



Study the Voltammetric Behavior of Symmetrical Tetradentate Schiff Bases

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ABSTRACT

Synthesis of symmetrical Schiff bases (1-4) employed by using condensation methods. Purity was monitored by TLC and column chromatographic techniques. In this present study cyclic voltammetric behavior of symmetrical Schiff bases (1-4) were studied. The cyclic voltammetric studies reveals that the –CH=N– group in Schiff bases is reduced and the process is quasireversible with kinetically controlled behavior. Based on the cyclic voltammetric data propose the possible mechanism for this redox behavior of schiff bases.

Keywords: Symmetrical Schiff bases, Voltammetric studies, Glassy carbon electrode.

INTRODUCTION

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone. The resultant compound, $R_1R_2C=NR_3$, is called a Schiff base. Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties [1,2]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [3, 4]. Schiff bases appear to be important intermediates in a number of enzymatic reactions involving interaction of the amino group of an enzyme, usually that of lysine residue, with a carbonyl group of the substrate [5]. Many biologically important Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [6-11]. Another important role of Schiff base structure is in transamination [12]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications [13-18]. In this present work we have synthesized four symmetrical schiff base ligands (**SB 1**, **SB 2**, **SB 3** & **SB 4**). These schiff base ligands are having much attention in the field of biological studies such antimicrobial, DNA cleavage, drug delivery etc and also it has lot of application with the metal complexes. All the four schiff bases have been characterized by cyclic voltammetric studies. Schiff bases containing the hetero atoms like oxygen, nitrogen, sulfur are of much importance and the metal complexes of salen ligands play a major role in homogeneous and heterogeneous catalysis in different solvents. But voltammetric studies of Schiff bases in aqueous and non- aqueous

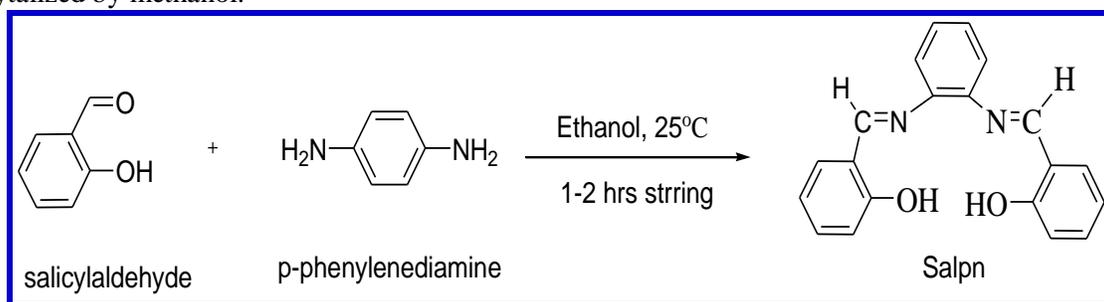
medium are very limited. The main focus is to study the reduction behavior of Schiff bases in aqueous and non-aqueous medium using glassy carbon electrode as a working electrode in Ag/AgCl as the reference electrode. Cyclic voltammetric diagnostic criteria for different types of reactions were applied and analyzed. The mass transport properties of these compounds during the electrochemical reactions are analyzed from the voltammetric data.

MATERIALS AND METHODS

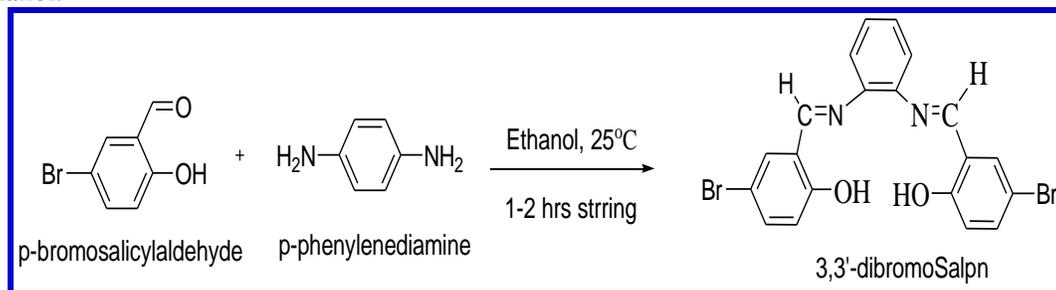
Salicylaldehyde, and the substituted salicylaldehydes (3-chloro, 3-bromo, 3-nitro, 3, 5-dichloro) were purchased from sigma Aldrich and p-phenylenediamine, were purchased from Merck (AnalaR grade). Ethanol, acetonitrile, hexane, ethyl acetate and Deionized water has been used as solvents for purification, recrystallization and solution makings. The redox potentials ($E_{1/2}$) of the schiff bases were measured in CH_3CN and aqueous CH_3CN medium using electrochemical Workstation (CH-Instrument), at 0.1M TBAP (tetrabutylammoniumperchlorate) as the supporting electrolyte and Ag/AgCl as the reference electrode.

Synthesis of Tetradentate Symmetrical Schiff Bases

Synthesis of Schiff Base 1: Schiff base (**SB 1**) was prepared by refluxing a mixture of 2 equivalent (1.164g) of salicylaldehyde and 1 equivalent (1.40g) of p-phenylenediamine in 10 ml of double distilled ethanol. Magnetically stirred well upto 2 h the yellow precipitate is formed. The yellow precipitate is filtered using Buckner funnel and then dried it. The product formation is monitored by TLC technique and recrystallized by methanol.



Synthesis of Schiff Base 2: Schiff base (**SB 2**) was prepared by refluxing a mixture of 2 equivalent of 3-bromosalicylaldehyde and 1 equivalent of p-phenylenediamine in 10 ml of double distilled ethanol. Magnetically stirred well upto 2 h the yellow precipitate is formed. The yellow precipitate is filtered using Buckner funnel and then dried it. The product formation is monitored by TLC technique and recrystallized by methanol.



Synthesis of Schiff Base 3: Schiff base (**SB 3**) was prepared by refluxing a mixture of 2 equivalent of 3-chlorosalicylaldehyde and 1 equivalent of p-phenylenediamine in 10 ml of double distilled ethanol. Magnetically stirred well upto 2 h the yellow precipitate is formed. The yellow precipitate is filtered using Buckner funnel and then dried it. The product formation is monitored by TLC technique and recrystallized by methanol.

composition of acetonitrile/water (90:10, 80:20, 70:30, 60:40, 50:50 (v/v) in the voltammetric behaviour of schiff base 4 are also shown in fig 2. In differential pulse voltammogram of schiff base 4 (Fig 4) shows, in high range of diagram, i.e., in oxidation part, there is a short peak in $E_a = 0.24$ V, $E_a = 0.80$ V also there is another peak in $E_a = 1.16$ V. In low range of diagram, i.e., in the reduction part, there is a short peak in $E_c = 0.14$ V range and there are two peaks with low height respectively $E_c = 0.41$ V, $E_c = 0.82$ V and $E_c = 1.122$ V. With a comparison of oxidation and reduction peaks, it can be resulted that there is a peak in reduction region like as a peak in oxidation region. Thus, its electrochemical behavior shows reversibility of ligand. The peak (about -1.5 V) may most probably be due to the reduction of $-C=N-$ (azomethine) group. The voltammograms of SB 4 was recorded at different scan rates (50, 100, 200, 300, 400 and 500 mVsec^{-1}) in (Fig 3) using glassy carbon as the working electrode and Ag/AgCl (saturated KCl) as the reference electrode. TBAP (tetra butyl ammonium perchlorate) is used as the supporting electrolyte. Cyclic voltammograms show the quasi reversible nature of the peaks. The cyclic voltammetric peak parameters are given in table 1. Absence of reversibility is evident from $E_{pa} - E_{pc}$ values which are more than 56 mVsec^{-1} for all cases. The anodic and cathodic peak potentials of the system are given in table 1. The Peak currents (cathodic & anodic) of Schiff base (SB 1, SB 2, SB 3 & SB 4) with different scan rates (50,100, 150,200,250, 300, 350 mVsec^{-1}) in acetonitrile at room temperature using glassy carbon as the working electrode and Ag/AgCl (saturated KCl) as the reference electrode are shown in Tables 2-5. The anodic peak potential is moving towards anodic direction and cathodic peak potentials are moving towards cathodic direction with increasing sweep rates. The cathodic peak current decreases and anodic peak current increases with increase in scan rates. The $i_{pc}/v^{1/2}$ and $i_{pa}/v^{1/2}$ values are not constant and $i_{pc}/v^{1/2}$ values are decreasing and $i_{pa}/v^{1/2}$ values are increasing with scan rate. These observations indicate that the overall electrode process is kinetically controlled. The plots i_{pa} vs. $v^{1/2}$ (Fig 5) and i_{pc} vs $v^{1/2}$ (Fig 6) of SB 4 in acetonitrile medium support the absence of diffusion controlled processes. The plots are close to linearity and not passing through the origin.

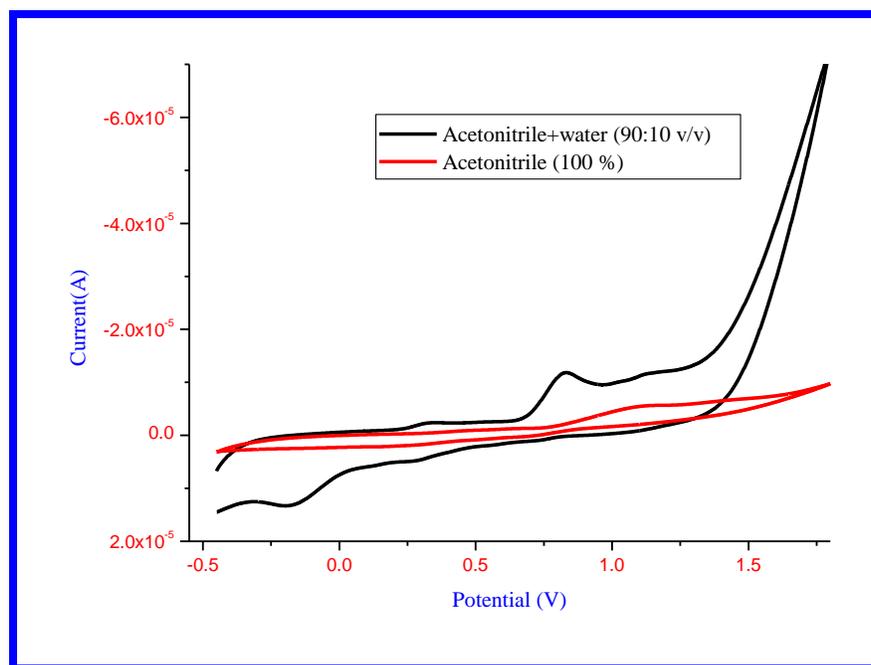


Fig 1. Cyclic voltammogram of Schiff base (SB 4) in A). CH_3CN (100%) B). $\text{CH}_3\text{CN}+\text{H}_2\text{O}$ 90:10 v/v at scan rate 50 mVs^{-1} with TBAP (supporting electrolyte). potentials are referred to Ag/AgCl

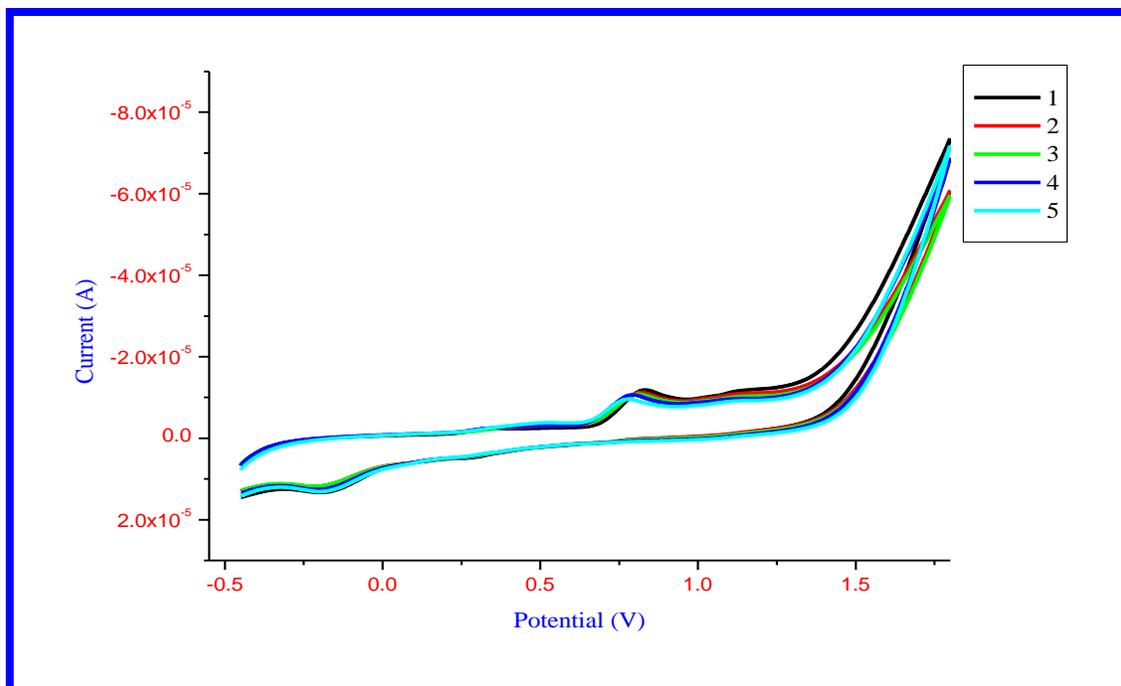


Fig 2. Cyclic voltammogram of Schiff base (SB 4) in $\text{CH}_3\text{CN}+\text{H}_2\text{O}$ at scan rate 50mVs^{-1} with TBAP (supporting electrolyte). potentials are referred to Ag/AgCl. solvent composition 1). 90:10 2). 80:20 3). 70:30 4). 60:40 5). 50:50 (v/v).

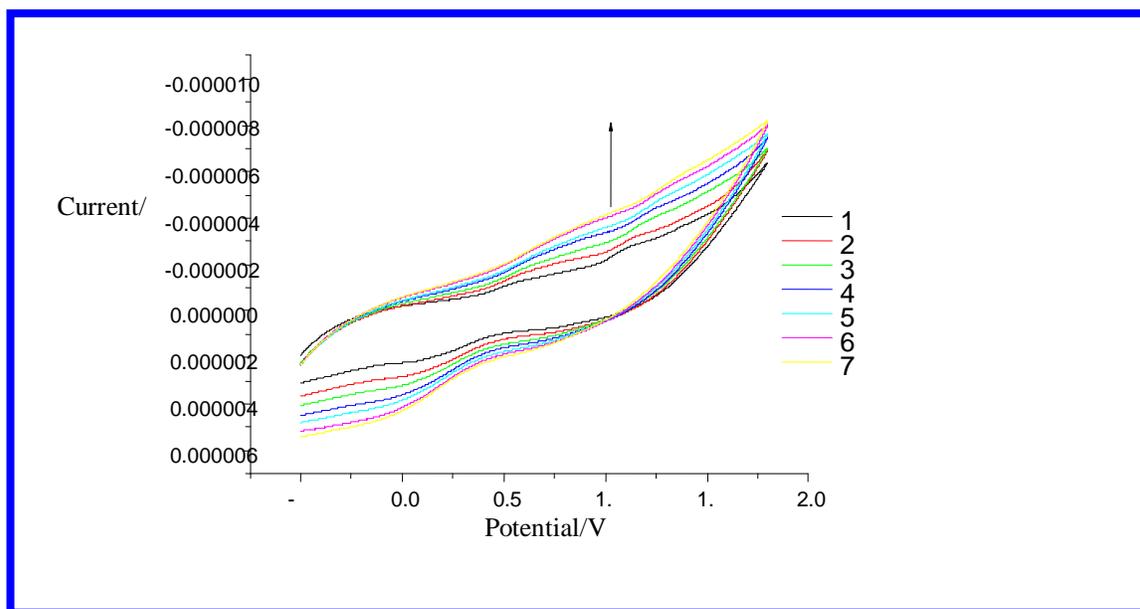


Fig 3. Cyclic voltammogram of Schiff base (SB 4) in acetonitrile at different scan rate (50, 100, 150, 200, 250, 300, 350 mV s^{-1}) with TBAP (supporting electrolyte). potentials are referred to Ag/AgCl.

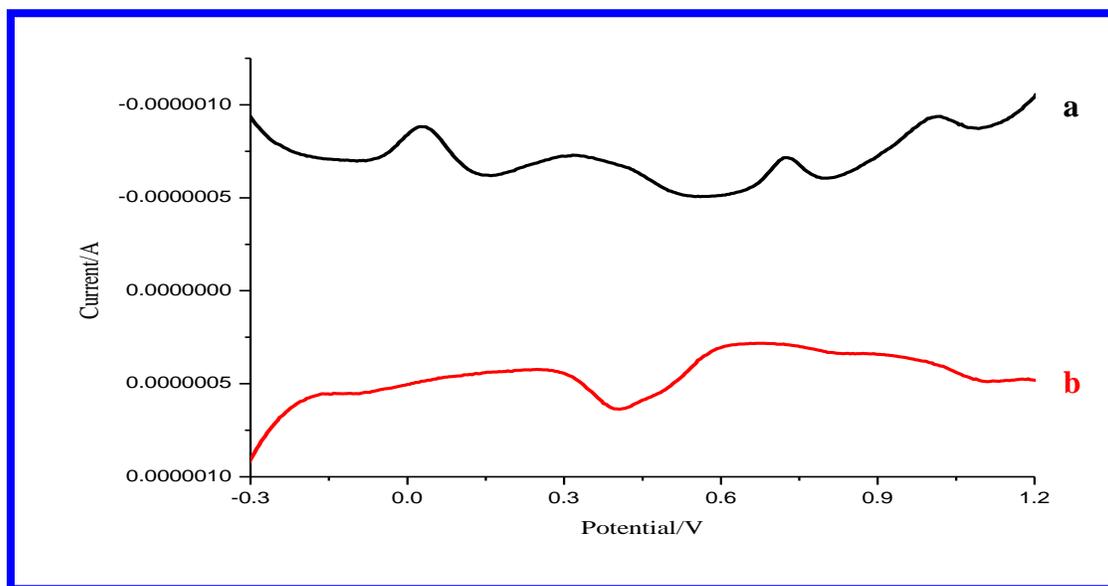


Fig 4. Differential pulse voltammogram of (SB 4) in acetonitrile at scan rate 100mV s^{-1} with TBAP (supporting electrolyte). potentials are referred to Ag/AgCl. a). oxidation peak potential E_{p_a} . b). reduction peak potential E_{p_c} .

Table 1. The Peak potential & peak currents (cathodic & anodic) of Schiff base 1-4 with scan rate (50 mVsec^{-1}) in acetonitrile and acetonitrile+ water at room temperature reference electrode Ag/AgCl (saturated KCl)

Schiff bases	Peak potential (cathodic & anodic) of Schiff bases 1-4 in acetonitrile		Peak potential (cathodic & anodic) of Schiff bases 1-4 in acetonitrile+ water	
	E_{p_c} (V)	E_{p_a} (V)	E_{p_c} (V)	E_{p_a} (V)
SB 1	-0.24,0.38,0.94,1.24	-0.26,0.59,0.94, 1.39	-0.17,0.34	0.37,0.89
SB 2	0.41,0.88,1.15,1.52	0.29,0.85,0.49,1.134	-0.15,0.40	0.26,0.72
SB 3	0.19,0.33,0.49,1.15	0.49,0.84,1.15	-0.64,0.31	-0.31,0.036,0.48,-0.59
SB 4	0.14,0.60,0.82,1.22,	0.24, 0.80,1.16	-0.06,0.42,0.54,0.74,1.12	0.04,0.24,0.54,0.94

Table 2. The Peak currents (cathodic & anodic) of Schiff base (SB 1) with different scan rates (50,100, 150,200,250, 300, 350 mVsec^{-1}) in acetonitrile at room temperature SB 1= $[2 \times 10^{-6}\text{ M}]$, reference electrode Ag/AgCl (saturated KCl).

SB:1 in Acetonitrile	Scan rate(v) mVsec^{-1}	$v^{1/2}\text{mVsec}^{-1}$	$i_{p_c} \times 10^{-6}$ (A)	Log i_{p_c} (A)	$i_{p_a} \times 10^{-6}$ (A)	Log i_{p_a} (A)
	50	7.07	2.667	-5.5739	-2.252	5.6474
	100	10.00	3.499	-5.4560	-3.064	5.5137
	150	12.25	4.331	-5.3634	-3.688	5.4332
	200	14.14	5.083	-5.2938	-4.188	5.3779
	250	15.80	5.835	-5.2339	-4.812	5.3176
	300	17.32	6.416	-5.1927	-5.436	5.2647
	350	18.71	6.997	-5.1550	-5.876	5.2309

Table 3. The Peak currents (cathodic & anodic) of Schiff base (SB 2) with different scan rates (50,100, 150,200,250, 300, 350 mVsec⁻¹) in acetonitrile at room temperature SB 2= [2X10⁻⁶ M], reference electrode Ag/AgCl (saturated KCl).

SB 2 in Acetonitrile	Scan rate(v) mVsec ⁻¹	v ^{1/2} mVsec ⁻¹	ip _c x10 ⁻⁶ (A)	Log ip _c (A)	ip _a x10 ⁻⁶ (A)	Log ip _a (A)
	50	7.07	2.121	-5.6734	-1.709	5.7672
	100	10.00	2.718	-5.5657	-2.624	5.5810
	150	12.25	3.124	-5.5052	-3.208	5.4937
	200	14.14	3.656	-5.4369	-3.835	5.4162
	250	15.80	3.938	-5.4047	-4.376	5.3589
	300	17.32	4.250	-5.3716	-4.749	5.3233
	350	18.71	4.468	-5.3498	-5.208	5.2833

Table 4. The Peak currents (cathodic & anodic) of Schiff base (SB 3) with different scan rates (50,100, 150,200,250, 300, 350 mVsec⁻¹) in acetonitrile at room temperature SB 3= [2X10⁻⁶ M], reference electrode Ag/AgCl (saturated KCl).

SB 3 in Acetonitrile	Scan rate(v) mVsec ⁻¹	v ^{1/2} mVsec ⁻¹	ip _c x10 ⁻⁶ (A)	Log ip _c (A)	ip _a x10 ⁻⁶ (A)	Log ip _a (A)
	50	7.07	1.932	-5.7139	-2.051	5.6880
	100	10.00	2.299	-5.6384	-2.701	5.5684
	150	12.25	2.566	-5.5907	-3.200	5.4948
	200	14.14	3.199	-5.4949	-3.699	5.4319
	250	15.80	3.601	-5.4424	-4.349	5.3616
	300	17.32	4.234	-5.3732	-4.899	5.3098
	350	18.71	4.733	-5.3248	-5.236	5.2810

SB 4 in Acetonitrile	Scan rate(v) mVsec ⁻¹	v ^{1/2} mVsec ⁻¹	ip _c x10 ⁻⁶ (A)	Log ip _c (A)	ip _a x10 ⁻⁶ (A)	Log ip _a (A)
	50	7.07	2.880	-5.5406	-7.723	5.1122
	100	10.00	3.476	-5.4589	-8.851	5.0530
	150	12.25	4.071	-5.3902	-9.974	5.0011
	200	14.14	4.438	-5.3528	-11.100	4.9546
	250	15.80	4.942	-5.3060	-12.000	4.9208
	300	17.32	5.582	-5.2532	-12.750	4.8944
	350	18.71	6.133	-5.2123	-13.500	4.8696

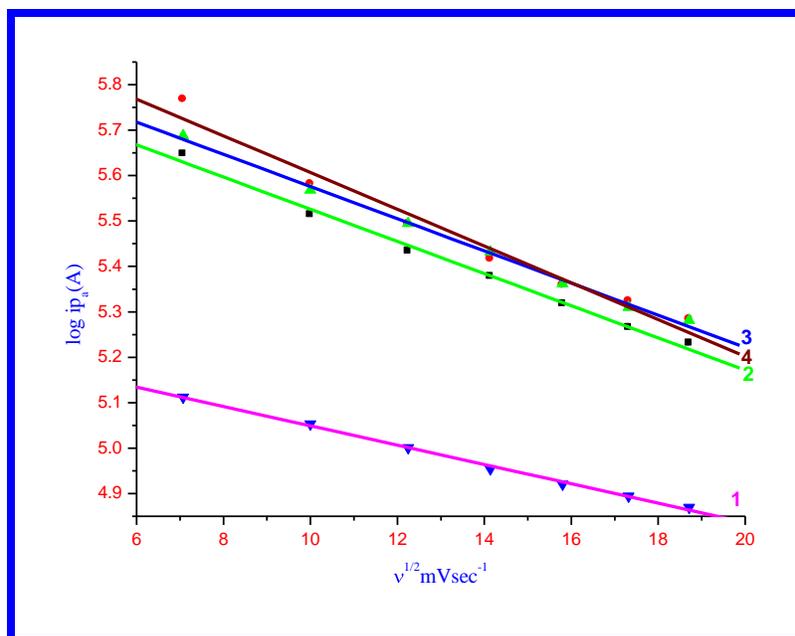


Fig 5. Plot of $\log i_{pa}$ vs. $v^{1/2}$ of Schiff base **1-4** in acetonitrile. Reference electrode Ag/AgCl (satdKCl) at 298K.

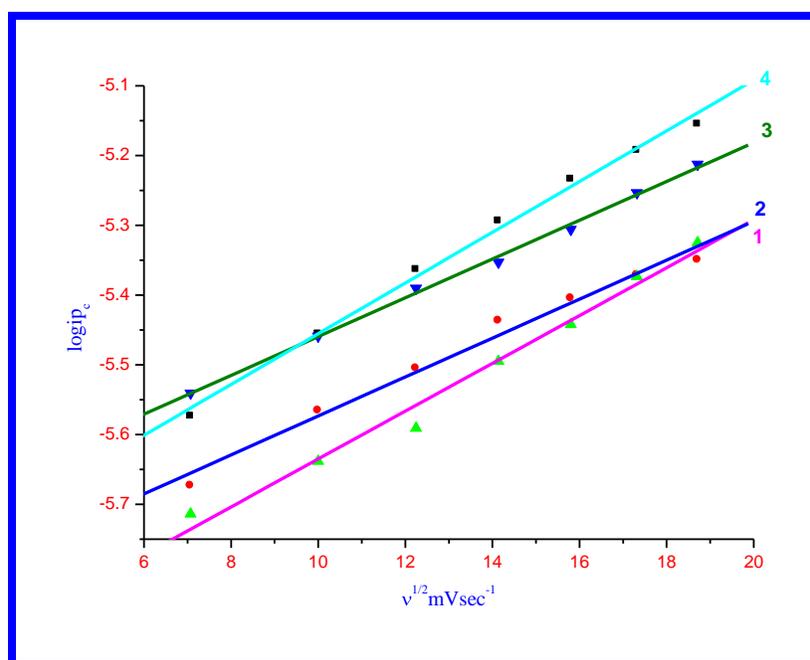
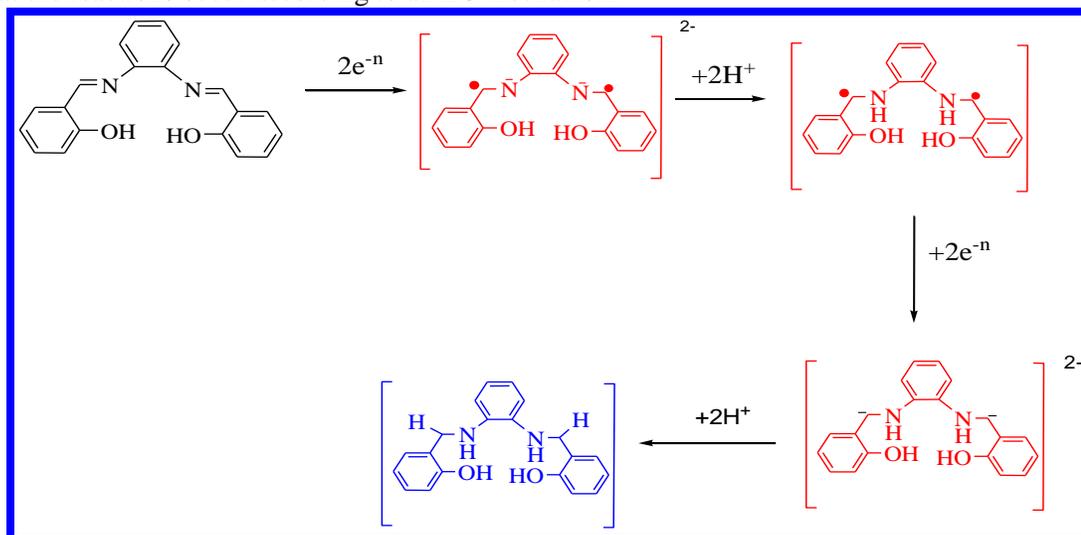


Fig 6. Plot of $\log i_{pc}$ vs. $v^{1/2}$ of Schiff base **1-4** in acetonitrile. Reference electrode Ag/AgCl (satd KCl) at 298K.

Mechanism : As can be seen from the mechanism given in Scheme 1, the first step is the 2e reduction of the azo methane group of tetradentate symmetrical schiff bases , in which the $-C=N-$ bond opens resulting a $-C=N^{2-}$ -dianion. Then, the dianion binds $2H^+$, resulting in the formation of a hydrazine compound ($-CH-NH-$). In the second step, the imine groups of Schiff bases form a radical anion ($C=N\cdot$) with a 1electron transfer. Then, the negatively charged nitrogen atom binds to a proton resulting in $C-NH$. This radical carbon atom takes one more electron giving carbanion C^--NH . Finally, the carbanion reacts with a

proton from the solution, resulting in an amine (CHNH). According to these data, it can conveniently be claimed that the reactions occur according to an EC mechanism



Scheme 1. Electron transfer mechanism of schiff bases

APPLICATIONS

Growth of bacterial pathogens on selected concentrations of schiff bases were checked to determine the minimum concentration that inhibits the growth of the organism. The antimicrobial activity was studied against pathogenic bacterial strains both Gram positive (*S. aureus*) bacterium and Gram negative bacteria (*E. coli*). Antibacterial potential of schiff bases were assessed in terms of zone of inhibition of bacterial growth. Based on the results the schiff base was effective against Gram negative (*E. coli*) bacterium than Gram positive bacterium (*S. aureus*). The schiff base is having an excellent inhibitive action against Gram negative bacterium (*E. coli*) than Gram positive bacterium (*S. aureus*). Sanjay chhibber[31] had reported that majority the infections caused by bacteria in humans are treated by instituting antimicrobial treatment. However, as a result of indiscriminate use of broad-spectrum antibiotics, bacteria have evolved resistance against many of these agents. These results prove that the antibacterial potential of schiff bases will be an effective alternative for the conventional antibiotics and emerging infection causing pathogens.

CONCLUSIONS

The electrochemical behaviors of different Schiff bases are studied in acetonitrile solvent. Cyclic voltammetric behavior of the selected Schiff bases are studied in glassy carbon as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode and TBAP is used as the supporting electrolyte. While the could be seen from the cyclic voltammograms, the peaks belong to the $-C=N-$ and $-C=N-(ads)$ groups, respectively, It could also be concluded that the reduction potentials and currents depended on the electron withdrawing groups and hydrogen bonding on either side of the $-C=N-$ groups.

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REFERENCES

- [1] S. Patai (Ed.), *J. Wiley & Sons*, London, **1970**.
- [2] E. Jungreis, S. Thabet, *Analytical Applications of Schiff bases*, Marcell Dekker, New York, **1969**.
- [3] C. Spinu, M. Pleniceanu, C. Tigae, *Turk. J. Chem.* **2008**, 32,487.
- [4] B. Clarke, N. Clarke, D. Cunningham, T. Higgins, P. McArdle, M. Ni Cholchu, M. O’Gara, *J. Organometallic Chem.* **1998**, 559, 55.
- [5] A.L. Lehlinger, *Principles of biochemistry*, Worth, New York, **1975**.
- [6] S.N. Pandeya, D. Sriram, G. Nath, E. De Clercq, *Pharm. ActaHelv.* **1999**, 74, 11.
- [7] S.N. Pandeya, D. Sriram, G. Nath, E. de Clercq, *Arzneimittelforsch.* **2000**, 50, 55.
- [8] W.M. Singh, B.C. Dash, *Pesticides.* **1988**, 22, 33.
- [9] J.L. Kelley, J.A. Linn, D.D. Bankston, C.J. Burchall, F.E. Soroko, B.R. Cooper, *J. Med. Chem.* **1995**, 38, 3676.
- [10] G. Turan-Zitouni, Z.A. Kaplancikli, A. Özdemir, P. Chevallet, *Arch. Pharm. Chem. Life Sci.* **2007**, 340, 586.
- [11] M.T.H. Tarafder, A. Kasbollah, N. Saravanan, K.A. Crouse, A.M. Ali, K.T. Oo, *J. Biochem. Mol. Biol. Biophys.* **2002**, 6, 85.
- [12] G.H. Schmid, *Organic Chemistry*, New York, **1996**.
- [13] K. Singh, M.S. Barwa, P. Tyagi, *Eur. J. Med. Chem.* **2007**, 42, 394.
- [14] P.G. Cozzi, *Chem. Soc. Rev.* **2004**, 33, 410.
- [15] S. Chandra, J. Sangeetika, *J. Indian Chem. Soc.* **2004**, 81, 203.
- [16] M.B. Ferrari, S. Capacchi, G. Pelosi, G. Reffo, P. Tarasconi, R. Albertini, S. Pinelli, P. Lunghi, *Inorg. Chim. Acta.* **1999**, 286, 134.
- [17] E. Canpolat, M. Kaya, *J. Coord. Chem.* **2004**, 57, 1217.
- [18] M. Yildiz, B. Dulger, S.Y. Koyuncu, B.M. Yapici, *J. Indian Chem. Soc.* **2004**, 81, 7.
- [19] R.S. Nicholson, I. Shain, *Anal. Chem.* **1964**, 36, 706.
- [20] J. M. V. Scott, W. H. Jura, *Can. J. Chem.* **1967**, 45, 2375.
- [21] L. V. Kononenko, V. D. Bezuglyi, V. N. Dmitrieva, *Zh. Obshch. Khim.* **1968**, 38, 2153.
- [22] P. Martinet, J. Simonet, J. Tendil, *C. R. Acad. Sci. Ser. C.* **1969**, 268, 303.
- [23] V. N. Dmitrieva, L. V. Kononenko, V. D. Bezuglyi, *Teor. Eksp. Khim.* **1965**, 1, 456.
- [24] V. D. Bezuglyi, L. V. Kononenko, A. F. Forunova, V. N. Dmitrieva, B. L. Timan, *Zh. Obshch. Khim.* **1969**, 39, 1680.
- [25] V. N. Dmitrieva, N. A. Rozanel’skaya, B. M. Krasovitskii, B. I. Stepanov, V. D. Bezuglyi, *Zh. Obshch. Khim.* **1971**, 41, 60.
- [26] V. N. Dmitrieva, V. B. Smelyakova, B. M. Krasovitskii, V. D. Bezuglyi, *Zh. Obshch. Khim.* **1966**, 36, 405.
- [27] N. F. Levchenko, L. S. Afanasiadi, V. D. Bezuglyi, *Zh. Obshch. Khim.* **1967**, 37, 666.
- [28] S. Cakir, E. Bicer, M. Odabasoglu, Ç. Albayrak, *J. Braz. Chem. Soc.* **2005**, 16, 711.
- [29] O.Çakir, E. Biçer, *Portugaliae Electrochim. Acta*, **1998**, 16, 11.
- [30] S. Yagmur, *The investigation of the Electrochemical Behaviours of Phenazopyridine Hydrochloride and some of its Schiff Bases*, Çanakkale Onsekiz Mart University, Graduate School of Science and Engineering Chair for Chemistry, PhD Thesis of Science, Canakkale, **2010**.
- [31] Chhibber, S.: Biocontrol of antibiotic resistant bacteria using Bactriophage: an emerging approach, Antimicrobial resistance: from emerging threat to reality Eds: Lawrance R.; Gulati A. K and Abraham G.: Narosa Publishing House Pvt.Ltd. **2009**, 7.