POLAROGRAPHIC REDUCTION OF CINCHOMERONIC ACID

P. Yadagiri Swamy, G. Veerabhadram and K.S. Sastry

Department of Chemistry, University College of Science, Osmania University, Hyderabad - 500 007

The electrochemical reduction of cinchomeronic acid at dme has been studied in the buffer solution of various pH values. The half-wave potential is found to shift to more negative value, whilst limiting current is found to decrease with the increase in the pH of the buffer solution. The reduction wave is diffusion controlled and irreversible. The values of kinetic parameters for the electrode reaction are computed using Meites-Israel method.

The electrochemical reduction of pyridine carboxylic acids was a subject of many investigations[1-4]. Tissier and Agoutin[5] studied the variations of diffusion current and half-wave potential with pH and deduced the values for the three equilibrium constants of cinchomeronic acid. Campanella and Chicchierini[6] made polarographic studies of dipicolinic acid and interpreted the data on the basis of equilibria among the six species, in which the acid could exist in aqueous solution. Brown et al[7] investigated the electrochemical reduction of picolinic, dipicolinic acids and their aldehydes at a mercury pool cathode to hydroxy-methyl pyridines. Recently, the general polarographic behaviour and reduction mechanism of dipicolinic acid was reported from this laboratory[8].

The present investigation is devoted to the study of polarographic behaviour of cinchomeronic acid.

EXPERIMENTAL

Cinchomeronic acid (3,4-pyridine dicarboxylic acid) was obtained from SIGMA Chemical Company, U.S.A. All the chemicals used were of A.R grade.

The buffer solutions of pH<3 were obtained by mixing in various proportions of hydrochloric acid and sodium acetate. The buffer solutions of pH<3 were prepared from Britton - Robinson[9] modified universal buffer solutions. The ionic strength was maintained at 0.6 M by adding the required amount of potassium chloride. The pH values of the solutions were checked with a pH meter, LI-12 model of Elico make. Cinchomeronic acid concentration in polarographic solution was 1 mM. Triton-X-100 (5 $x10^{-4}$ %) was used as a maximum supressor.

A manual polarograph type CL02 A, and polyflex galvanometer type PL 50, (Toshniwal) were used for measurements.

The solution was deaerated with nitrogen gas. A capillary delivered 2.835 mg of mercury per second at a corrected mercury column height of 17.08 cms. The drop time was 3.8 seconds (in distilled water, open circuit). SCE was used as reference electrode. The temperature of study was 30 ± 0.1°C.

REULTS AND DISCUSSION

Cinchomeronic acid is found to give a single well-defined cathodic wave in the pH range 1 to 5 and again above pH of 9. However, two waves are observed in the pH range 5 to 9. The polarograms at various pH values are shown in Figure 1.

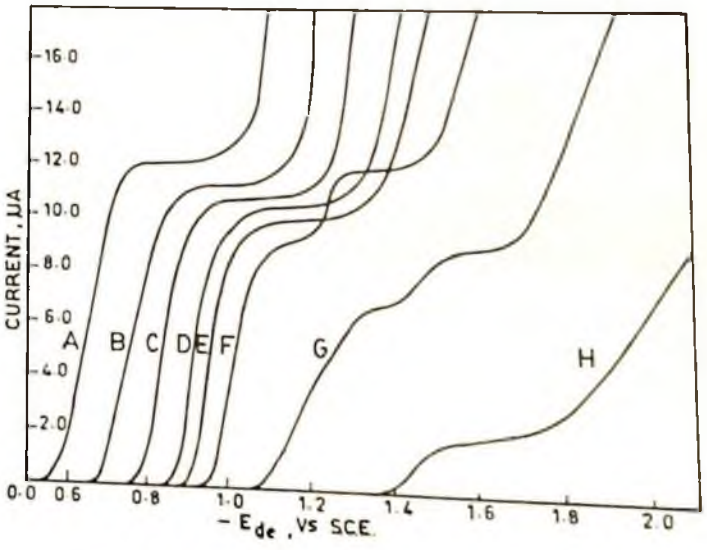


Fig. 1 Polarograms of 1 mM of Cinchomeronic Acid at pH values of (A) 1.34 (B) 2.32 (C) 3.01 (D) 4.26 (E) 4.92 (F) 5.39 (G) 8.02 (H) 9.24

The total limiting current is found to decrease with the increase in pH of the buffer solution. The decrease is small upto a pH 8 and thereafter limiting current decreases rapidly.

Similar observation was made by Tissier and Agoutin[5]. Multiple waves may be due to the presence

TABLE 1

KINETIC PARAMETERS OF 1 mM OF CINCHOMERONIC ACID IN DIFFERENT BUFFER SOLUTION AT 30°C

pH	I Diffusion current constant	$-E_{1/2}$ volts	$-E^{\circ}_{1/2}$ volts	$\frac{0.06015}{\alpha n_a}$ (S_1)	αn_a	$k^{\circ}_{f,h}$ cm.sec
1.34	4.79	0.647	0.626	0.0519	1.16	1.56×10^{-11}
2.32	4.44	0.765	0.743	0.0562	1.07	4.93×10^{-13}
3.01	4.24	0.811	0.791	0.0578	1.04	1.43×10^{-13}
4.26	4.14	0.919	0.901	0.0654	0.92	4.46×10^{-14}
5.39 a)	3.52	1.021	1.001	0.0661	0.91	1.70×10^{-15}
b)	1.05	1.240	1.220	0.0633	0.95	1.72×10^{-19}
8.02 a)	2.75	1.180	1.160	0.0725	0.83	1.12×10^{-16}
b)	0.80	1.480	1.460	0.0676	0.89	5.18×10^{-22}
9.24	0.75	1.420	1.400	0.0835	0.72	7.87×10^{-18}

a) First wave b) Second wave

$\Delta E_{1/2}$ is 0.057 mV/pH unit in the pH range 1-2.7
0.088 " " 2.7-9.5

of different species, viz H_3A^+, H_2A and HA^-, these different species giving different waves.

The $E_{1/2}$ shifts to more negative value with the increase in the pH of the medium indicating participation of protons in the rate determining step. The plot of $E_{1/2}$ vs pH consists of two linear portions intersecting at pH of 2.60 with slopes of 0.057 V/pH in the range of pH 1-2.6 and 0.088 V/pH in the pH range of 2.6 to 10.

The value 2.60 observed as intersecting point in the $E_{1/2}$ - pH plots can be assigned to the pK value of the cinchomeronic acid[5].

The plots of limiting current vs $\sqrt{h}$ are straight lines passing through the origin at each of the pH values of 1.34, 2.57, 4.26 and 8.02 indicating diffusion controlled nature of reduction in every case.

The effect of concentration on the diffusion current of both the wave within the range of 0.2 to 1 mM has been studied at pH values of 1.09, 2.32, 4.26 and 8.52 and found to be linear and passing through the origin.

Electrode Reaction

The plots of $-E_{d.e.}$ vs log $[i/(i_{\alpha}-i)]$ at various pH values are found to be linear. But their slopes (S_1 in Table 1) indicates irreversible nature of the reduction.

The kinetic parameters for the electrode reaction have been obtained by using the methods of Meites and Israel[11]. The values obtained for the $k^{\circ}_{f,h}$ (heterogeneous formal rate constant) at various pH values are tabulated in Table 1. The value of the diffusion coefficient for the calculation of $k^{\circ}_{f,h}$ has been obtained using the Stokes Einstein relation[12]. The value of $k^{\circ}_{f,h}$ is found to decrease with increase in the pH of the solution. This trend shows that the electrode reaction tends to become more and more irreversible with increasing pH. This trend is also observed with the decrease in αn_a values.

The mechanism of the electrochemical reduction process has been evaluated from polarographic and controlled potential electrolysis data. The controlled potential electrolysis of cinchomeronic acid conducted in this laboratory has shown the main product to be an aldehyde (4e process) in acidic media of pH<4 and an alcohol (8e process) in acidic media pH>4.

A mechanism for the reduction of pyridine carboxylic acid at rotating disc electrode is given by Bhatti and Brown[15]. They described that the first charge transfer step as irreversible and that the rate-determining step is either a subsequent electrochemical charge transfer or a bimolecular chemical step. Our results are in agreement with this mechanism.

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