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Electrochemical Behaviour of Quinaldic Acid at Dropping Mercury Electrode and Hanging Mercury Drop Electrode

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The polarographic and cyclic voltammetric studies of quinaldic acid are made at dropping mercury electrode and hanging mercury drop electrode in buffer solutions of various pH values. The polarographic half wave potentials and cyclic voltammetric peak potentials are shifted to more negative values, whilst limiting currents and peak currents are found to decrease with the increase in the pH of the buffer solution. The polarographic wave and cyclic voltammetric peaks are found to be irreversible and diffusion controlled. The values of kinetic parameters are computed using Meites-Israel method.

Key Words: Electrochemical behaviour, Quinaldic acid, Hanging mercury drop electrode.

INTRODUCTION

Electrochemical reduction of carboxylic acids in general and pyridine carboxylic acids in particular at dropping mercury electrode were a subject of interest for several researchers[1-5]. Alen *et al.*[6] reported the limiting current and half-wave potentials of 2-pyrazine carboxylic acid during structural elucidication of studies of Leocovarin[6]. The detailed polarographic behaviour of pyridine carboxylic acids were reported from this laboratory[7,8]. 2-Quinoline carboxylic acid and their various derivates are extensively used in the identification and estimation of several transition metals and metal chelates.

The present work involves the study of electrochemical reduction of the quinaldic acid at dme, hmde and macro mercury pool cathode in order to know the extent of reversibility, the kinetics and products of electrode reaction. A suitable mechanism is envisaged for electrochemical reduction process.

EXPERIMENTAL

Quinaldic acid was obtained from E. Merck Chemical Company Ltd., Germany. All the other chemicals used were of A.R. grade. The buffer solutions of pH < 3 were obtained by mixing variuos proportions of hydrochloric acid and sodium acetate. The buffer solutions of pH > 3 were prepared from Britton Robinson[9] modified universal buffer solutions. A constant ionic strength was maintained at 0.6 M by adding the required amount of potassium chloride Triton X-100 (5×10^{-4}) was used as maximum suppressor. The pH values of the solutions were checked with a pH meter supplied by Digisum Electronics, Hyderabad. The polargrams were recorded with a *d.c.* recorder polarograph, model CL 25 supplied by Elico Pvt. Ltd. Hyderabad. The solutions were deaerated with nitrogen gas. The capillary used, delivered 1.425 mg of mercury per second at a mercury column height of 55 cms. The drop time was 4.2 seconds (in distilled water, open circuit). The SCE was used as refrence electrode.

Cyclic voltammetric experiments were carried out with Princeton Applied Research Company model 370 electrochemistry system. The cell used was 377A system consisting of E 410 hanging mercury drop electrode, a platinum wire as counter electrode and SCE as reference electrode.

Macroscale electrolysis at the mercury pool cathode was carried out at a constant potentials using potentioscan wenking model POS 73 supplied by Gerhard Bank Elektronik, Germany.

RESULTS AND DISCUSSION

Polarography: Quinaldic acid (2-quinoline carboxylic acid) is found to give a single well defined cathodic wave in the buffer range of pH values 1 to 5.29 and in the buffer range of pH 6.50 to 9 two cathodic waves are observed. The polarograms of 1 mM quinaldic acid are shown in Fig. 1. The limiting current is increased to a maximum value of 9.5 μA and therafter a gradual decease is observed. The general nature of the plots of i_d *vs.* pH shows that the electrode reaction is governed by the rate of the proton transfer[10]. The different waves observed are assigned to the presence of various[11] species H_3A^+, H_2A and HA^-.

The half wave potential ($E_{½}$) values are found to shift to more negative side with the increase in the pH of the solution. The plots of $E_{½}$ *vs.* pH indicate two linear portions interacting at a pH of 5.10. This is ascribed to the dissociation constant of the acid and is in agreement with the literature value[12].

The plots of limiting current *vs.* $h^{½}$ (h is the corrected height of mercury column) studied at pH values 1.20, 2.52, 3.50 and 8.48 are straight lines passing through the origin indicating diffusion controlled nature of the wave.

The effect of concentration on the diffusion current of quinaldic acid has been studie in the range of 0.25 to 1.25 mM at pH values of 1.20, 2.52 and 3.50. The i_d *vs.* concentration plots are linear, passing through the origin which confirms diffusion controlled nature of the wave.

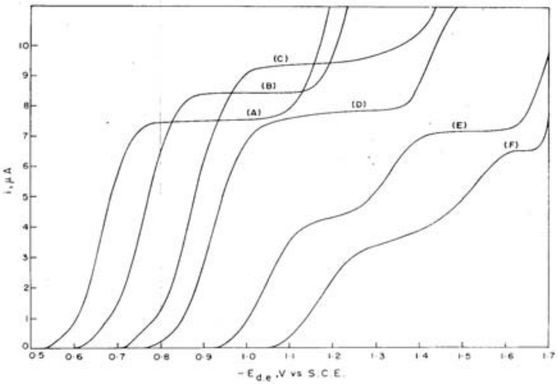

Fig. 1. Polarograms of 1 mM quinaldic acid at pH values of (A) 1.20, (B) 2.52, (C) 3.50, (D) 5.29, (E) 6.50 and (F) 8.48

Electrode process: The plots of $-E_{de}$ *vs.* log i/i_d-i at various pH values are found to be linear, but their slope values (given S_1 in Table-1) are more than expected for a reversible wave. This indicates the electrode reaction may be irreversible. The value of transfer coefficient, α approximated from the value of αn_a given in Table-1 is found to be ≤ 0.5 supporting the irreversible nature of the wave. This has also been verified by Tomes criteria[13].

Kinetic parameter: The kinetic parameters for the electrode reaction have been obtained by using the method of Meites-Israel[14]. The values obtained for the heterogeneous formal rate constant, $k^0_{f,h}$ and activation free energy change, ΔG at various pH values are given in Table-1. The value of diffusion coefficient for the calculation of $k^0_{f,h}$ has been obtained by reported method[15]. The value of $k^0_{f,h}$ is found to decerase with the increase in the pH of the buffer solution, whilst the ΔG value is found to increase. This shows the electrode reaction tends to become more and more irreversible with the increase in the pH of the buffer solution. This trend is also observed with decrease in the αn_a values.

TABLE-1
KINETIC PARAMETERS OF QUINALDIC ACID (1 mM) IN DIFFERENT BUFFER SOLUTIONS AT 30ºC

pH	I, id/C.m.$^{2/3}$t$^{1/6}$ μA.mM^{-1}mg$^{-2/3}$t$^{-1/6}$		$-E_{1/2}$ (V)	$\frac{0.06015}{\alpha n_a}$ (S_1)	αn_a	Z_H^+	Apparent n_a α = 0.5	$k^0_{f,h}$ cm s^{-1}	ΔG Kcal mol^{-1}
1.20	4.75		0.70	0.086	0.69	0.64	1.39	5.07×10^{-9}	18.21
2.52	5.30		0.78	0.095	0.63	0.58	1.26	2.34×10^{-9}	19.01
3.50	5.86		0.85	0.105	0.57	0.52	1.14	1.95×10^{-9}	19.18
5.29	4.91		0.94	0.118	0.51	0.64	1.02	1.31×10^{-9}	19.36
6.50	2.77	(F)	1.06	0.135	0.45	0.56	0.89	9.44×10^{-10}	19.56
	2.75	(S)	1.33	0.140	0.43	0.54	0.86	1.83×10^{-11}	21.93
8.48	2.38	(F)	1.18	0.148	0.41	0.51	0.81	4.97×10^{-10}	19.94
		(S)	1.47	0.149	0.40	0.50	0.81	6.21×10^{-12}	22.58

Cyclic voltammetry: Cyclic voltammetric experiments of quinaldic acid (1 mM) are carried out at hanging mercury drop electrode (hmde).

The cyclic voltammograms as shown in Fig. 2 are recorded in the buffer solutions of various pH values *viz.*, 1.12, 2.52 and 4.41 at the scan rates of 10, 20, 50 and 100 mV/s. In all these buffers well defined single and broad cathodic peak is observed. No anodic peak is observed in the reverse scan. The cathodic peak potential (Ep_c) shifts to more negative value with increase in pH of the buffer solutions and scan rate as shown in Table-2. This indicates the departure of the system from equilibrium. The peak current increase with increases in scan rate. The plots of ip_c *vs* $\upsilon^{½}$ (scan rate) are straight lines passing through the origin, confirming the diffusion controlled nature of cyclic voltammogram. Contrary to the behaviour of a reversible system quinaldic acid is characteristic for its irreversible nature, with dependence of Ep_c on sweep rate,[16,17] besides $\Delta E_p \neq 60/n$ mV and $ip_c / ip_a \neq 1$. Thus, the observance of single cathodic peak (*i.e.* absence of anodic peak in the reverse scan) and the shift in peak potential with scan rate as well as pH, clearly rules out the possibility of a fast electron transfer which is characteristic of a reversible behaviour, thus confirming the electrode reaction to be irreversible.

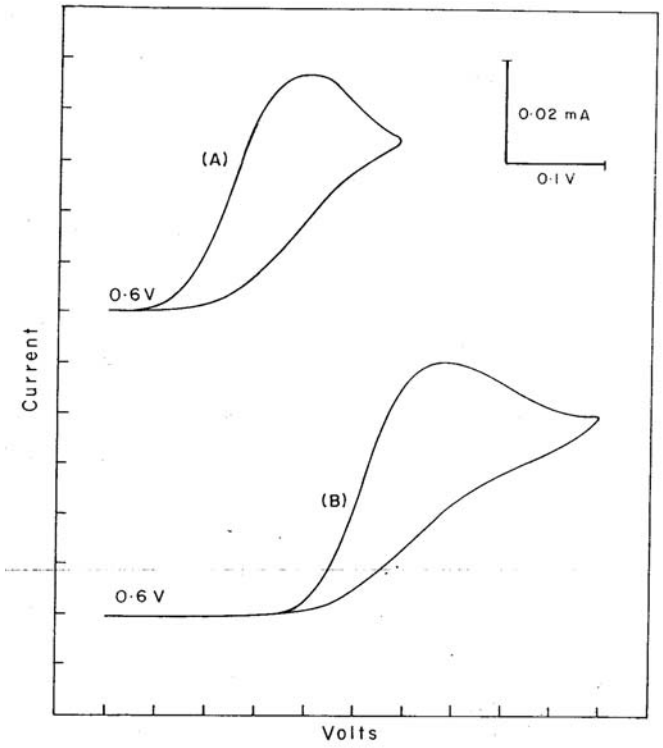

Fig. 2. Cyclic voltammograms of 1 mM quinaldic acid at the pH values (A) 2.52 (B) 4.41 with the scan rate 50 mV/s.

TABLE-2
EFFECT OF SWEEP RATE ON THE PEAK POTENTIAL AND PEAK CURRENT OF 1 m OF QUINALDIC ACID

Sweep rate (υ) mV/s	Cathodic peak potential ($-Ep_c$) V	Cathodic peak current (${}^{i}p_c$) × 10^2 mA	${}^{i}p_c/\upsilon^{1/2}$
	pH = 1.10		
10	0.750	3.0	0.95
20	0.761	3.6	0.92
50	0.768	6.5	0.85
100	0.775	9.2	0.92
	pH = 2.52		
10	0.801	2.4	0.76
20	0.810	3.0	0.67
50	0.818	4.0	0.56
100	0.826	5.0	0.50
	pH = 4.41		
10	0.912	2.7	0.85
20	0.921	3.6	0.80
50	0.934	5.0	0.71
100	0.940	7.0	0.68

Controlled potential electrolysis: The controlled potential electrolysis of quinaldic acid has been carried out at mercury pool cathode using potentiostatic technique in buffer solutions of various pH values. The potential corresponding to the plateau of the polarogram is applied to the working electrode. The electrochemical reduction is followed by means of polarography at regular intervals of time. The products of electrolysis are identified by infrared spectra. The carbonyl absorption is found at 1720 cm^{-1}, while the hydroxyl group absorption is observed at 3200 cm^{-1}. The product is found to be mainly an aldehyde in strongly acidic media and alcohol in weakly acidic media. The isolation of aldehyde in the strongly acidic media is explained on the basis of protection of an initially formed aldehyde as a hydrate or a non-reducible derivative[4].

Mechanism of electrochemical reaction: The polarographic and cyclic voltammetric studies indicate the electrochemical process to be irreversible. The analysis of polarographic data shows the involvement of single electron and proton in the rate determining step. Controlled potential electrolysis indicates the consumption of 2e for aldehyde and 4e for alcohol per molecule in strong and weak acid buffers respectively.

A mechanism for the reduction of pyridine carboxylic acids at rotating disc electrode is given by Bhatti and Brown[18]. They described that the first charge transfer step is reversible and that the rate determining step is either a subsequent electrochemical charge transfer or a bimolecular chemical step. On the basis of the kinetic data they proposed the mechanism as,

$$\mathrm{RCOOH} \rightleftharpoons \mathrm{R\ COO^{-}} + \mathrm{H^{+}}$$

$$\mathrm{RCOOH} + \mathrm{H^{+}} + \mathrm{e^{-}} \rightleftharpoons \mathrm{R\dot{C}(OH)_2\ ads.}$$

$$\mathrm{R\dot{C}(OH)_2} + \mathrm{e^{-}} \xrightarrow{\text{slow}} \mathrm{\bar{C}R(OH)_2} \xrightarrow[\mathrm{H^{+}}]{\text{fast}} \mathrm{RCH(OH)_2}$$

The further step for the reaction of aldehyde to alcohol would involve two electrons and two protons.

$$\mathrm{RCHO} + 2\mathrm{H^{+}} + 2\mathrm{e^{-}} \longrightarrow \mathrm{RCH_2OH}$$

Our results are in agreement with this mechanism.

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