118,127,131 and 132 ppm represent the benzene ring carbons. The peak at 158 ppm shows the presence of hydroxyl group substituted carbon in the benzene ring. A peak at 165 ppm is due to the imine group carbon(C=N). The ^{1}H NMR spectrum of the Schiff base was shown in Fig. 3b. The chemical shifts are present in the down field when compared with the internal reference TMS. A small peak present at 8.29 ppm it shows the phenolic hydroxyl proton exhibit in the Schiff base. Peaks appeared in the range of 6.8-7.1 ppm reviles that presence of aromatic protons. Signal at 2.2- 2.7 ppm shows that presence of aliphatic protons in the amine chain. A peak at 1.25 ppm is due to the methyl group protons which is present in the aromatic ring.

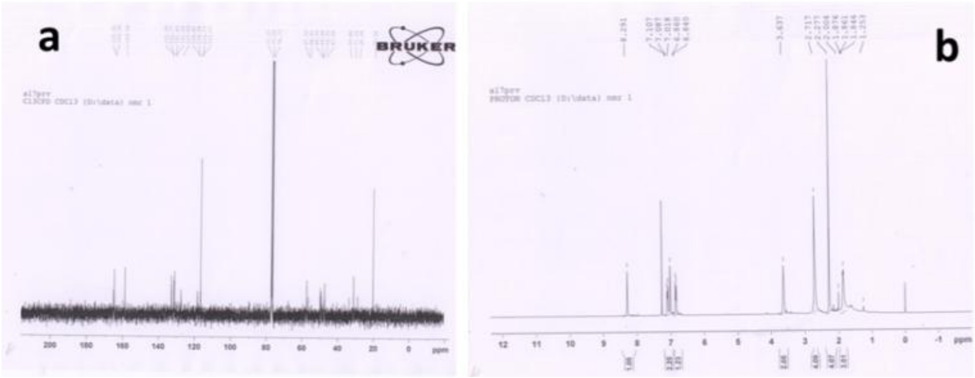

Fig. 3: (a) C^{13} NMR and (b) H^{1} NMR spectrum of the Schiff base

D. Electrochemical sensing of pyrocatechol

The electrochemical sensing behaviour of Schiff base towards pyrocatechol (PC) was examined by CV. 5 µL of 0.001 M Schiff base was coated on the GCE surface by the drop coating method. Fig. 4a displays the

CV's of bare, and Schiff base modified GCE in presence of 1 mM PC in 0.1 M PBS, and Fig. 4b shows the effect of scan rate on the Schiff base modified GCE. The Fig. 5a displays the CV's of modified GCE in PBS only, and Schiff base modified GCE in presence of 1 mM PC in 0.1 M PBS, The Fig. 5b shows the graphical representation of electrocatalytic reaction. The Fig. 4a shows shift in potential and enhanced peak current when compare with the bare GCE. It indicates that electrocatalytic ability of the modified electrode. This electrocatalytic effect was enhancing due to the larger surface area available on the modifying GCE. The influence of scan rate on the electrochemical response of 1 mM PC at the Schiff base modified GCE was investigated. The study showed that the reduction peak current moved negatively, but the oxidation peak was not showing any characteristic response. Based on that, reduction peak was accounted for detection of PC. Moreover, the reduction peak currents were linearly proportional to the square root of scan rate in the range from 10 to 500 mV s−1. The R value is -0.98, It reveals that the Schiff base layer on the GCE has good electrocatalytic activity and fast electron transfer at pH 7. It also suggests that the electrode reaction based on the hydrogen bond formation between the Schiff base and the PC. The catalytic reaction facilitates electron transfer between PC and the Schiff base modified electrode, as a result the electrochemical reduction of PC becomes easier. In the electrocatalytic reaction the diffusion process was carried by the sensing material. The diffusion current Ipc = -0.291-0.314x .The reason is that the Schiff base could increase the rate of electron transfer and lower the over potential of PC at the bare electrode. Thus, it is clear that Schiff base modified GCE can be successfully used for the electrochemical sensing of PC [8,9].

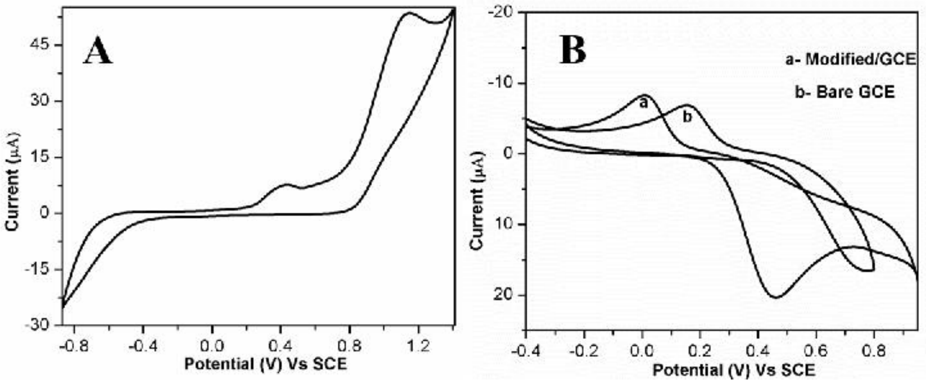

Fig-4: (A) Eletrochemical behaviour of the Schiff base at 50 mVs^{-1} (B) CV of bare and modified GCE in presence of 1 mM PC at the scan rate of 50 mVs^{-1}.

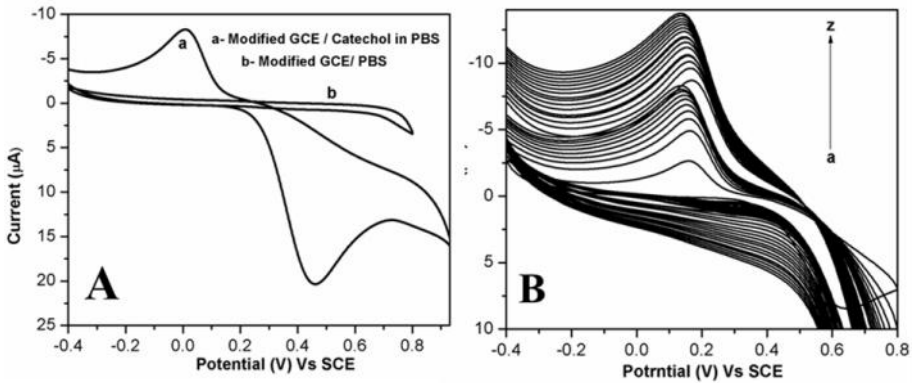

Fig-5: (A) CV of modified GCE in presence and absence of 1 mM PC at the scan rate of 50 mVs^{-1}.
(B) Effect of scan rate for the sensing of 1 mM PC by modified GCE the scan rate from 10-500 mVs^{-1}

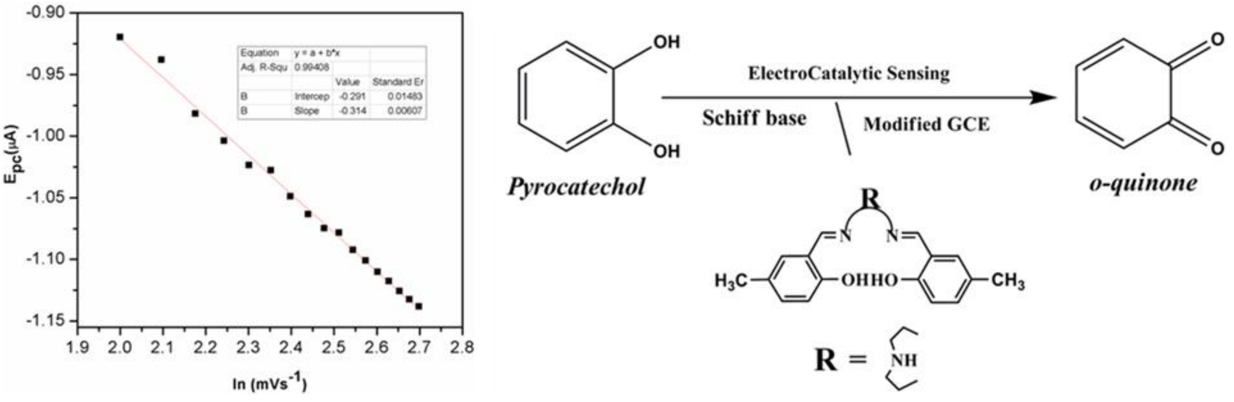

Fig. 6: (A) Plot of scan rate vs current and (B) graphical representation of electrocatalytic reaction.

IV. CONCLUSION

In conclusion, salen type Schiff was synthesized by microwave method and their coordination chemistry and electrochemical sensing property have been investigated by UV-visible, FT-IR, NMR spectroscopy techniques and CV. The Schiff base was used to sensing the pyrocatechol. From the electrochemical sensing experiment, it can be concluded that the Schiff base has good sensing activity towards the pyrocatechol. Hence, the GCE modified with Schiff base will be good sensor for pyrocatechol.

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