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CYCLIC VOLTAMMETRIC STUDY OF α–METHYLDOPA AT CARBON PASTE ELECTRODE

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The cyclic voltammetric behaviour of α-methyldopa at a silicon oil carbon paste electrode has been reported. This allowed the development of a quantitative method to determine α-methyldopa in LiCl, KCl, NaCl, HCl, H_2SO_4 and CH_3COOH as supporting electrolytes. For qualitative characteristics, α-methyldopa showed an ECC mechanism in terms of electron transfer reaction (placing it in DPI zone) at carbon paste electrode. The values of transfer coefficients α and β were determined. The larger ΔE_p values were obtained due to the use of unmodified carbon paste electrode (CPE) has decreased the rate of electron transfer at the surface of the test electrode. The first order rate constant values (k_o) were within $0.10\text{-}7.78 \pm 0.1 \times 10^{-3}\ s^{-1}$. Adsorption of analyte was also determined at CPE using repeated scan method.

Keywords: Cyclic voltammetric, silicon oil carbon and hypertension.

INTRODUCTION

The importance of α-methyldopa [L-3-(3,4-dihydroxy-phenyl)-2-methyl alanin] is significant for its anti-hypertensive character owing to its ability to control hypertension. A detailed reference is cited by Andreali *et al* (1990) pertaining to the selection of anti-hypertensive drugs. De Rope and Ames (1966) reported results pertaining to its biological aspects reveal that it is a competitive inhibitor of dopadecarboxylase when metabolized in the rat brain to chatecholamines along with α-methyl dopamine and α-methyl norpinephrine. Yu and Scott (1973) revealed that α-methyldopa acts as a substrate in the process of pigment formation of melanocytes of hair follicles where it follows oxidation process at high pH resulting in a polymeric melanin-like pigment. Report in the literature described by Sassetti and Fudenberg (1971) reflects its characteristics similar to that of naturally occurring congeners.

Early work pertaining to voltammetric and polarographic studies on the determination of α-methyldopa revealed its oxidation at different electrodes. Pungor *et al* (1971), for instance, determined α-methyldopa along with other drugs while performing voltammetry at a silicon rubber based graphite electrode. Voltammetric behaviour of α-methyldopa has been studied at Pt and carbon electrodes in aqueous systems by Ozkan & Biryol (1990) and Ali et al. (1992). Similarly, Young *et al* (1980) reported anodic oxidation of α-methyldopa at carbon paste electrode in McIlvaine buffer, and 1M $HClO_4$ using cyclic voltammetry. Literature reveals a large no of articles cited on the determination of catecholamines. For instance, Rein *et al* (2001) and Maeda (2000) reported electrochemical behaviour of catecholamines (L-dopa) using cyclic voltammetry for their quantitative study. Marazuela *et al* (1999) performed cyclic voltammetry and amperometry for the detection of catecholamines using flow injection method at modified micro electrode surface. Liu *et al* (2000) published results of amperometry on catecholamines by capillary electrophoresis at a micro electrode. Takahashi and Imato (1999) worked on the voltammetric response of catecholamine along with ascorbic acid at a modified graphite electrode. In pharmaceutical formulations, Caruso *et al* (1999) reported determination of epinephrine and dopamine using a biosensor based modified carbon paste electrode. Similarly, cyclic voltammetry was performed by Uchiyama *et al* (1997) for separate determination of catecholamines and aniline through cyclization of dopamine and epinephrine using selective carbon electrode current response. Potentiometry and voltammetry were also reported by Odashima *et al* (1999) and Nazarova *et al* (2001). Modified carbon paste electrodes have been used for their better qualitative as well as quantitative response in pharmaceuticals or other purpose. Hu *et al* (2003) applied diacetydioxime modified carbon paste electrode in differential pulse stripping voltammetry for lead and cadmium detection. Gherghi *et al* (1985) studied interaction between actinomycin D and DNA on carbon paste electrode and on hanging mercury drop electrode. Oni *et al* (2002) reported voltammetric determination of vitamin B_1 in the tablets at a carbon paste electrode. Fiorucci *et al* (2002) worked on the study of tryptophan in pharmaceutical formulation while performing direct voltammetry at a carbon paste electrode. Similarly, Yanez *et al* (2002) determined nitrendipine with β-cyclodextrin modified carbon paste electrode by stripping differential pulse voltammetry. The present work includes the cyclic voltammetric studies of α-methyldopa at a silicon oil impregnated carbon paste electrode in CH_3COOH, HCl, H_2SO_4, KCl, LiCl, and NaCl. Attempt was made to determine kinetic parameter (k_o), α and β (transfer coefficients) for the oxidation-reduction reaction. The successive cycling at the test electrode was also performed to understand the nature of adsorption.

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EXPERIMENTAL

Various acids and ionic salts of analytical grade were used as a supporting electrolyte for the cyclic voltammetric study of α-methyldopa. These include H_2SO_4 (B.D.H.), HCl (B.D.H), CH_3COOH (B.D.H.), KCl (E. Merck), NaCl (E. Merck), and LiCl (E. Merck). A stock solution of analyte was prepared by dissolving 0.1g α-methyldopa (M. S. D.; Pharmaceutical grade) in 100mL volumetric flask using supporting electrolytes. It was diluted further to the desired concentration.

Cyclic voltammeter, bioanalytical systems (BAS; Model CV-1B) with an XY-chart recorder was used for the cyclic voltammetric studies of α-methyldopa. The used three electrode assembly was a carbon paste electrode, Ag│AgCl reference electrode and a platinum wire counter electrode. The carbon paste electrode (BAS; MF-2011) was packed with the silicon oil impregnated carbon paste (BAS; CF-1010) according to the instructions of BAS manual. Baselines were obtained by filling 10mL of the supporting electrolyte in the cell after flushing the nitrogen (99.99%) through the solution for 10 min. Cyclic voltammograms in the potential range 1.25 to –0.7V were recorded at different scan rates by maintaining temperatures at 25, 35 and 45±1°C. Then, cyclic voltammograms of α-methyldopa were recorded in the electrolytes as usually. Effect of pH and temperature on the redox behaviour of α-methyldopa was also studied.

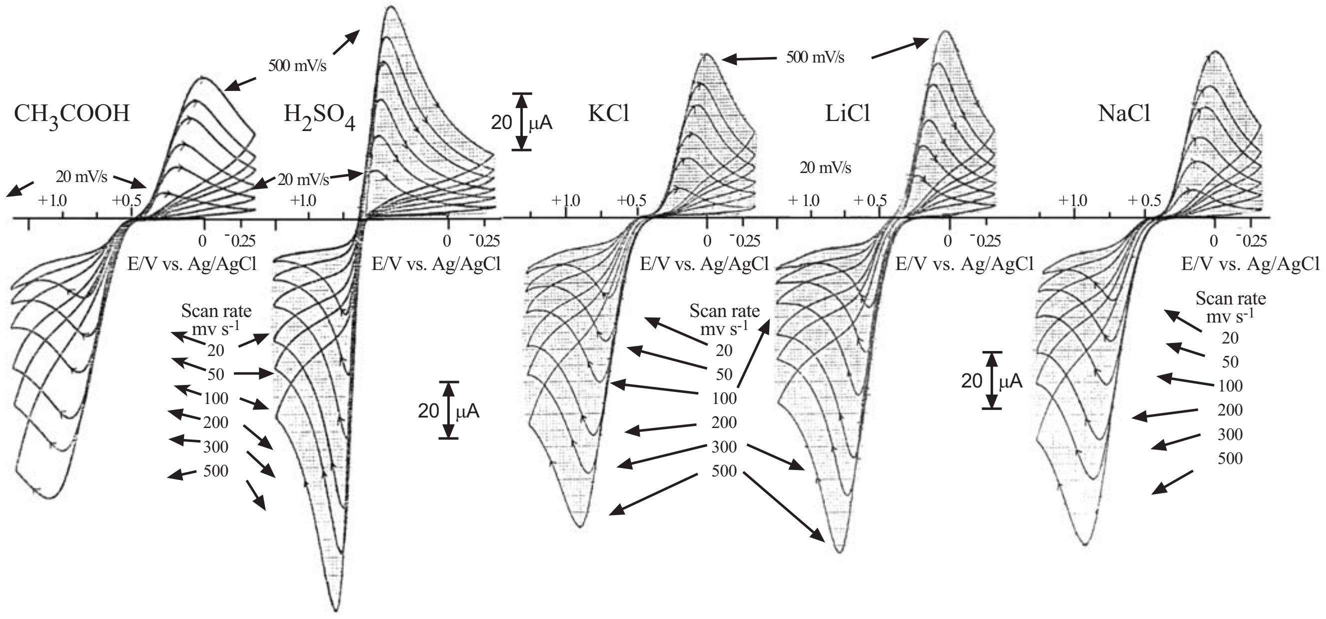

Fig. 1: First-scan cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgC1 reference electrode with different scan rates in various supporting electrolytes at 25°C.

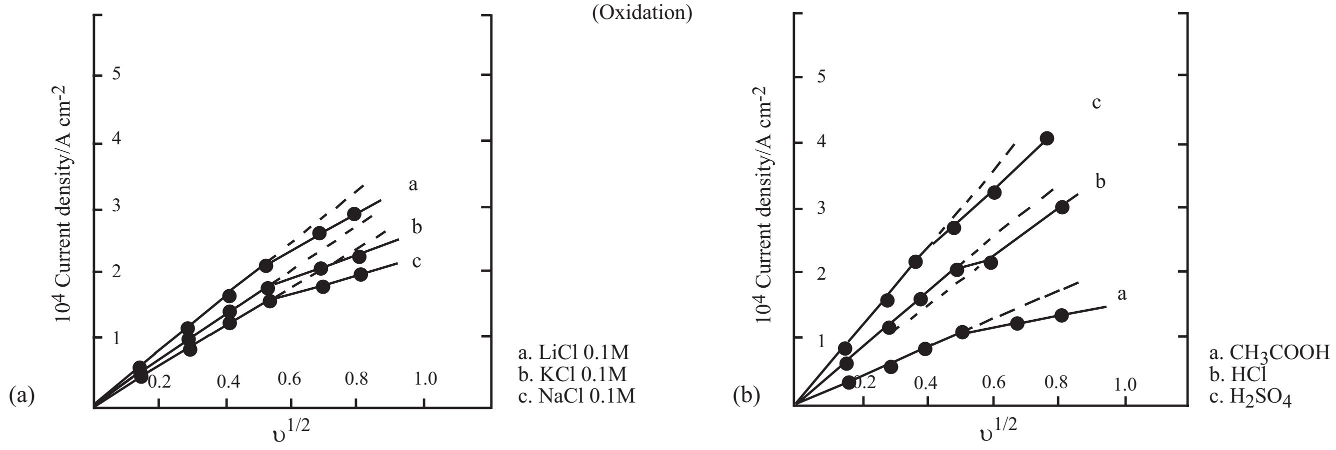

Fig. 2: Variation of anodic peak current density (J_a) with square root of sweep rate υ from the cyclic voltammograms of α-methyldopa (4.73 x l0^{-3} M) at a carbon paste electrode vs. AgAgCl reference electrode in various supporting electrolytes at 25°C.

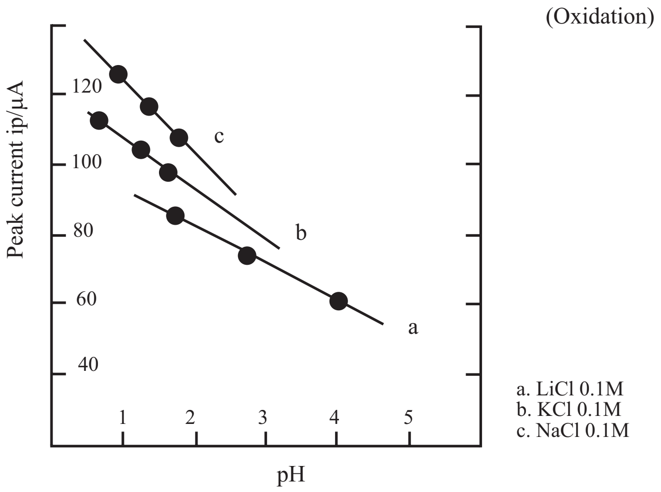

Fig. 3

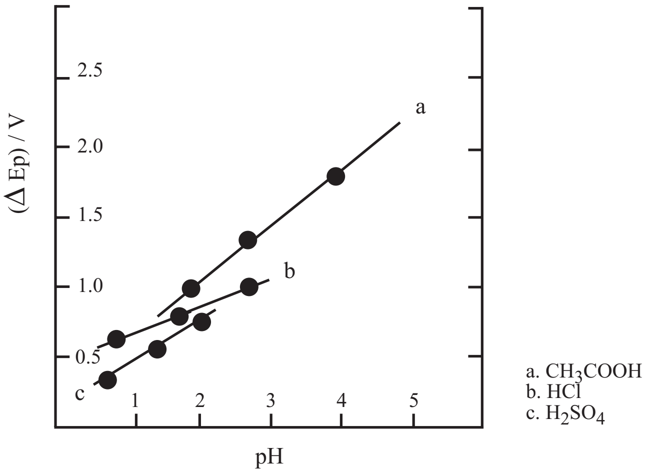

Fig. 4

Fig. 3: Variation of anodic peak current (i_{pa}) with pH from the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgCl reference electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

Fig. 4: Variation of (ΔE_p) with pH from the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgCl reference electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

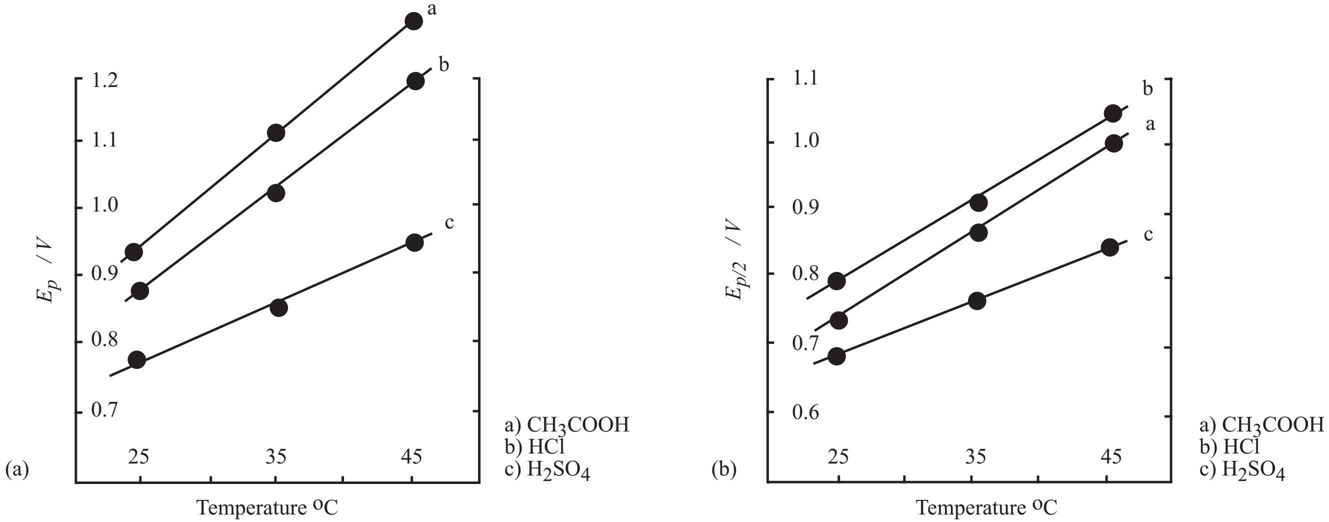

Fig. 5: Effect of temperature on (E_p) and ($E_{p/2}$) from the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgCl reference electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

RESULTS AND DISCUSSION

The single scan cyclic voltammograms of α-methyldopa observed in LiCl, HCl, and CH_3COOH supporting electrolytes are shown in fig.1. It is notable that similar behaviour is appeared in other studied electrolytes also. The voltammograms represent that the present case involves two-electron transfer process which can be shown as:

$$C_{10}H_{13}NO_4 \Leftrightarrow [C_{10}H_{13}NO_4]^{2+} + 2e^- + 2H^+ \quad .....(1)$$

Considering the mechanism of the electrode reaction, the values of λ as derived from $I_p^a(II)/I_p^c(I)$ values which placed this system in DPI zone having λ=0.031, with a fact that the electrode reaction behaves like an unperturbed reaction with $n=n_1$. The α-methyldopa system also fulfills the diagnostic test of a quasi-reversible system. For example, the current density j_p enhances nonlinearly with the square root of scan rate instead of a linear fashion as given in fig.2. Secondly, the ratio of the anodic peak current density j_{pa} to the cathodic current density j_{pc} is equal to one within the limits of experimental errors as explained by Greef *et al* (1985). Thirdly, Reinmuth (1962) and Bard & Faulkner (1980) reported that the difference E_{pa}-E_{pc} is greater than 59/n mV and increases with rate of potential scan υ. However, there are some reports in the literature that an ECC mechanism system may simultaneously follow the quasi-reversible electron transfer process reported by Bard & Faulkner (1980).

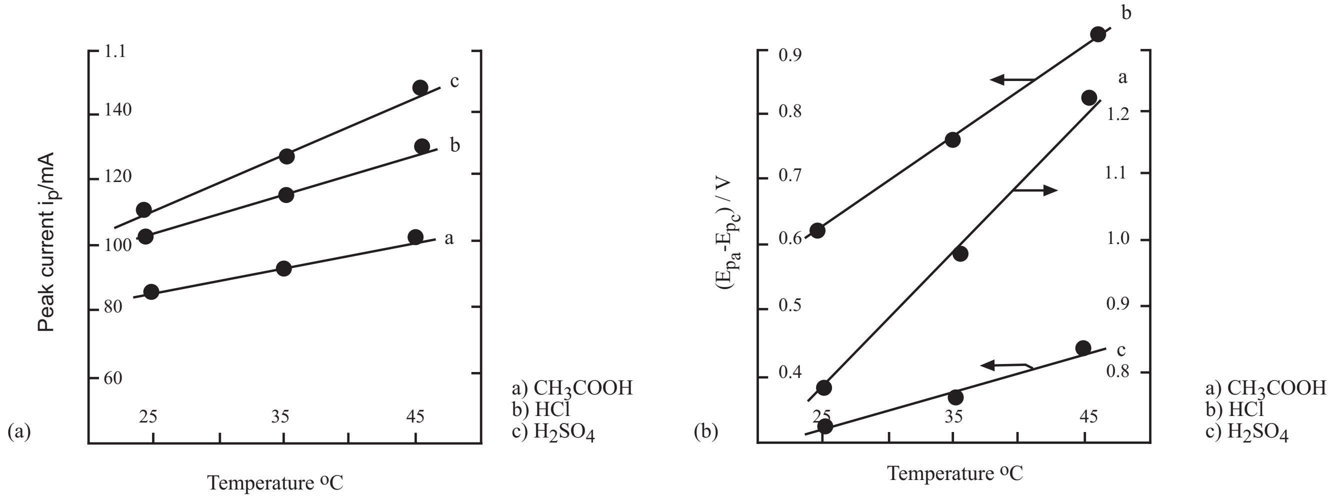

Fig. 6: Effect of temperature on a) i_p and b) peak separation (ΔE_p) from the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgCl reference electrode with in various supporting electrolytes at 25°C.

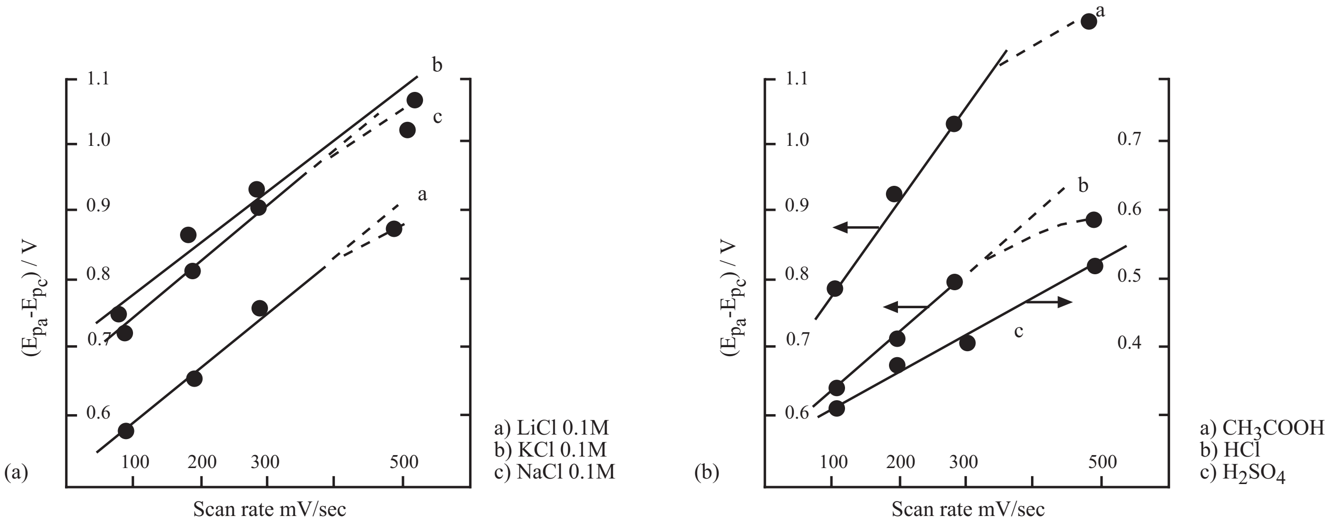

Fig. 7: Effect of potential scan rate on (ΔE_p) from the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode vs. Ag AgCl reference electrode with 100 mV/ scan rate in various supporting electrolytes at 25°C.

Table 1

Diagnostic tests of a quasi-reversible system

Criteria for a quasi-reversible system		Results obtained from α-methyldopa	
1.	/Jp/ is not proportional to $\upsilon^{1/2}$ but Increases as with Increase in $\upsilon^{1/2}$	1.	/Jp/ is not proportional to $\upsilon^{1/2}$ but increases with $\upsilon^{1/2}$
2.	/Jpa/Jpc/ =$_1$b provided $\alpha_a = \alpha$ c = 0.5	2.	/Jpa/Jpc/ =$_1$b
3.	E_{pa} - E_{pc} is greater than59/nmV and increases as υ increases	3.	E_{pa} - E_{pc} > l00mV and increases as υ increases
4.	E_{pc} shifts negatively on increasing υ	4.	On increasing υ the E_{pc} shifts negatively

Diagnostic test for totally irreversible systems

1. J_{pc} is proportional to $\upsilon^{1/2}$ 2. E_{pc} shifts -30/ α na mV per decade increases in υ. 3. /$E_p - E_{p/2}$/ = 48/ α na mV

The first order rate constant (k_o) was determined by using values of $I_p^a(II)/I_p^c(I)$ in the working curve shown in the literature and taking the help of $\lambda = (k_o/\upsilon)(RT/nF)$. The value of k_o was equal to 0.31±0.01 sec^{-1} at 50mV/s.

The peak current decreased linearly with the increase in the pH of the supporting electrolyte in acetic acid is similar to the reported work by Ruiz & Pingarron Carrazon (1992), Gonzalea *et al* (1990), Frsang & Tomcsanyi (1967) and Bai

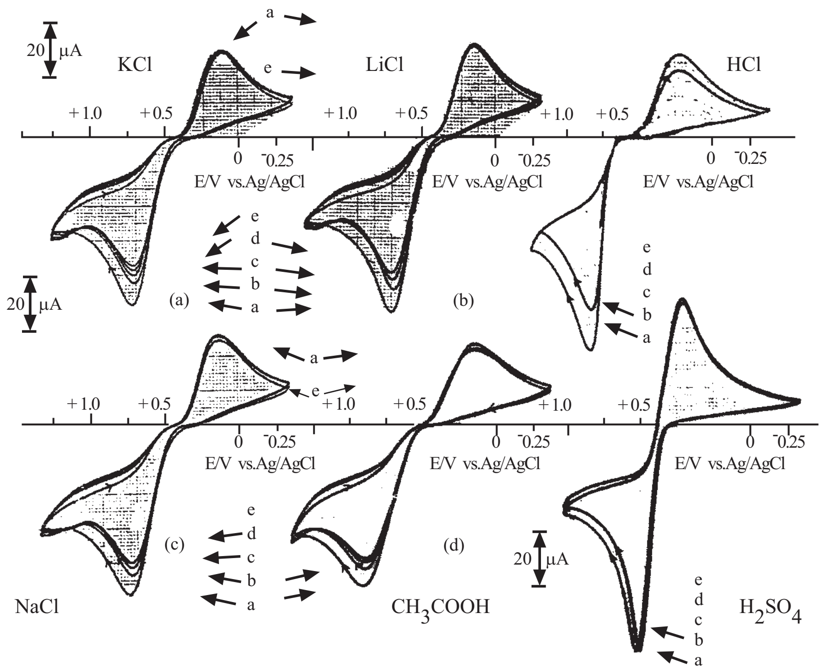

Fig. 8: Repeated-scan cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C (a = 1st cycle and e = 5th cycle).

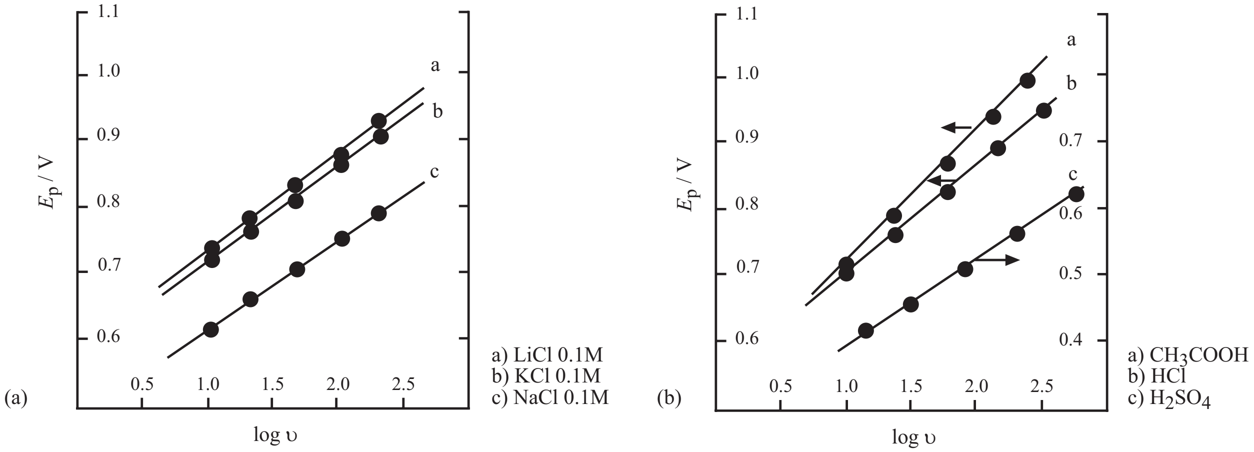

Fig. 9: The dependence of E_p on log υ for the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode with 100 mV/s scan rates in various supporting electrolytes at 25°C.

et al (1990). This behaviour was noticed at all scan rates as shown in fig.3. The same response was observed in HCl and H_2SO_4 system at all scan rates and temperatures. The dependence of peak separation (ΔE_p) on pH of aqueous solutions of HCl, H_2SO_4, and CH_3COOH is shown in fig.4. In all these cases, a linear increase in peak separation was observed while increasing the pH of these aqueous solutions at 25°C due to slow conversion of C to D as given by Bard & Faulkner (1980).

The peak potential increased by increasing the temperature in all these supporting electrolytes. This is shown in fig.5a. In case of $E_{p/2}$, a similar response was also found with the temperature change as given in fig.5b.

The effect of temperature on the anodic and cathodic peak currents (i_{pa} and i_{pc}) is shown in fig.6a. The anodic peak height increased linearly with the increase in temperature at all scan rates. The cathodic peak current values showed the similar trend at all scan rates in these supporting electrolytes similar to the reported work of Mn^{2+} in H_3PO_4-KOH buffer system (Frsang and Tomcsanyi, 1967).

The value of (E_{pa}-E_{pc}) in all these systems increased by increasing the temperature from 25 to 45°C at all scan rates and pH similar to the findings of Sun and Mottola. Fig.6b shows the dependence of temperature on peak separation from the cyclic voltammograms of α-methyldopa in these supporting electrolytes.

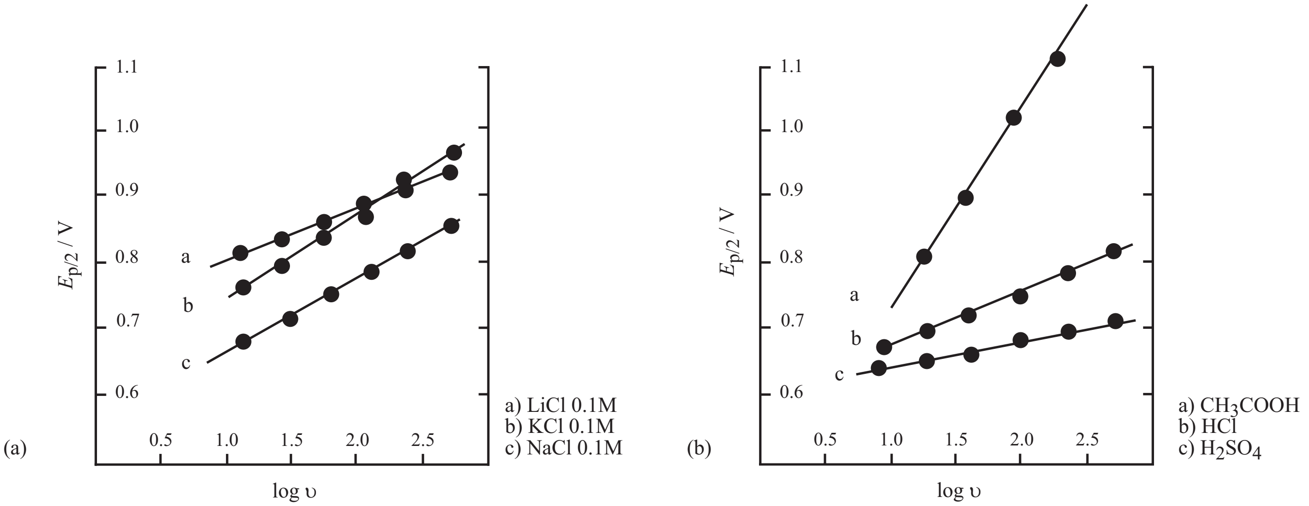

Fig. 10: The dependence of $E_{p/2}$ on log υ for the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

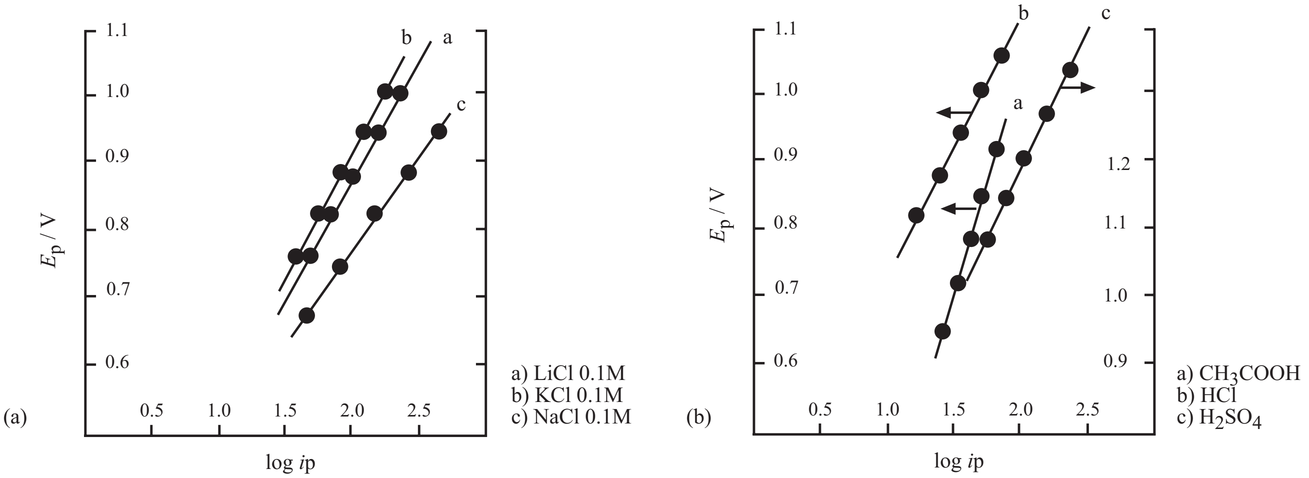

Fig. 11: The dependence of E_p on log i_p, for the cyclic voltammograms of α-methyldopa (4.73 x 10^{-3} M) at a carbon paste electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

A plot of peak separation (ΔE_p) vs. potential scan rate in all these supporting electrolytes is shown in fig.7. The value of peak separation increased by increasing potential scan rates. Table 2 shows the effect of potential scan rates on ΔE_p values of α-methyldopa. This tendency was found in all supporting electrolytes while a maximum response was seen in acetic acid which is in accordance with the Frsang & Tomcsanyi (1967) and Sun & Mottola (1991) work. Such a change reveals that α-methyldopa in acetic acid system behaves almost irreversibly on the basis of very large ΔE_p values.

The shape of cyclic voltammograms of α-methyldopa in all supporting electrolytes remained almost similar in terms of E_a and E_c on repeated scanning at 100 mV/s except in HCl and H_2SO_4 systems. Only a decrease in anodic and cathodic peak heights was noticed in successive cycles. However, a constant value was achieved up to the 4th to 5th cycle. This is exhibited in fig.8. The same response has been reported by Santos and Baldwin (1988) in case of mono/disaccharide at a carbon paste electrode. Since no pre or post peak appeared in the repeated cycling which is the qualitative test for a chemical adsorption of analyte as given by Reinmuth (1962), therefore, no adsorption effect either weak or strong was registered at the carbon paste electrode in these supporting electrolytes.

The peak potential E_p increased as the concentration of the supporting electrolytes decreased in all the supporting electrolytes. However, an increase in i_p was found in the region 1M to 0.1M concentration of the supporting electrolytes, while further decrease in the concentration of supporting electrolytes caused a linear decrease in the peak current comparative to the work described by Gardea-Tarresdey *et al* (1988) and Santos & Baldwin (1988).

The peak potential (E_p) and peak ($E_{p/2}$) of α-methyldopa showed a linear relation with potential scan rate (log υ) which is illustrated in fig. 9 and 10. Similarly, E_p, vs. log i_p relation showed a linear response as given in fig.11. Table 3 provides information regarding E_p shift per decade increase in the potential scan rate as published by Klingler & Kochi (1980).

Table 2

The values of ΔE_p and time taken for voltage scan during Epa-Epc values from the cyclic voltammograms of α-methyldopa [4.2 x 10^{-3} M] in various supporting electrolytes with different pH values at 25°C

Scan Rate	LiCL at pH = 6.2		NaCl at pH = 6.0	
mV/s	ΔEp / mV	Time / sec	ΔEp/mV	Time / sec
20	375 ± 10	91.98 ± 0.05	600 ± 10	84.38 ± 0.05
50	450 ± 10	36.75 ± 0.05	675 ± 10	35.8 ± 0.05
100	575 ± 10	18.38 ± 0.05	725 ± 10	18.25 ± 0.05
200	650 ± 10	9.02 ± 0.05	808 ± 10	9.06 ± 0.05
300	750 ± 10	6.04 ± 0.05	900 ± 10	5.96 ± 0.05
500	863 ± 10	3.68 ± 0.05	1013 ± 10	3.55 ± 0.05

Scan Rate	KCl at pH = 6.0		H_2SO_4 at pH = 1.4	
mV/s	ΔEp / mV	Time / sec	ΔEp/mV	Time / sec
20	550 ± 10	90.05 ± 0.05	370 ± 10	69.38 ± 0.05
50	638 ± 10	37.0 ± 0.05	408 ± 10	27.75 ± 0.05
100	738 ± 10	18.48 ± 0.05	463 ± 10	14.13 ± 0.05
200	850 ± 10	8.19 ± 0.05	563 ± 10	6.88 ± 0.05
300	913 ± 10	6.04 ± 0.05	600 ± 10	4.62 ± 0.05
500	1030 ± 10	3.55 ± 0.05	680 ± 10	2.78 ± 0.05

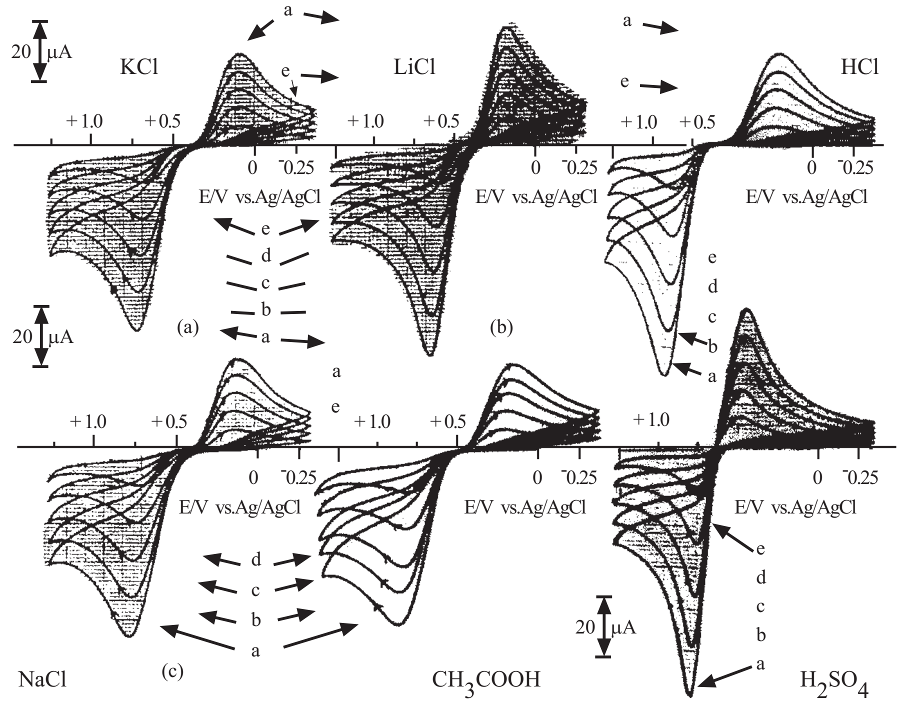

Fig. 12: The single-scan cyclic voltammograms of various concentrations of α-methyldopa (a = 4.73 x10^{-5} M, b=0.8a, c=0.6a, d=0.4a, and e=0.2a) at a carbon paste electrode with l00mV/s scan rate in various supporting electrolytes at 25°C.

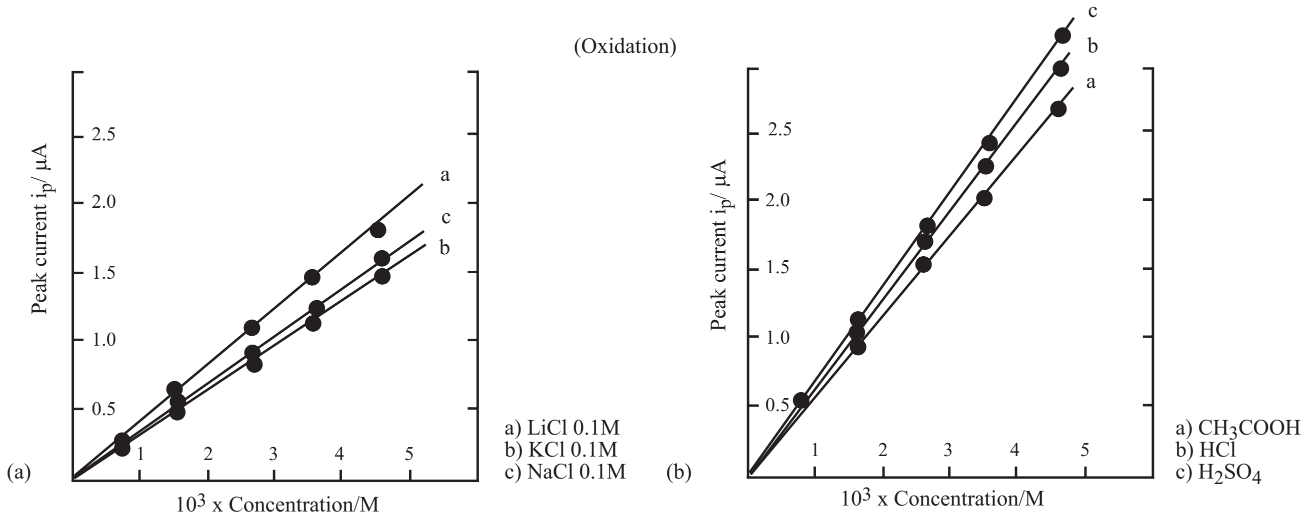

Fig. 13: Calibration curves obtained from the single-scan cyclic voltammograms of various concentrations of α-methyldopa (a=4.73 x 10^{-5} M, b=0.8a, c=0.6a, d=0.4a, and e=0.2a) at a carbon paste electrode with 100 mV/s scan rate in various supporting electrolytes at 25°C.

Table 3

The values of E_p shift per decade increase in scan rate for α-methyldopa in different supporting electrolytes with different scan rates at 25°C

Scan Rate	LiCL at pH = 6.2		NaCl at pH = 6.0	
mV/s	E_p / mV	E_p / mV shift ^{a}	E_p / mV	E_p / mV shift ^{a}
20	650 ± 10	138 ± 14.1	775 ± 10	113 ± 14.1
50	675 ± 10		800 ± 10	
200	788 ± 10	350 ± 14.1	888 ± 10	188 ± 14.1
500	1025 ± 10		988 ± 10	

Scan Rate	KCl at pH = 6.0		CH_3COOH at pH = 2.9	
mV/s	E_p / mV	E_p / mV shift ^{a}	E_p / mV	E_p / mV shift ^{a}
20	758 ± 10	142 ± 14.1	863 ± 10	137 ± 14.1
50	788 ± 10		863 ± 10	
200	900 ± 10	225 ± 14.1	1000 ± 10	300 ± 14.1
500	1013 ± 10		1163 ± 10	

Scan Rate	HCl at pH = 0.9		H_2SO_4 at pH = 0.9	
mV/s	E_p / mV	E_p / mV shift ^{a}	E_p / mV	E_p / mV shift ^{a}
20	813 ± 10	87 ± 14.1	750 ± 10	50 ± 14.1
50	825 ± 10		750 ± 10	
200	900 ± 10	175 ± 14.1	800 ± 10	108 ± 14.1
500	1000 ± 10		858 ± 10	

a = E_p shift per decade increase in scan rate.

In case of irreversible electron transfer reaction reported by Klingler & Kochi (1980), Nicholson & Shain (1964), the peak potential or half peak potential has been plotted against the potential scan rate with a slope enumerating the transfer coefficients. Beside this, E_p vs. log i_p relationship from its slope reported by Klingler & Kochi (1980) specified evaluation of αn_a and βn_b values as shown in tables 4-7. In the present study, the values of transfer coefficients αn_a and βn_b computed by Klingler's method are tabulated from the above mathematical relations and are consistent. The dependency of E_p and $E_{p/2}$ on log υ and E_p on log i_p encircles it in the domain of an irreversible electron transfer process. However, results from the diagnostic criteria for ECE mechanism and for quasi-reversible system are more

Table 4

The values of α na and β nb by different methods for α-methyldopa [4.2 x 10^{-3} M] in various supporting electrolyte at different pH and temperatures

pH	Temp.	α na Values			
	°C	$48/(E_p-E_{p/2})$	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
6.2 (LiCl)	25	0.38 ± 0.12	0.18 ± 0.01	0.27 ± 0.005	0.17 ± 0.005
6.0 (LiCl)	45	0.37 ± 0.27	0.16 ± 0.005	0.44 ± 0.01	0.20 ± 0.01
6.0 (NaCl)	25	0.28 ± 0.10	0.25 ± 0.01	0.37 ± 0.005	0.24 ± 0.01
6.0 (NaCl)	35	0.38 ± 0.10	0.31 ± 0.01	0.17 ± 0.005	0.61± 0.005
6.0 (KCl)	25	0.34 ± 0.11	0.23 ± 0.005	0.30 ± 0.01	0.20 ± 0.01
6.0 (KCl)	35	0.27 ± 0.08	0.11 ± 0.01	0.16 ± 0.01	0.70 ± 0.005

pH	Temp.	β nb Values			
	°C	$48/(E_p-E_{p/2})$	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
6.2 (LiCl)	25	0.38 ± 0.12	0.11 ± 0.01	0.32 ± 0.005	0.09 ± 0.01
6.0 (LiCl)	45	0.26 ± 0.07	0.23 ± 0.005	0.60 ± 0.01	0.20 ± 0.01
6.0 (NaCl)	25	0.27 ± 0.08	0.20 ± 0.01	0.32 ± 0.005	0.17 ± 0.005
6.0 (NaCl)	35	0.36 ± 0.12	0.10 ± 0.01	0.15 ± 0.01	0.07± 0.01
6.0 (KCl)	25	0.30 ± 0.11	0.17 ± 0.01	0.30 ± 0.01	0.13 ± 0.005
6.0 (KCl)	35	0.23 ± 0.07	0.07 ± 0.005	0.10 ± 0.005	0.05 ± 0.005

Table 5

The values of β na and β nb by different methods for α-methyldopa [4.2 x 10^{-3} M] in CH_3COOH as supporting electrolyte at different pH and temperatures

pH	Temp.	α na Values			
	°C	$48/(E_p-E_{p/2})$	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
2.9	25	0.27 ± 0.09	0.14 ± 0.02	0.23 ± 0.002	0.13 ± 0.002
3.5	25	0.19 ± 0.07	0.11 ± 0.01	0.33 ± 0.002	0.05 ± 0.01
4.0	25	0.15 ± 0.12	0.07 ± 0.01	0.13 ± 0.002	0.06 ± 0.01
2.9	45	0.24 ± 0.14	0.05 ± 0.003	0.10 ± 0.01	0.10± 0.01
3.4	45	0.10 ± 0.02	0.07 ± 0.002	0.07 ± 0.004	0.25 ± 0.01
3.9	45	0.17 ± 0.05	0.07 ± 0.01	0.08 ± 0.003	0.04 ± 0.003

pH	Temp.	β nb Values			
	°C	$48/(E_p-E_{p/2})$	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
2.9	25	0.23 ± 0.08	0.14 ± 0.02	0.36 ± 0.01	0.11 ± 0.002
3.5	25	0.14 ± 0.09	0.06 ± 0.003	0.13 ± 0.003	0.05 ± 0.01
4.0	25	0.17 ± 0.02	0.04 ± 0.01	0.08 ± 0.003	0.02 ± 0.002
2.9	45	0.15 ± 0.03	0.05 ± 0.004	0.07 ± 0.01	0.05± 0.004
3.4	45	0.12 ± 0.03	0.08 ± 0.01	0.40 ± 0.003	0.06 ± 0.01
3.9	45	0.09 ± 0.02	0.05 ± 0.002	0.09 ± 0.002	0.06 ± 0.003

acceptable. Any deviation from the reported diagnostic criteria may be due to the consequence of the selection of carbon paste electrode instead of using a conventional mercury test electrode at which these facts have been reported. For example, large variation in low values of transfer coefficients from theoretical calculations as well as from cv profiles in case of high scan rates and in acetic acid system are mainly due to this fact. Additionally, there may be the involvement of surface functional groups as discussed above reported by Engstrom & Strasser (1984), Blaedel & Jenkins (1974), Rivas & Pingarron Carrazon (1992) and Duca & Bejan (1991), which make the electron transfer process slow (making it an irreversible one).

The peak current i_{pa} and i_{pc} vs. concentration of α-methyldopa showed a linear response in all supporting electrolytes within the concentration range 4.2x10^{-3} to 8.4x10^{-6} M. Figs. 12, 13 show that the profiles of cyclic voltammograms of α-methyldopa having i_{pa} values were found to be proportional to its concentration. This represents

Table 6

The values of α na and β nb by different methods for α-methyldopa [4.2 x 10^{-3} M] in HCl as supporting electrolyte at different pH and temperatures

pH	Temp.	α na Values			
	^{o}C	$48/(E_p-E_{p/2})$	E_p vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
0.9	25	0.32 ± 0.14	0.19 ± 0.01	0.37 ± 0.005	0.16 ± 0.005
1.8	25	0.38 ± 0.12	0.30 ± 0.01	0.59 ± 0.01	0.31 ± 0.005
2.7	25	0.26 ± 0.09	0.20 ± 0.01	0.43 ± 0.01	0.19 ± 0.01
0.9	35	0.45 ± 0.09	0.26 ± 0.01	0.35 ± 0.01	0.35 ± 0.01
1.7	35	0.42 ± 0.06	0.26 ± 0.01	0.31 ± 0.005	0.26 ± 0.01
2.6	35	0.37 ± 0.10	0.19 ± 0.01	0.31 ± 0.005	0.15 ± 0.005
0.8	45	0.28 ± 0.09	0.17 ± 0.01	0.29 ± 0.01	0.18 ± 0.005
1.7	45	0.40 ± 0.15	0.10 ± 0.01	0.14 ± 0.01	0.14 ± 0.01
2.6	45	0.28 ± 0.02	0.13 ± 0.01	0.32 ± 0.01	0.19 ± 0.005

pH	Temp.	β nb Values			
	^{o}C	$48/(E_p-E_{p/2})$	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
0.90	25	0.47 ± 0.17	0.22 ± 0.005	0.30 ± 0.01	0.14 ± 0.01
1.8	25	0.47 ± 0.17	0.23 ± 0.005	0.33 ± 0.01	0.19 ± 0.01
2.7	25	0.23 ± 0.09	0.13 ± 0.01	0.27 ± 0.005	0.16 ± 0.01
0.9	35	0.58 ± 0.07	0.25 ± 0.01	0.33 ± 0.005	0.23 ± 0.005
1.7	35	0.38 ± 0.18	0.21 ± 0.005	0.23 ± 0.005	0.16 ± 0.005
2.6	35	0.30 ± 0.08	0.15 ± 0.01	0.2 ± 0.01	0.12 ± 0.01
0.8	45	0.27 ± 0.08	0.14 ± 0.005	0.23 ± 0.005	0.10 ± 0.005
1.7	45	0.15 ± 0.05	0.07 ± 0.01	0.14 ± 0.005	0.05 ± 0.01
2.6	45	0.17 ± 0.04	0.09 ± 0.01	0.15 ± 0.01	0.06 ± 0.005

that the diffusion of α-methyldopa is the rate limiting step in the electron transfer reaction as explained by Bard & Faulkner (1980), Ruiz & Pingarron Carrazon (1992) and Gonzalea *et al* (1990).

Young *et al* (1980) reported CV of α-methyldopa in perchloric acid and McIlvaine buffers as a two electrons two protons transfer process. They proved α-methyldopa as an ECC mechanism by considering it an electrochemical oxidation, a chemical cyclization, and a chemical redox transfer process similar to the reported work by Gardea-Tarresdey *et al* (1988) and Duca & Bejan (1991). The values of various parameters they reported were like αn_a = 1.17, $\boldsymbol{D}=0.39\times10^{-5}cm^2/s$, $n_a=2$, $\alpha=0.59$ with $k_o=0.018$ to 0.19 sec^{-1} at 25°C (from $I_{t1/2}/C$ vs. t relation and $n_{app.}/n_o$ curves). In the present work, α values were between 0.6 to 0.4. That shows n ≅1.0 ±0.1 with $\alpha=0.5\pm0.05$ provided $n_1=n_2=1$ in ECC mechanism. The value of k_o in the present work is within the reported range (0.13 s^{-1} at 50mV/s).

CONCLUSION

Electrochemical study (cyclic voltammetry) of α-methyldopa was performed at an unmodified carbon paste test electrode vs. Ag │AgCl reference electrode. Base-lines obtained at this electrode were found to be horizontally straight with an extended anodic potential range. The quantitative and qualitative characteristics of α-methyldopa in various supporting electrolytes were determined such as α, β, and k_o [from $I_p^a(II)/I_p^c(I)$ values]. For qualitative characteristics, α-methyldopa showed an ECC mechanism in terms of unperturbed electron transfer reaction (placing it in DPI zone) at carbon paste electrode. The values of transfer coefficients, α and β were determined. The larger

Table 7

The values of α na and β nb by different methods for α-methyldopa [4.2 x 10^{-6}M] in H_2SO_4 as supporting electrolyte at different pH and temperatures

pH	Temp.	α na Values			
	°C	48/(E_p-$E_{p/2}$)	E_p vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
0.9	25	0.43 ± 0.12	0.25 ± 0.01	0.36 ± 0.01	0.24 ± 0.01
1.4	25	0.41 ± 0.10	0.27 ± 0.005	0.43 ± 0.01	0.30 ± 0.01
2.0	25	0.33 ± 0.09	0.16 ± 0.01	0.23 ± 0.005	0.18 ± 0.005
0.9	35	0.44 ± 0.25	0.44 ± 0.005	0.78 ± 0.01	0.39 ± 0.01
1.6	35	0.40 ± 0.08	0.31 ± 0.005	0.44 ± 0.005	0.33 ± 0.01
2.4	35	0.39 ± 0.10	0.18 ± 0.01	0.29 ± 0.01	0.18 ± 0.005
0.8	45	0.31 ± 0.07	0.20 ± 0.01	0.32 ± 0.01	0.23 ± 0.01
1.6	45	0.35 ± 0.13	0.12 ± 0.01	0.21 ± 0.005	0.12 ± 0.01
2.4	45	0.33 ± 0.22	0.14 ± 0.01	0.35 ± 0.005	0.22 ± 0.01

pH	Temp.	β nb Values			
	°C	48/(E_p-$E_{p/2}$)	Ep vs. log v	$E_{p/2}$ vs. log v	E_p vs. log i_p
0.9	25	0.56 ± 0.08	0.37 ± 0.005	0.59 ± 0.01	0.33 ± 0.005
1.4	25	0.58 ± 0.21	0.27 ± 0.005	0.43 ± 0.01	0.21 ± 0.005
2.0	25	0.35 ± 0.11	0.20 ± 0.01	0.33 ± 0.005	0.30 ± 0.01
0.9	35	0.45 ± 0.1	0.60 ± 0.005	0.75 ± 0.01	0.54 ± 0.005
1.6	35	0.43 ± 0.26	0.21 ± 0.005	0.74 ± 0.01	0.20 ± 0.01
2.4	35	0.31 ± 0.11	0.17 ± 0.01	0.60 ± 0.01	0.14 ± 0.01
0.8	45	0.32 ± 0.1	0.23 ± 0.005	0.23 ± 0.005	0.20 ± 0.005
1.6	45	0.29 ± 0.05	0.14 ± 0.01	0.15 ± 0.01	0.10 ± 0.005
2.4	45	0.20 ± 0.06	0.10 ± 0.01	0.17 ± 0.01	0.11 ± 0.005

ΔE_p values were obtained due to the use of unmodified carbon paste electrode hence decreased the rate of electron transfer at the surface of the test electrode. The first order rate constant values (k_o) were generally within 0.10 to 7.78 ± $0.1x10^{-3}$ s^{-1} at different scan rates (50-500mV/s). Adsorption of analyte was also determined at CPE using repeated scan method.

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