

## Electrochemical sensing of phenolic compounds based on polymerized acyclic Schiff base modified glassy carbon electrode

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**Abstract** : Acyclic Schiff base was synthesized by microwave irradiation method. It was characterized by UV-Visible, FT-IR, and NMR spectroscopy techniques, the electrochemistry of the Schiff base was studied by cyclic voltammetry. The synthesized Schiff base was electrochemically polymerized, then used for electrochemical sensing of phenolic compounds. The polymerized Schiff base possesses high sensitivity towards the determination of phenolic compounds such as catechol, resorcinol and hydroquinone. The ability of polymerized Schiff base to form hydrogen bonding with phenolic compounds 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** : Microwave irradiation, Schiff base, electrochemical sensing, hydroquinone.

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### Introduction

A great interest was shown to synthesis the cyclic or acyclic Schiff bases in the last few decades, due to their pertinent role in basic structural elucidation and application in various science fields. These Schiff bases have good result in the catalysis, biological, medicinal applications, etc. An outstanding efforts have been taken in recent studies for the synthesis of more Schiff base to their additional application in the electrochemical sensors field<sup>1,2</sup>. The Schiff bases both acyclic and cyclic can be synthesized by the simple condensation reaction of aldehyde and diamine, the synthetic procedure was designed to reduce the as much by products and towards the desired product. These Schiff bases has peerless host nature for the complex formation with the metal ion. The metal complexes are widely exhibit various catalytic property, good magnetic and optical properties<sup>3-5</sup>. Currently, a new interest going on to synthesis the Schiff base by microwave assisted method. This method was useful to be in all accepts (time, energy and solvent conservation)<sup>6</sup>. The Schiff base was electrochemically polymerized and used for sensing of phenolic compounds. The ability of poly-

merized Schiff base to form hydrogen bonding with phenolic compounds is one of the reasons for sensing of phenolic compounds at low potential. The phenolic compounds play an important role in plant secondary metabolisms and act as antioxidants. The phenolic compounds may be an antioxidants via different mechanisms. The various types of mechanisms are free radical scavenging, singlet oxygen quenching, hydrogen donation, metal ion chelation or as substrates for attack by superoxides. The phenolic compounds are sensing by different techniques one of the method is chromatographic method<sup>7</sup>. These methods are having complicated process, it needs more number of chemicals and expensive. The electrochemical method is simple alternative technique for the sensing of phenolic compounds. In this electrochemical method has some advantages than the other analytical techniques. It has good response, minimum cost effective, simple process and minimum requirement of chemicals. In the electrochemical methods many reports in which glassy carbon electrode and gold electrode have been used to estimate the phenolic compounds<sup>8</sup>. In our present work GCE surface was modified by the electrochemically poly-

rized acyclic Schiff base. The sensing of phenolic compounds by the modified GCE exhibits better response than the bare GCE. The proposed electrochemical sensors displays high sensitivity and rapid response for the phenolic compounds and not necessity to use any other electron mediators.

## Results and discussion

### FT-IR spectral analysis :

The FT-IR spectrum of the precursor compound shows a sharp band at  $1639\text{ cm}^{-1}$  due to the presence of imine (C=N) group. Schiff base shows a band at  $3792\text{ cm}^{-1}$  due to the phenolic OH groups. The Schiff base shows a band at  $2934\text{ cm}^{-1}$  is due to the presence of alkanes (C-H) stretching. A band exhibit in the range of  $2851\text{--}2800\text{ cm}^{-1}$  shows that presence of internal hydrogen bond between the imine nitrogen and hydroxyl hydrogen (C=N $\cdots$ HO). The band in the region of  $1207\text{--}1165\text{ cm}^{-1}$  in the ligand is due to the presence of aliphatic amine (C=N stretch) group. The ligand shows a sharp band in the region of  $1578\text{--}1491\text{ cm}^{-1}$  is due to aromatic (C-C) stretching in-ring. The complete disappearance of aldehydic group of the precursor and the appearance of imine (CH=N-) group in the ligands show the effective Schiff base condensation between the aldehyde group of the precursor compound and the amine groups<sup>9</sup>.

### Electronic spectra :

The electronic spectra of the Schiff base in methanol

solution was recorded in the region of 200–800 nm. In this electronic spectra Schiff base exhibit three bands. A band at 260 nm is due to the  $n\rightarrow\pi^*$  transition in the C=C and C=N chromophores. Second band appears at 220 nm due to  $\pi\rightarrow\pi^*$  transition. These transitions are shifted to red shift because of the presence of conjugations in the Schiff base. A band at 370 nm is reviles that the intramolecular hydrogen.

### NMR spectral analysis :

The  $^{13}\text{C}$  NMR spectrum of the Schiff base was record in  $\text{CDCl}_3$  the carbon shows various level peaks based on their chemical environmental. The  $^{13}\text{C}$  NMR spectrum of Schiff base is shown in Fig. 2(a). Peaks are appeared in the down field when compared with the internal reference 20.35 ppm is due to the methyl carbon, peaks at 31.24, 47.46, 57.50 ppm is shows the aliphatic carbons which are present in the amine chain. In the range of 116, 127, 131 and 132 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 164 ppm is due to the imine group carbon (C=N). The  $^1\text{H}$  NMR spectrum of the Schiff base was shown in Fig. 2(b). It's also recorded in the  $\text{CDCl}_3$  used as solvent. The chemical shifts are present in the down field when compared with the internal reference TMS. A small peak present at 13.26 ppm it shows the phenolic hydroxyl proton exhibit in the Schiff base. Peaks appeared in the range of 6.8–7.2 ppm reviles that presence of aromatic

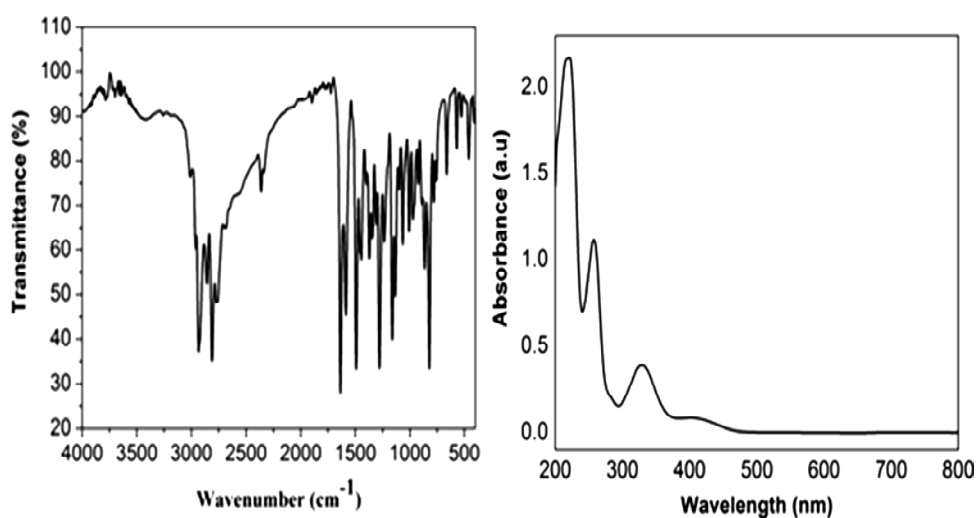


Fig. 1. FT-IR and UV-Visible spectra of Schiff base.

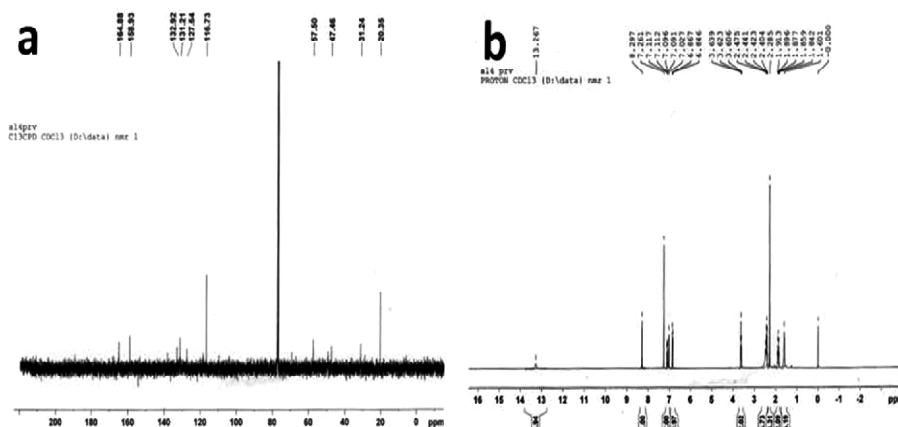


Fig. 2. (a) <sup>13</sup>C NMR spectra of Schiff base, (b) <sup>1</sup>H NMR spectra of Schiff base.

protons. Signal at 2.2–3.6 ppm shows that presence of aliphatic protons in the amine chain. A peak at 1.9 ppm is due to the methyl group protons which is present in the aromatic ring.

*Electrochemical sensing of phenolic compounds :*

The electrochemical sensing of hydroquinone (HQ) were determine by CV. The Schiff base was electrochemically polymerized in presence of TBAP (tetrabutylammoniumperchlorate) using GCE as working electrode. The Schiff base was polymerized on the GCE surface it was the modified electrode for sensing HQ (hydroquinone). Fig. 3 shows the cyclic voltammogram's of bare, and polymerized Schiff base modified GCE containing 1 mM HQ in presence of 0.1 M PBS. The figure shows variation in potential and amplified peak current when compare with the bare GCE. It reviles that electrocatalytic

capability of the modified electrode. This electrochemical sensing 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 HQ at the polymerized Schiff base modified GCE was probed. The study of scan rate effect was shows that the oxidation peak current migrates positively and the reduction peak current migrates negatively. Moreover, both the oxidation and reduction peak currents were linearly proportional to the square root of scan rate in the range from 10 to 100 mV s<sup>-1</sup>. It reveals that the polymerized Schiff base layer on the GCE has good electrochemical activity and fast electron transfer at pH 7. It also suggests that the electrode chemical reaction based on the hydrogen bond formation between the Schiff base and the HQ. The catalytic reaction facilitates electron transfer between HQ and

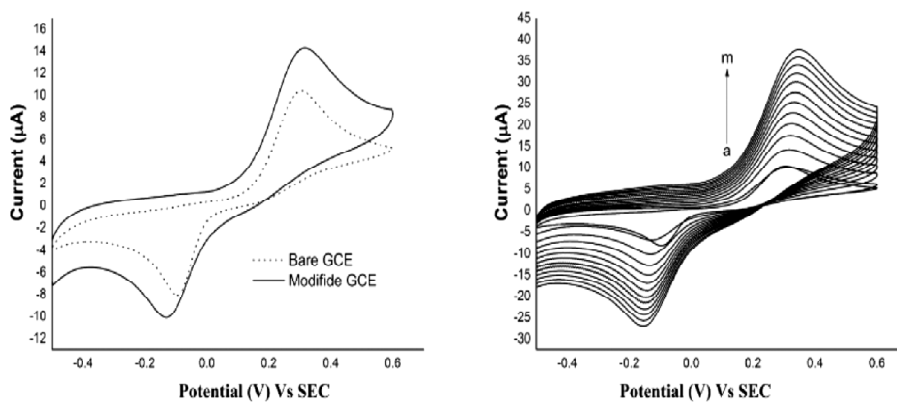


Fig. 3. Cyclic voltammetric response of 1 mM HQ of bare GCE and modified GCE, comparison of scan rate.

the polymerized Schiff base modified electrode, as a result the electrochemical oxidation of HQ becomes easier. The reason is that the polymerized Schiff base could increase the rate of electron transfer and lower the overpotential of HQ at the bare electrode. Thus, it is clear that polymerized Schiff base modified GCE can be successfully used for the electrochemical sensing of HQ<sup>10,11</sup>.

## Experimental

### Chemical and reagent :

5-Methylsalicylaldehyde was synthesized by the given literature method. The solvents methanol and acetonitrile was purchased from Qualigens in analytical grade. Tetrabutylammoniumperchlorate was purchased from Fluka and recrystallized from hot methanol. *N,N*-Bis-(3-aminopropyl)piperazine was purchased from Aldrich.

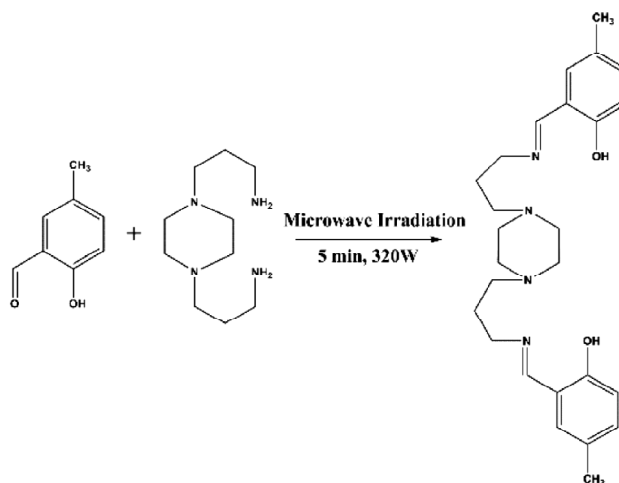
### General synthesis of 5-methylsalicylaldehyde :

A mixture of glycerol (150 g, 1.63 mol) and boric acid (35 g, 1.76 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 75 mL of 80% ethanol. Yield : 8.2 g (26%); m.p. 55 °C.

*Synthesis of ligands (9E)-N-(2-hydroxy-5-methylbenzylidene)-3-(4-((E)-3-(2-hydroxy-5-methylbenzylidene-amino)propyl)piperazin-1-yl)propan-1-amine :*

10 ml methanol solution of *N,N*-bis-(3-aminopropyl)-piperazinediamine (0.2 g, 1 mmol) was added dropwise to the stirred methanol solution of 5-methylsalicylaldehyde (0.2720 g, 2 mmol) an yellow colour solution was obtained. The solution was kept in microwave oven about 5 min at 320 W, the above reaction shown in Scheme 1. The resulting product was cooled to room temperature a yellow colour precipitate was formed it was filtered. The precipitate was washed with hexane and dried. The curde

product was recrystallized by ethanol. It gives a yellow crystals.



Scheme 1

## Conclusion

In conclusion, acyclic Schiff base have been 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 electrochemically polymerized. The polymerized Schiff base was used to sensing the phenolic compounds. From the electrochemical sensing experiment, it can be concluded that the polymerized acyclic Schiff base has good sensing activity towards the hydroquinone. Hence, the GCE modified with polymerized Schiff base will be good sensor for phenolic compounds.

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