Electrochemical Behaviour of Picolinic Acid at dme

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The electrochemical reduction of picolinic acid has been studied in the 1:1 aquo-organic mixtures of various organic solvents of methanol, ethanol, n-propanol, dioxane, dimethyl-formamide, dimethylsulfoxide and ethyleneglycol in the buffer solutions of pH values of 1.15 and 3.05. The limiting current is found to decrease whilst half-wave potential is found to shift to more negative value in the presence of organic solvent. Similar result is observed with increase in the percentage of ethanol also. The limiting current is diffusion controlled and the reduction process is irreversible. The kinetic parameters have been calculated using Meites and Israel method.

The polarographic behaviour of isonicotinic acid and picolinic acid was studied widely(1-4). Tompkins and Schmidt(1) studied the effect of pH on the polarographic wave of picolinic acid. Based on varitation of i_d with pH, Jellinek(2) discussed the mechanism in terms of recombination taking place at the electrode electrolyte interface. Volke and Volkova(3) discussed the polarographic wave heights and half-wave potentials of these acids in terms of the equilibria of the pyridine-pyridinium and carboxylic acid-carboxylate base pairs. Lund showed(4) that the major product of the reduction of isonicotinic acid at controlled potential in acid aqueous buffer solution is the isonicotinic aldehyde. Brown et al(5) investigated the reduction of picolinic and dipicolinic acids and their aldehydes at a mercury-pool cathode to hydroxy methylpyridines.

In the present work the polarographic study of picolinic acid has been conducted in various aquo-organic mixtures to understand the effect of medium on the diffusion current, half-wave potential and kinetics.

EXPERIMENTAL

Picolinic acid was obtained from Koch-light Laboratories, England. All the chemicals used were of AR grade. The organic solvents were used after necessary purifications (6-8). The concentration of picolinic acid was 1 mM. The buffer solution of pH 1.15 was obtained by mixing hydrochloric acid and sodium acetate. The buffer solution of pH 3.05 was obtained from Britton-Robinson (9) modified universal buffer solutions. Potassium chloride was used as a supporting electrolyte. The pH value of the solutions were checked with a pH meter. Triton X - 100 (5×10^{-4} %) was used as a maximum suppressor.

The polarograph was a manual polarograph type CL02 A, and polyflex galvanometer type PL 50, supplied by Toshniwal Instruments, Bombay. The pH meter was a digital model DL-707, supplied by Digisun Electronics, Hyderabad. The viscosity of the solutions was measured with 'Ostwald's viscometer' and the the values thus obtained are comperable with reported values.

The dissolved oxygen from the solution was flushed out by passing purified nitrogen gas before each polarogram was taken. The capillary delivered 2.835 mg of mercury per second at a corrected mercury column height of 17.08 cms. The droptime was 3.8 seconds (in distilled water,open circuit). The potentials were measured against a SCE.

The measurements were made at a constant temperature of 30 ± 0.1°C maintained with a thermostat.

RESULTS AND DISCUSSION

The polarographic behaviour of 1 mM of picolinic acid in the presence of 1:1 aquo-organic mixtures of various organic solvents like methanol, ethanol, n-propanol, dioxane, dimethylformamide, dimethylsulfoxide and ethyleneglycol has been studied in the buffered (at pH values of 1.15 and 3.05) solutions. In all these cases, a single well defined cathodic wave is obtained. The polarograms of picolinic acid in the presence of various organic solvents at pH 1.15 are shown in Figure 1.

There is a marked decrease in the value of diffusion current with the addition of the organic solvent and the extent of decrease depends on the nature of the organic solvent. This decrease in the diffusion current may be attributed to the increase in the viscocity of the solution. The $i_d\eta^{1/2}$ values are given in Table 1.

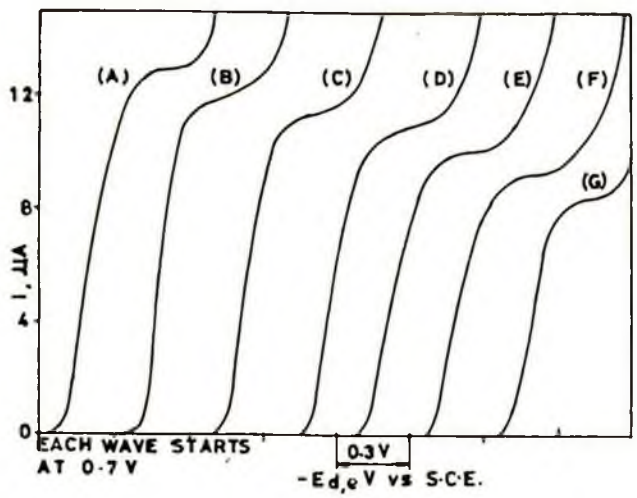


Fig. 1 polarograms of 1 mM of picolinic acid at a pH of 1.15 in 1:1 aquo-organic mixtures of various organic solvents (A) Methanol, (B) Dioxane, (C) Ethanol, (D) Dimethylformamide, (E) n-Propanol, (F) Dimethylsulfoxide, (G) Ethyleneglycol

The half-wave potential is shifted to more negative values in the presence of organic solvents and are shown in Table 1.

The diffusion controlled nature of the polarographic wave is evident from the linearity of i_d vs $h^{1/2}$ plots.

The conventional log plots are straight lines, but their slopes are more than the theoretically expected values of a reversible wave. This indicates the irreversible nature of the electrodic reaction.

The $k^\circ_{f,h}$ (formal heterogeneous rate constant) values are calculated using the method of Meites and Israel(10) and are shown in Table 1. The values of $k^\circ_{f,h}$ are found to decrease in the presence of organic solvents. The $k^\circ_{f,h}$ value decrease with the increase in the chain length of alcohols. The diffusion coefficient values are calculated from the relation:

$$\eta_{aq}^{1/2} / \eta_{org}^{1/2} = D_{org}^{1/2} / D_{aq}^{1/2} \qquad \ldots(1)$$

Where η = Viscocity of the solution
D = diffusion coefficient.

The deduced 'αn_a' (α = transfer coefficient, n_a = no. of electrons involved in rate determining step) values are shown in Table 1 which are comparable to the values deduced in the absence of organic solvents. This shows that the mechanism of electrochemical reaction is similar even in the presence of organic solvents although a marked shift in diffusion current and $E_{1/2}$ is observed.

The effect of changing of concentration of ethanol on the polarographic reduction of picolinic aci has been studied at pH 3.05. Various percentages of ethanol with water have been used for this purpose. The limiting current is found to decrease with increase in the alcohol content of the medium as shown in figure 2. The magnitude of the decrease in diffusion current depends on the percentage of ethanol added without altering the actual process.

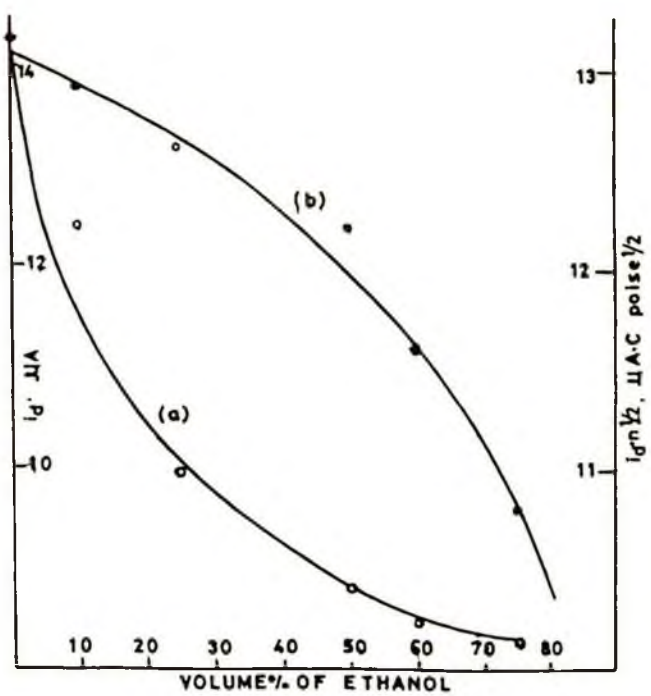


Fig. 2 Plots of (a) and (b) n vs volume percentage of for the polarographic reduction of picolinic aci pH of 3.05.

The decrease in the diffusion current may be attributed to the decrease in effective diffusion coefficient. Decrease in the value of the diffusion coefficient may result either from the increase in the viscocity of the solution or the change in the size of the solvated species(11).

TABLE 1

EFFECT OF VARIOUS AQUO-ORGANIC MIXTURES (1:1) ON THE POLAROGRAPHIC WAVE OF 1 mM OF PICOLINICE ACID

Solvent	i_d μA	$-E_{1/2}$ V	$i_d \eta^{1/2}$ μA.C.poise$^{1/2}$	r. °A	D x 10^6 cm^2 sec^{-1}	αn_a	$k^\circ_{f,h}$ x 10^{11} cm. sec^{-1}
			pH = 1.15				
Water	15.03	0.880	13.45	1.31	23.02	0.701	7.47
Methanol	12.73	0.882	14.74	1.41	14.21	0.699	5.28
Ethanol	11.23	0.885	15.60	1.25	9.92	0.691	4.70
n - propanol	9.99	0.895	14.61	1.43	8.93	0.683	4.16
Dioxane	11.98	0.875	15.66	1.24	11.15	0.699	5.35
DMF	10.61	1.005	15.08	1.34	9.43	0.675	0.34
DMSO	9.11	0.890	14.69	1.41	7.32	0.683	4.31
Ethylene-glycol	8.49	0.878	14.08	1.54	6.92	0.691	4.73
			pH = 3.05				
Water	14.32	1.040	12.81	1.44	17.26	0.572	5.67
Methanol	10.40	1.042	12.04	2.10	9.42	0.567	3.40
Ethanol	8.79	1.049	12.21	2.04	6.73	0.557	3.27
n - propanol	7.72	1.065	11.29	2.38	5.19	0.551	2.40
Dioxane	9.43	1.035	12.32	2.00	7.75	0.562	4.04
DMF	8.36	1.130	11.88	2.15	6.09	0.547	0.78
DMSO	6.96	1.080	11.23	2.41	4.22	0.555	1.34
Ethylene-glycol	6.43	1.038	10.67	2.67	3.60	0.558	3.02

Since in different cases these two effects may tend either to reinforce or compensate each other, a quantitative interpretation of the separate influence of each may be difficult.

The plots of $i_d\eta^{1/2}$ vs ethanol concentration (percentage) are shown in figure 2. They show a decrease in the current with the increase in the ethanol content of the medium. The decrease in the limiting current may be ascribed to the decrease in the effective diffusion coefficient. The increase in the volume of the reducible species is most probably due to the higher tendency of these species to be solvated by the molecules of ethanol than water(12). The change in current should, accordingly be the resultant effect of the increase in viscosity and the molecular volume which in turn lowers and diffusion coefficient. The equations of Ilkovic(13) and Stokes-Einstein(14) can be used in order to get the following final form(12).

$$i = 708\, n\, Cm^{2/3}\, t^{1/6} \left[\frac{(3.38 \times 10^{-5})}{(4/3\,\pi r^3 N)^{1/3}\eta} \right]^{1/2} \quad \ldots(2)$$

Where i_d = diffusion current (μA)
n = number of electrons involved in the reduction process,
C = concentration of the depolarizer (mM),
r = radius of the diffusing particle (cm),
m = flow rate (mg. sec^{-1}),
N = Avagadro's number.

Equation (2) can be simplified as

$$r = K^2/i_d^2\eta \quad \ldots(3)$$

Where $K = (3.53\, n\, C\, m^{2/3}\, t^{1/6})\, 10^{-4}$

The data shown in Table 2 clarifies that the change in the radius (r) of the reducible species is a function of ethanol concentration in the

TABLE 2

EFFECT OF ETHANOL CONCENTRATION ON THE POLAROGRAPHIC WAVE OF 1 mM OF PICOLINIC ACID AT THE pH OF 3.05

% of ethanol	i_d ,μA	$-E_{1/2}$,V	r in A°	$Dx10^6$ $cm^2.sec^{-1}$	αn_a	$k^\circ_{f,h}$ x10^{11} $cm.sec^{-1}$
10	12.40	1.032	1.83	13.40	0.567	4.82
25	9.95	1.036	1.92	8.63	0.562	4.16
50	8.79	1.049	2.04	6.73	0.557	3.27
60	8.45	1.056	2.26	6.22	0.557	2.71
75	8.32	1:070	2.60	6.03	0.555	2.33

medium. The radius of the reduced species is found to increase with the increase in the ethanol content of the medium.

The half-wave potential is found to shift to more negative value with the increase in the percentage of ethanol as shown in Table 2 and figure 3. This can be attributed to several factors, namely dielectric constant (ϵ), solvation of ions and adsorption of organic solvent at the electrode surface. The variation of $E_{1/2}$ with 'ϵ' is given by the Takahashi relation(15), viz:

$$E_{1/2(s)} = E_{1/2(w)} - K\left[\frac{1}{\epsilon_{(w)}} + \frac{1}{\epsilon_{(s)}}\right] \quad ---(4)$$

in which $E_{1/2(w)}$ and $E_{1/2(s)}$ are the half-wave potentials in aqueous and aquo-organic mixtures respectively and 'K' is a constant.

If the dielectric constant is the dominant factor, the shift in $E_{1/2(s)}$ would be a linear function of $1/\epsilon_{(s)}$. The plots of $E_{1/2(s)}$ vs $1/\epsilon_{(s)}$ are linear as shown in Figure 3, which shows that the dielectric constant is a dominant factor for the changes observed in the present study.

The addtition of ethanol to water causes a destruction of the normal structure of water(12). The destruction of the associated molecules readily influences the hydration layer surrounding ions leading to a shift of $E_{1/2}$ to less negative values. However, the shift of $E_{1/2}$ to more negative values, observed in the present work may also be due to the adsorption of the organic solvents molecules to some extent at the electrode surface. The accumulation of solvent molecules near the electrode surface retards the adsorption of the reducible species and also blocks the reactive centres on electrode surface. Thus the reduction process requires higher energy and hence the $E_{1/2}$ shifts to more negative potentials.

The kinetic parameters $k^\circ_{f,h}$ & αn_a values are given

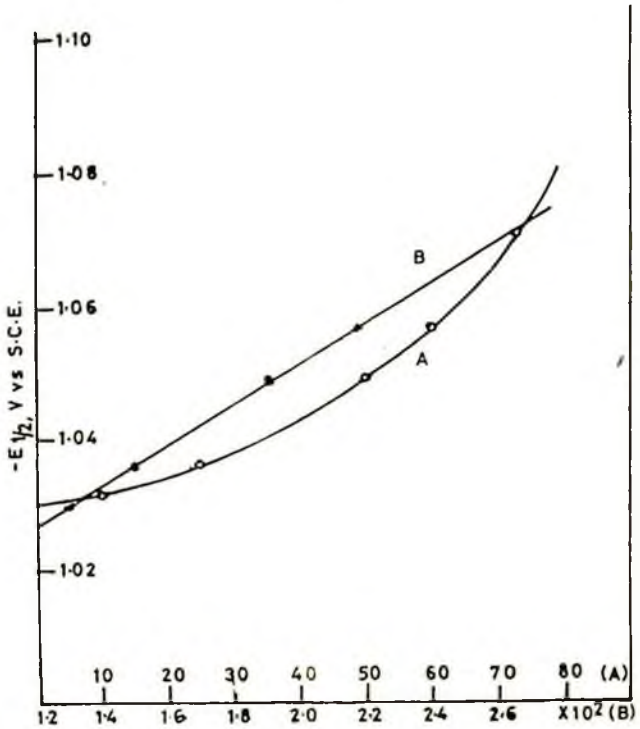


Fig. 3 Plots of E vs (A) volume percentage of ethanol and (B) reciprocal dielectric constant for the polarographic reduction of picolinic acid at a pH of 3.05.

in Table 2. The $k^\circ_{f,h}$ value is found to decrease with the increase in the concentration of ethanol, which show the increase in irreversibility. This is further supported by the decrease in αn_a values with increase in the percentage of ethanol.

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