SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF SCHIFF BASES CONTAINING 4-AMINOBENZOIC ACID MOEITY

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ABSTRACT

The use of Schiff bases in material science, therapeutics and sensor has been achieved due to its electrochemical potentials. In this study, Schiff bases of 4-((2-hydroxybenzylidene)amino)benzoic acid (G1) and 4-((5-bromo-2-hydroxybenzylidene)amino)benzoic acid (G2) were synthesized from 4-aminobenzoic acid. The compounds were characterized using FTIR, ESI-MS and 1H NMR which confirm the synthesized compounds. The electrochemical behaviour of both ligands was studied in triethylammonium phosphate acetonitrile solution. The cyclic voltammetry of G1 and G2 Schiff bases resembled voltammograms with one or two quasi-reversible redox processes, indicating redox potentials of the ligands. The electrochemical screening showed that the ligands would exhibit significant binding interactions with molecules such as metal ions and biological models.

Keywords: 4-aminobenzoic acid, cyclic voltammetry, electrochemical, redox activity, Schiff base

INTRODUCTION

Schiff bases are interesting class of ligands that have shown interdisciplinary domains as they possess a diversity of donor atoms that exhibit remarkable activity. Such activities include corrosion inhibition, catalysts, biological activity, chemo-sensor, material science [1-8]. The use of Schiff bases in material science necessitated its importance in electrochemistry. Electrochemistry is the science of how electricity and chemicals interact in redox reactions. The design and synthesis of Schiff bases that contain redox-active centres for electrochemical applications is increasing, as this field of chemistry examines redox processes, to understand reaction intermediates, and to obtain the stability of reaction products [9, 10]. Ray et al, [11] reported an efficient electron transfer from gold electrode to cytochrome c immobilized on an electrode which was achieved through monolayers of thiol-containing Schiff base. It was observed that cytochrome c molecules possibly bind to Schiff base complexes through electrostatic interaction between surface lysine residues of the protein and the carboxylate and metal ion coordination of the monolayer of the Schiff base complex. Heterogeneous electron transfer between the gold electrode and cytochrome c in the thin film mediated by the layer of the Schiff base was found to be faster than several earlier reports on electrode modifiers as promoters.

Several Schiff bases have played significant roles in electrochemistry. [12,13]. Ejiah et al in 2023 [14] reported the electrochemical behaviour of 2-aminophenol Schiff bases towards metal ions in solution. The electro-activeness of the ligands was evident in their
application as a chemo-sensor. Ourari and co-workers [15] have reported electrochemistry and indirect electrocatalytic properties of a novel organometallic Schiff base nickel(II) complex. Electrochemical behaviour of Schiff base as an anti-corrosive molecule for mild steel in H₂SO₄ medium have been reported by Kumari et al. [16]. Electrochemical impedance spectroscopy showed the inhibition by adsorption of inhibitor molecules on mild steel surface. Polarization study reveals that Schiff base acted as mixed-type inhibitor.

Nimal in 2020 studied electrochemical characterization of biologically important Schiff bases [17]. Biological applications of Schiff bases have been found to be related to their oxidation potential, this is due to transfer of a hydrogen atom through a proton coupled electron transfer reaction [18]. Izham et al, in 2022 [2] reported potential valuable Schiff bases for electrochemical-DNA sensor for the future. Recent review by Altuner et al, [19] revealed more interesting electrochemical and fluorescence applications of Schiff bases.

At present, electrochemical study of Schiff bases due to their easy reaction procedure and low-cost materials necessitated this research. Interestingly, we found little or no report on the electrochemical activity of 4-aminobenzoic acid Schiff base ligands. Herein, we report synthesis, characterization and electro-activity of Schiff bases derived from 4-aminobenzoic acid and salicylaldehyde and 5-bromosalicylaldehyde. This report also highlights the effect of substituent group on the electrochemical behaviour of the ligands.

**MATERIALS AND METHODS**

**Materials**

The chemicals and reagents used were purchased from Sigma-Aldrich chemical Co Ltd and used without further purification. They include ethanol, salicylaldehyde, 5-bromosalicylaldehyde, 4-aminobenzoic acid, n-hexane and ethyl acetate. The melting points of all the synthesized compounds were determined using the Stuart melting point apparatus model in Chemistry Department, University of Lagos, Nigeria. FT-IR spectra of the compounds were recorded on a Spectrum Two FT-IR Spectrometer directly on small samples of the compounds in the range 4000 to 400 cm⁻¹. ¹H-NMR spectra in DMSO-d₆ solution of the ligands were recorded on a Bruker Avance III 400 MHz. Chemical shifts were reported in ppm relative to TMS as internal standard. Electrospray Ionisation (ESI) analyses were performed in positive ionisation mode on a Micromass LCT Time of Flight Mass Spectrometer. All the characterizations were carried out at the University of Birmingham, United Kingdom.

Electrochemical studies were performed using a platinum electrode as the auxiliary electrode, glassy carbon electrode (GCE) as the working electrode, and Ag/AgCl electrode as the reference electrode using Epsilon Ec. Vet. 213.77 Xp voltammetry machine at the Chemistry Department of the University of Lagos.

Electrochemical parameters:
EpsilonEc.Vet.213.77Xp,
Scan rate (mV s⁻¹): 50-250 mV;
number of segments: 2; quiet time (s): 2; scale: μA; reference electrode (Ag/AgCl electrode), working electrode (GCE), counter electrode (platinum electrode), supporting electrolyte, triethylammonium phosphate (TEAP); solvent, acetonitrile.

**Synthesis of Schiff Bases**

**Synthesis of 4-((2-hydroxybenzylidene)amino)benzoic acid (G1)**

An ethanolic solution of 10 ml of 4-aminobenzoic acid (2.5 mmol, 0.343 g), 10 ml salicylaldehyde (2.5 mmol, 0.2 ml) was added. The reaction mixture was kept under reflux for 6 hours at 70°C. The reaction was monitored by TLC using n-hexane and ethyl acetate solvent system in the ratio 3:2. The mixture obtained was cooled at room temperature and the red crystal formed were collected by filtration, recrystallized using ethanol.

**Synthesis of 4-((5-bromo-2-hydroxybenzylidene)amino)benzoic acid (G2)**

An ethanolic solution of 10 ml of 4-aminobenzoic acid (0.343 g, 2.5 mmol), 10 ml 5-bromosalicylaldehyde (0.39 g, 2.5 mmol) was added. The reaction mixture was kept under reflux for 6 hours at 70°C. The reaction was monitored by TLC using n-hexane and ethyl acetate solvent system in the ratio 3:2. The mixture obtained was cooled at room temperature and the orange crystals formed were collected by filtration, recrystallized using ethanol.

**Electrochemical Studies of G1 and G2 Schiff bases**

Electrochemical study of G1 and G2 was carried out using cyclic voltammetry. A solution of triethylammonium phosphate (0.0231 g) was prepared in 100 ml acetonitrile. Then, 10 ml triethylammonium phosphate solution for each of G1 and G2 (0.1 mmol) was prepared. Thereafter, 5 ml each of the prepared solutions was electrochemically analysed using cyclic voltammetry.

**RESULTS AND DISCUSSION**

**Synthesis of G1 and G2 Schiff bases**

The general synthesis scheme for G1 and G2 is provided in Scheme 1.

![Scheme 1: General Synthesis of 4-((2-hydroxybenzylidene)amino)benzoic acid (G1) and 4-((5-bromo-2-hydroxybenzylidene)amino)benzoic acid (G2)](image)

G1 = R, H; G2, = R, Br

The Schiff bases were obtained in good yields from the reactions of 4-aminobenzoic acid with salicylaldehyde (G1), 5-bromosalicylaldehyde (G2) in a 1:1 stoichiometric ratio Scheme 1.
The formation of the desired ligands was confirmed by $^1$H NMR, FTIR and ESI-MS. The physical properties of the synthesized Schiff base $G_1$ and $G_2$ are presented in Table 1. The compounds have sharp melting point and gave a good yield in the range of 73-76%.

**Table 1. Physical data of Schiff bases $G_1$ and $G_2$**

<table>
<thead>
<tr>
<th>Schiff bases</th>
<th>Color</th>
<th>Melting Point (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_1$</td>
<td>Yellow</td>
<td>265-267</td>
<td>76</td>
</tr>
<tr>
<td>$G_2$</td>
<td>Orange</td>
<td>272-274</td>
<td>73</td>
</tr>
</tbody>
</table>

**FTIR and $^1$H NMR Spectra of $G_1$ and $G_2$ Schiff bases**

The FTIR spectra of the synthesized Schiff bases $G_1$ and $G_2$ (summarized in Table 2) showed bands in the range expected for the ligand. The absorption band in the range 1618-1622 cm$^{-1}$ assigned to the “C=N” functional group confirms the formation of Schiff base. The compounds displayed band in the range 3069-3070 cm$^{-1}$ and 1175 cm$^{-1}$ which are characteristics of O-H and C-O groups respectively. The carbonyl group of the acidic moiety of amine was observed at 1674-1678 cm$^{-1}$. The absence of the band between 1720-1740, further confirms the formation of a Schiff base (Fig. 1 and 2).

$^1$H NMR spectra revealed resonated protons at the expected values, confirming the purity and structure of $G_1$ and $G_2$ ligands. Both Schiff bases exhibits a singlet in the region 8.87-8.96 δ attributed to the imine proton. The protons of OH group resonated at 10.10-10.32 δ as expected (Fig. 3 and 4).

![Figure 1: FTIR spectra of G1 Schiff base](image-url)
Figure 2: FTIR spectra of G2 Schiff base

Figure 3: $^1$H NMR spectra of G1 Schiff base
Figure 4: $^1$H NMR spectra of G2 Schiff base

<table>
<thead>
<tr>
<th>Schiff bases</th>
<th>R</th>
<th>V(O-H)</th>
<th>V(C=O)$_{acid}$</th>
<th>V(C=N)</th>
<th>V(C-O)</th>
<th>(C=N) (δ, ppm)</th>
<th>(O-H) (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>H</td>
<td>3069</td>
<td>1678</td>
<td>1622</td>
<td>1175</td>
<td>8.87</td>
<td>10.10</td>
</tr>
<tr>
<td>G2</td>
<td>Br</td>
<td>3070</td>
<td>1674</td>
<td>1618</td>
<td>1175</td>
<td>8.96</td>
<td>10.32</td>
</tr>
</tbody>
</table>

**Table 2.** FTIR and $^1$H NMR bands of Schiff bases G1 and G2

**ESI-MS spectra of G1 and G2 Schiff bases**

ESI-MS spectra confirmed the exact mass of ligands G1 $C_{14}H_{11}NO_3 [M+1H]^+$ m/z = 242.07, found 242.06 and G2 $C_{14}H_{10}BrNO_3 [M+1H]^+$ m/z = 319.98, found 319.96 (Fig. 5 and 6).
Figure 5: ESI-MS spectra of G1 [M + 1H]+ m/z = 242.07.

Figure 6: ESI-MS spectra of G1 [M + 1H]+ m/z = 319.98.

Electrochemical Study of G1 and G2 Schiff bases

Electrochemical studies of G1 and G2 Schiff bases were carried out in triethylammonium phosphate supporting electrolyte (0.0231 g in 100 ml acetonitrile), using a standard three electrode cell with convention as follows: Working electrode- glassy carbon electrode; Reference electrode- Ag/AgCl (in saturated 3 M KCl solution); Counter electrode: Platinum wire. A potential window of -1000 mV to 1000 mV was applied, and the working parameters were kept constant as alterations in scan rate of the two different ligands were applied.

The cyclic voltametric studies conducted in the analysis depicts an electroactive behaviour of the ligands, following a typical quasi reversible process with peak separation of about 300 mV. A peak separation of beyond 59 mV between the anodic and cathodic process is indicative of a quasi-reversible process [20]. Given that the anodic and cathodic peak heights differ is another indication that the process is not a fully reversible process. Notwithstanding, an electroactive redox process, as revealed by the presence of anodic and cathodic peaks on the cyclic voltammogram [21].

Analysing the redox performance of the ligands at different scan rates Figures 7a–e (50 mV to 250 mV), we observe an expected shift to more positive peak. Measurements at higher scan rates also produced better resolved peak of the redox process within the potential range of 500 mV to 900 mV Figures 7c–e. Higher scan rates are observed to facilitate a better diffusion process, thus enhancing mass transport of the active species to the electrode surface, leading to a more prominent and better-defined peaks as observed in the voltammograms [21].
Fig. 7 (a–e) Cyclic voltammogram for 25 mM G1 in acetonitrile containing triethylammonium phosphate (TEAP) as a supporting electrolyte at a scan rate of 50 mV to 250 mV.

For the bromo specie, there is an emergence of 2 cathodic peaks Figure 8j within the potential range of 500 mV to 900 mV as revealed at 250 mV scan rate. The emerging peak can be attributed to the contribution of the bromine atom to the ligand. As an electron-withdrawing specie, it can be seen to have a notable influence on the overall redox process of the ligand. Thus, improving its viability as a probe.

The peaks observed in the voltammetric process of both ligands can be attributed to oxidation of the 2-hydroxyl group, leading to a loss of electron and an abstraction of one proton, as reported by Ziyatdinova et al. [22]
(g)

(h)
CONCLUSION

We have successfully developed 4-aminobenzoic acid based G1 and G2 Schiff bases. The cyclic voltammetry results revealed interesting redox activity of each ligand. It was observed that presence of bromine on the ring G2 increased electron transfer compared to G1, hence suggesting that G2 would present as a better electrochemical probe in material science.

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