



P-ISSN: 2349-8528
 E-ISSN: 2321-4902
www.chemjournal.com
 IJCS 2022; 10(6): 45-51
 © 2022 IJCS
 Received: 04-10-2022
 Accepted: 08-11-2022

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Electrochemical studies of synthesized glycine-4-tertbutylcyclohexanonimine at the working electrode

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Abstract

The present study has developed for investigation of cyclic voltammetric reduction of glycine-4-tert-butylcyclohexanonimine (GTBCHI) at GCE (working electrode) v/s Ag/AgCl in methanol and DMF media containing phosphate and BR buffer solutions at various pH and scan rates. The electron transfer process of GTBCHI at glassy carbon electrode (GCE) was found to be irreversible over the pH range 5-9. The relation between cathodic peak current and $v^{1/2}$ was shown straight line, indicating diffusion controlled process. The impacts of scan rate, media, pH and buffers on cathodic peak potential and cathodic peak current were examined.

Keywords: Electron transfer process, cathodic peak current, working electrode, diffusion controlled process

Introduction

Schiff base ligands have found to be a key point in the development of coordination chemistry^[1-6] due to formation of Schiff base complexes by their ability to bond through electron donating atoms such as N, O & S. In the Schiff base ligands, the presence of the lone pair of electrons on the nitrogen atom in the imine group having the chemical and biological importance^[7-9].

Electro analytical method has the benefits such as speedily response, good reproducibility and small detection limit^[10]. Electro analytical methods are used for study an analyse by applying the potential at the working electrode and measuring the current in an electrochemical cell containing the analyse^[11]. To analysis and determination of electrochemical behaviour of Schiff bases provides an opportunity for control of their behaviour under different condition. Cyclic voltammetry technique widely used to provide valuable information about the reduction and oxidation potentials and the nature of charge transfer processes.

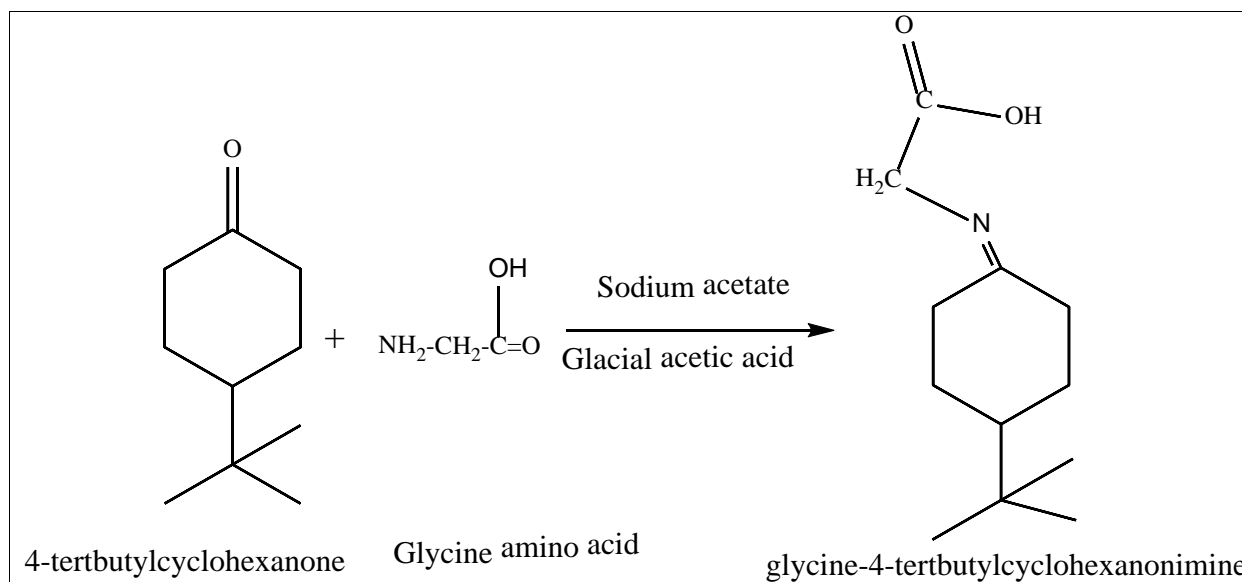
Experimental

Materials and methods

All chemical reagents were analytical grade. By using micro analytical technique, elemental analysis was carried out on C, H, N, elemental analyzer. IR spectra were obtained using KBr pellets on a spectrophotometer (SHIMADZU, Model 8400 S). By Elico Digital pH meter, the pH measurements were carried out. The cyclic voltammetric analysis were conducted using 3-electrode cell system with glassy carbon (working electrode), Pt (counter electrode), Ag/AgCl (reference electrode). The cyclic voltammetric measurements were carried out by fully computer system (Digital Constant Current Source).

Synthesis of glycine-4-tertbutylcyclohexanonimine (GTBCHI)-

The glycine-4-tertbutylcyclohexanonimine ligand was prepared via adding of glycine amino acid, sodium acetate and 4-tertbutylcyclohexanone in glacial acetic acid^[12]. The reaction mixture was refluxed on water bath, cooled and extracted. The product was separated by separating funnel and dried.



Scheme 1: Structure of Synthesized glycine-4-tertbutylcyclohexanimine (GTBCHI)

Result and discussion

Elemental analysis of ketimine (GTBCHI)-

Elemental analysis data of GTBCHI was found (cal.): M. Wt.; 211.15 (211.31), C; 75.65 (68.21), H; 10.00(10.02), N; 6.59 (6.63), O; 14.96 (15.14).

Infrared study of GTBCHI-

The imine stretching band appears at $1610\text{-}1620\text{cm}^{-1}$ in the spectra of GTBCHI. The disappearance of stretching vibration bands for carbonyl group and amino group^[13] showed that the condensation product formed by the reaction of 4-tertbutylcyclohexanone and glycine amino acid. The strong bands in the regions of $1700\text{-}1720\text{cm}^{-1}$ and $1370\text{-}1390\text{cm}^{-1}$ were observed respectively for asymmetric and symmetric carboxyl groups.

Cyclic voltammetric study of GTBCHI-

In electron transfer processes, the reduction potential and peak current are considered as an important parameter. It is strongly affected by the nature of the solvent and buffer, scan rate and pH. The various-scan cyclic voltammograms of the ketimine were recorded with variation of pH, buffer solutions (phosphate and BR) and solvents (methanol and DMF) at

GCE V/S Ag/AgCl. By the shape of the cyclic voltammograms, we examined that the cathodic peaks were showing with a well-defined current maximum, but no anodic peaks in the backward directions at various scan rates, suggesting irreversible responses of the two-electron reduction of the compound. The values of the reduction peak potential and peak current (E_{pc} , I_{pc}) and half-wave potential ($E_{p/2}$) were represented in tables 1-3. These following equations were used to calculate the kinetic variables.

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha_n F} = \left(\frac{47.7}{\alpha_n}\right) mV \quad (1)$$

$$I_p = 3.01 \times 10^5 n (\alpha_n)^{1/2} A C D_0^{1/2} \nu^{1/2} \quad (2)$$

$$E_p = -\frac{RT}{\alpha_n F} \left[0.78 + \ln \left(\frac{D_0^{1/2}}{k_{f,h}^{\circ}} \right) + \ln \left(\frac{\alpha_n F \nu}{RT} \right)^{1/2} \right] \quad (3)$$

Table 1: The scan rates effect on cyclic voltammetric parameters of glycine-4-tertbutylcyclohexanimine (GTBCHI) in methanol-phosphate buffered solution at different values of pH (5.8, 7 & 8)

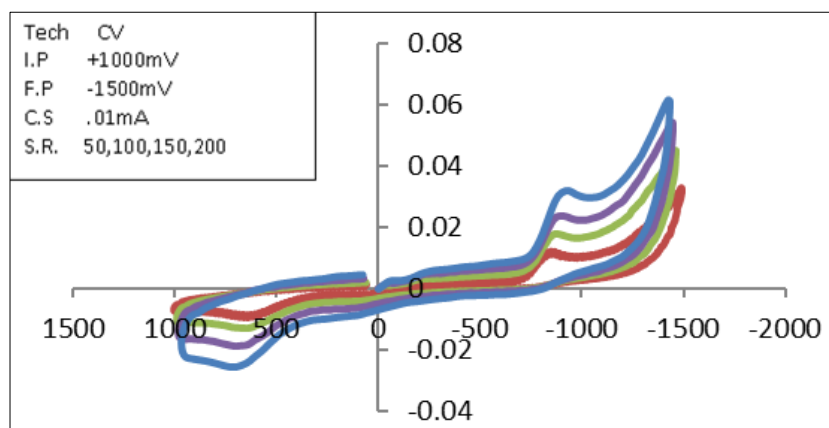
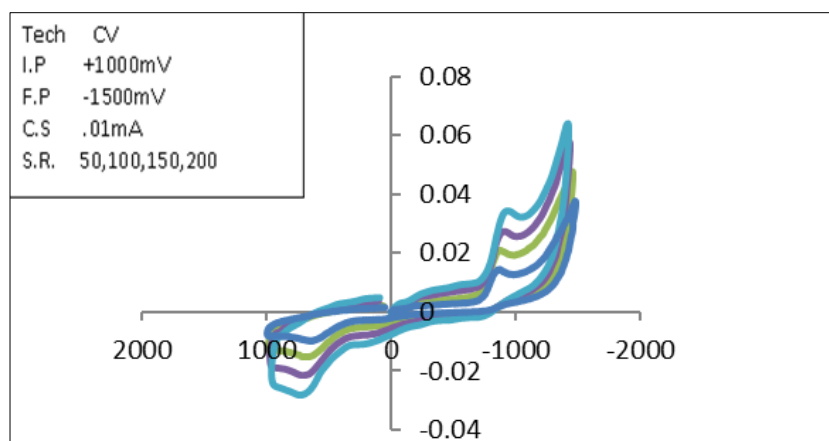
pH	ν (mV/Sec)	E_{pc} (mV)	I_{pc} (μA)	$E_{p/2}$ (mV)	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ (cm^2/Sec)	$k_{t,h}^{\circ}$ (cm/Sec)
5.8	50	-791.1	11.44	-699.1	1.61786	0.51876	14.13953	3.55×10^{-9}
	100	-811.7	16.62	-722.4	1.662	0.534155	14.31445	2.09×10^{-9}
	150	-821.3	20.63	-731	1.684432	0.528298	14.58785	2.56×10^{-9}
	200	-900.6	31.5	-791.2	2.227386	0.435975	21.2345	1.95×10^{-8}
7	50	-808.2	11.3	-748.4	1.598061	0.798059	11.26038	3.78×10^{-13}
	100	-831.7	22.43	-777.7	2.243	0.883006	15.02535	2.31×10^{-14}
	150	-864	28.62	-789.9	2.336813	0.643117	18.3424	3.10×10^{-11}
	200	-919.2	34.13	-815.7	2.413355	0.460736	22.38063	6.35×10^{-9}
8	50	-839.6	16.33	-755.6	2.071823	0.567722	19.29348	3.84×10^{-10}
	100	-852.5	28.14	-765.3	1.948	0.547269	23.94422	9.81×10^{-10}
	150	-876.6	32.01	-775.9	1.798742	0.473872	23.89937	8.18×10^{-9}
	200	-975	38.4	-820.6	1.938887	0.308938	30.7509	8.37×10^{-7}

Table 2: The scan rates effect on cyclic voltammetric parameters of glycine-4-tertbutylcyclohexanonimine in methanol-BR buffered solution at different values of pH (5, 7, 9)

pH	v mV/s	E _{p,c} (mV)	I _{p,c} (μA)	E _{p/2} (mV)	I _{p,c} / v ^{1/2}	α _n	D ₀ ^{1/2} (cm ² /s)	k ^o _{r,h} (cm/s)
5	50	-860.9	14.73	-770.77	2.083137	0.529236	18.0248	7.86x 10 ⁻¹⁰
	100	-867.02	24.49	-729.98	2.449	0.348074	26.12946	5.22x 10 ⁻⁷
	150	-920.2	32.68	-788.58	2.668311	0.362407	27.90072	2.03x 10 ⁻⁷
	200	-976.64	34.79	-800.64	2.460024	0.271023	29.74498	3.15x 10 ⁻⁶
7	50	-913.17	15.32	-784.43	2.166575	0.370514	22.40518	7.87x 10 ⁻⁸
	100	-957.27	28.4	-727.63	2.84	0.207716	39.22474	3.34x 10 ⁻⁵
	150	-1011.2	39.78	-807.57	3.248023	0.234214	42.24643	1.06x 10 ⁻⁵
	200	-1029.3	45.37	-827.57	3.208143	0.236478	41.52747	9.40x 10 ⁻⁶
9	50	-943.38	22.68	-754.09	2.071823	0.251994	40.1666	5.85x 10 ⁻⁶
	100	-974.81	31.88	-776.74	1.948	0.240824	40.89269	9.25x 10 ⁻⁶
	150	-1013.4	42.04	-809.2	1.798742	0.233572	44.70789	1.13x 10 ⁻⁵
	200	-1033.8	47.62	-827.5	1.938887	0.231172	44.08431	1.17x 10 ⁻⁵

Table 3: The scan rates effect on cyclic voltammetric parameters of glycine -4- tertbutylcyclohexanonimine in DMF -BR buffered solution at different values of pH (5,7 &9)

pH	v mV/s	E _{pc} mV	I _{pc} μA	E _{p/2} mV	I _{pc} / v ^{1/2}	α _n	D ₀ ^{1/2} cm ² /s	k ^o _{r,h} cm/s
5	50	-906.6	12.17	-843	1.721098	0.749529	12.51378	1.06x 10 ⁻¹³
	100	-941.8	15.78	-856.9	1.578	0.562036	13.24958	4.77x 10 ⁻¹¹
	150	-969.8	21.7	-891.9	1.771798	0.612088	14.25556	5.37x 10 ⁻¹²
	200	-997.8	27.52	-887.7	1.945958	0.433439	18.60572	3.62x 10 ⁻⁹
7	50	-968.83	10.68	-887.44	1.51038	0.586067	12.41909	7.22x 10 ⁻¹²
	100	-995.4	15.37	-912.32	1.537	0.574145	12.76851	8.99x 10 ⁻¹²
	150	-1016.6	21.31	-864.77	1.739954	0.314188	19.53981	2.29x 10 ⁻⁷
	200	-1045.9	25.11	-888.19	1.775545	0.302454	20.3226	3.04x 10 ⁻⁷
9	50	-984.84	12.33	-883.15	2.071823	0.469073	16.02637	5.14x 10 ⁻¹⁰
	100	-989.07	16.96	-867.26	1.948	0.391593	17.06025	1.29x 10 ⁻⁸
	150	-1040	24.5	-880	1.798742	0.298125	23.06208	3.79x 10 ⁻⁷
	200	-1047.8	27.89	-884.81	1.938887	0.29271	22.94521	4.91x 10 ⁻⁷

**Fig 1:** The various scan cyclic voltammograms responses of GTBCHI in methanol-phosphate buffered solution at pH5.8**Fig 2:** The various scan cyclic voltammograms responses of GTBCHI in methanol- phosphate buffered solution at pH 7

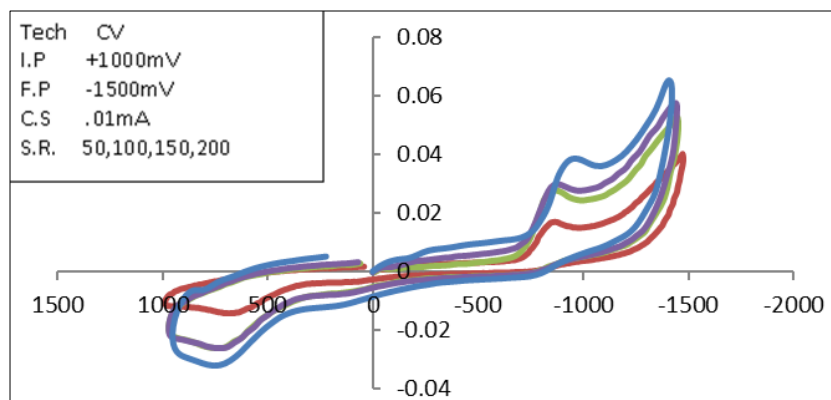


Fig 3: The various scan cyclic voltammograms responses of GTBCHI in methanol- phosphate buffered solution at pH 8

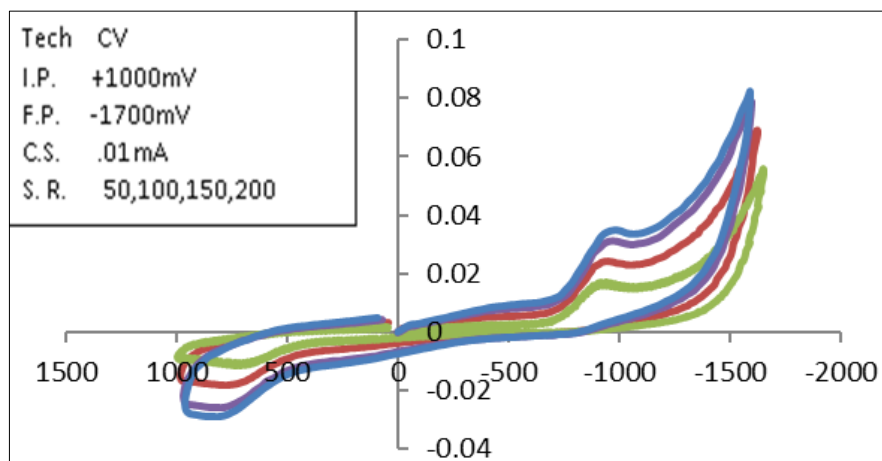


Fig 4: The various scan cyclic voltammograms responses of GTBCHI in methanol- BR buffered solution at pH 5

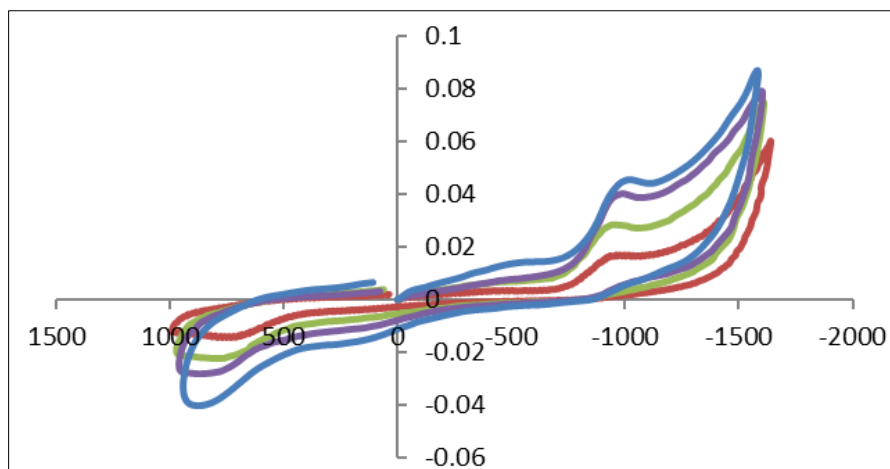


Fig 5: The various scan cyclic voltammograms responses of GTBCHI in methanol-BR buffered solution at pH 7

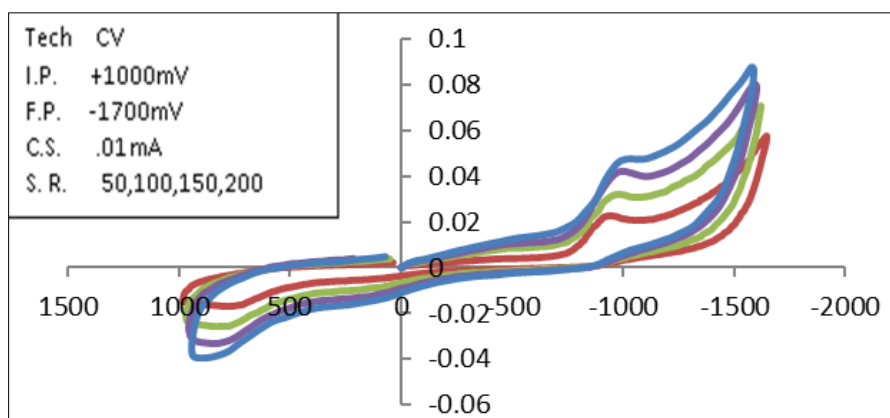


Fig 6: The various scan cyclic voltammograms responses of GTBCHI in methanol-BR buffered solution at pH 9

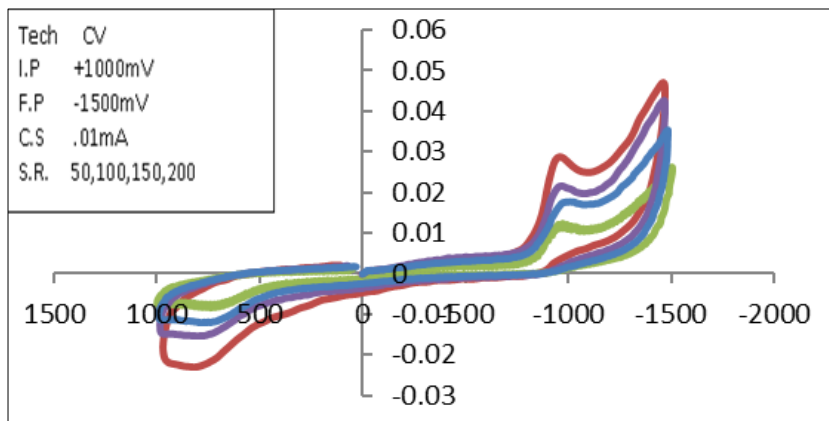


Fig 7: The various scan cyclic voltammograms responses of GTBCHI in DMF-BR buffered solution at pH 5

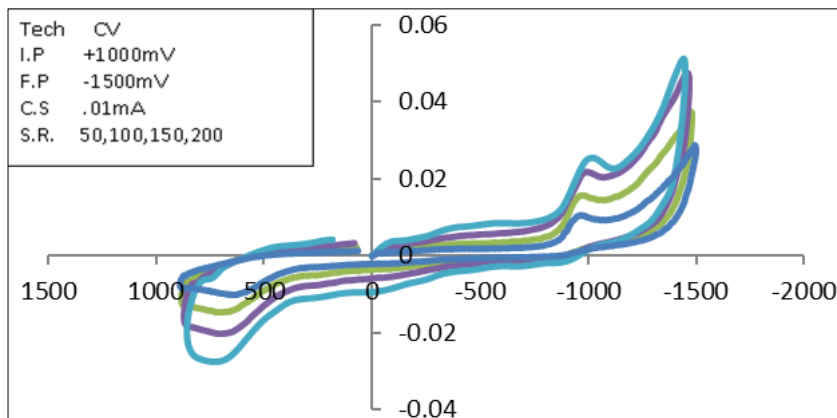


Fig 8: The various scan cyclic voltammograms responses of GTBCHI in DMF-BR buffered solution at pH 7

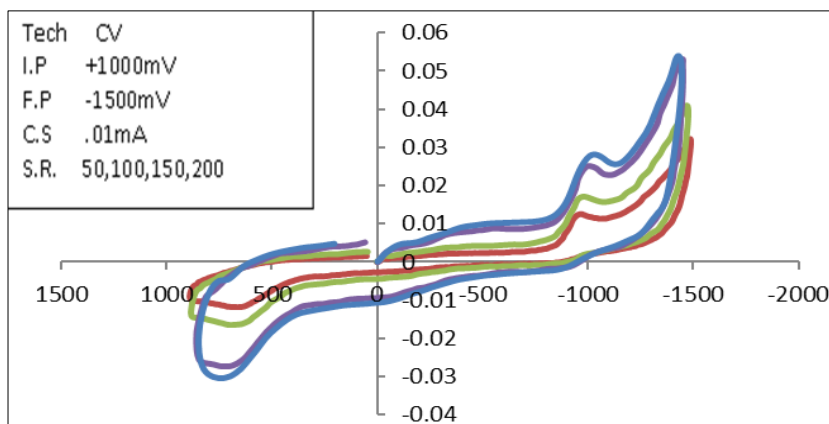


Fig 9: The various scan cyclic voltammograms responses of GTBCHI in DMF-BR buffered solution at pH 9

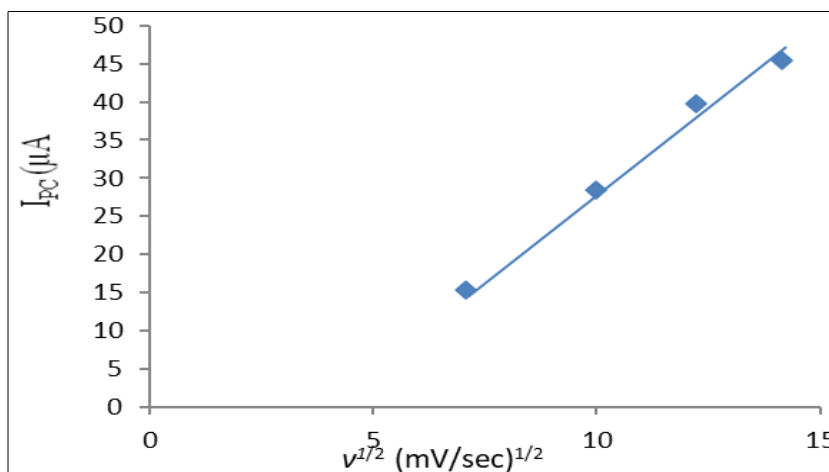


Fig 10: I_{pc} v/s $v^{1/2}$ of GTBCHI in methanol- BR buffered solution at pH 7

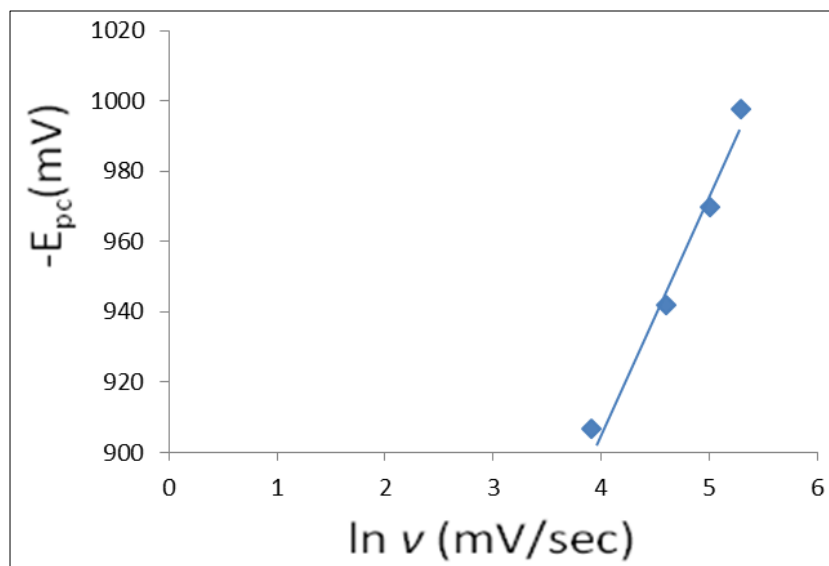


Fig 11: Peak potential (E_{pc}) versus ln v of GTBCHI by using various scan rates in DMF-BR buffered solution at pH 5

Influence of scan rate variation

A closer inspection of the voltammetric variables revealed that the shifting the potential of the reduction waves with higher negative values, related to the faster scan rate^[14]. This behaviour strongly will encourage totally electrochemically irreversibility of ketimine. The current intensity (I_{pc}) is proportional to the square root of the scan rate, which are consistent with the reaction rate, is controlled by linear diffusion^[15-17] in fig.10. The reduction potential (E_{pc}) varies with the logarithm of the scan rate and linear correlations are obtained, plotting E_{pc} versus ln v (fig.11).

Influence of buffered solutions

The variation of the buffer solutions to the reduction of the azomethine group was observed by recording cyclic voltammograms in the phosphate and BR buffer solutions with different scan rate using constant pH range (5-9) at GCE V/S Ag/AgCl electrode. The positive shift in reduction potential observed for phosphate buffer than BR buffer due to ionisation of buffer^[18], where the scan rate and pH were constant, indicated that the electrode process of ketimine is electrochemically unidirectional.

Influence of variation of solvents

In order to observe the effect of solvents on the voltammetric reduction of compound, the cyclic voltammograms were run in methanol and DMF medium with varying pH and scan rates. The reduction of ketimine becomes difficult at glassy carbon electrode in DMF than methanol which may be related to dielectric constant, polarity and viscosity of solvent^[19-20]. At the scan rate of 100mV/s and pH 5 in BR buffer, the values of reduction potential were observed -867.02 mV & -941.8 mV respectively in methanol and DMF medium. These electrochemical variables showed that the peak potential found to be less negative values with methanol, implying easier electron transfer process of ketimine.

Influence of pH variation

The electrochemical response of ketimine at different scan rates, buffers and solvents was investigated at varying pH (5-9). By comparing the values of reduction potential at different pH, it was observed that the peak potential is less negative at lower pH, indicating facile proton transfer takes place throughout the reduction process of compound^[21].

Conclusion

The ketimine was synthesized by reaction of glycine amino acid and 4-tert-butylcyclohexanone and characterised by elemental analysis and infrared study. Based on the electrochemical data of ketimine, it was observed that the peak potential depend upon scan rate, buffer, solvent and pH of the solution. The cyclic voltammograms of ketimine showed irreversible electrode process at GCE.

Acknowledgements

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, for giving good facilities for research.

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