POLAROGRAPHIC STUDY OF QUINOLINIC ACID AT VARIOUS TEMPERATURES

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The effect of temperature on the electrochemical reduction of quinolinic acid at dropping mercury electrode has been studied in the buffer solutions of various pH values and at different temperatures. The reduction process is diffusion controlled and irreversible. The kinetic parameters have been calculated by Koutecky-Cizek, Oldham-Parry, Meites-Israel and Gaur-Bhargava treatments. The effect of temperature on the kinetic and thermodynamic parameters has been investigated. The irreversibility decreases with the increase in the temperature.

The polarographic reduction of pyridine dicarboxylic acids was attempted by Tissier and Agoutin [1]. Its reduction at macro mercury pool-cathode [2] is reported. However, the effect of temperature on the electrode kinetics of the irreversible reduction of organic depolarizers has not attracted much attention.

In the present investigation an attempt is made to determine (a) the nature of the wave, (b) the formal heterogeneous rate constant ($k^\circ_{f,h}$) and (c) the other thermodynamic functions of quinolinic acid in various buffers with the variation in temperature. In the evaluation of $k^\circ_{f,h}$ values, various treatments are used in order to find the validity of the results obtained.

EXPERIMENTAL

Quinolinic acid was prepared using the procedure reported in the literature [3]. The details of experimental procedure were given in our earlier paper [4].

RESULTS AND DISCUSSION

The polarographic behaviour of 1 mM of quinolinic acid in the buffer solutions of various pH values viz., 1.06, 3.11, 4.28 and 6.44 at the temperature of 30°, 40°, 50° and 60° C have been studied.

Quinolinic acid gives two well defined cathodic waves at a pH of 1.06 and single wave at other pH's at all temperatures. The limiting current is found to be diffusion controlled at all temperature as evident from the linearity of the plots of i_d vs $h^{1/2}$ [5].

The diffusion current is found to increase with the increase in temperature. The temperature coefficient of diffusion current is found to be within the reasonable limits (Table 1 and 2) predicted by Meites for organic molecules [5]. The half-wave potential values are found to shift to more positive values with the increase in temperature.

The plots of $-E_{d.e.}$ vs log $[i/i_d - i)]$ are linear at all pH's and temperatures but their slopes are not in agreement with the theoretical values (0.015 V and 0.0075 V for 4 e and 8e reduction respectively) of a reversible wave. This indicates that the nature of the electrode reaction is irreversible.

Formal heterogeneous rate constants ($k^\circ_{f,h}$) have been evaluated using various methods such as Koutecky-Cizek [6], Meites-Israel [7], Oldham-Parry [8] and Gaur-Bhargava [9] in order to find the validity of the results obtained. The diffusion coefficient that is necessary for the calculation of $k^\circ_{f,h}$ at various temperatures have been calculated using the Stokes-Einstein [10] relation. The values of $k^\circ_{f,h}$ from different methods show the same trend and are in good agreement with each other. These values are given in Table 1 which confirm the irreversible nature of the wave. Further it is concluded from the increase in $k^\circ_{f,h}$ value with the increase in temperature, that the process of irreversibility decreases at higher temperatures. The increase in 'αn_a' with temperature also suggests that the increase in reversibility with the rise in temperature. This is because, the increase in the value of the product αn_a is attributed to the sole increase in the value of 'α' i.e. transfer coefficient [11].

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TABLE 1

THERHODYNAMIC PARAMETERS OF QUINOLINIC ACID REDUCTION, BY DIFFERENT TREATMENT
[QUINOLIC ACID] 1 mM

Parameters	pH 3.11				pH 6.44			
	303°K	313°K	323 K	333°K	303°K	313°K	323°K	323°K
$E_{1/2}$ Volts Traditional log plots	0.976	0.973	0.969	0.964	1.355	1.351	1.347	1.344
Oldham-Parry plots	0.979	0.975	0.970	0.965	1.358	1.354	1.349	1.346
αn_a	0.937	0.974	1.011	1.051	0.727	0.755	0.782	0.810
Temp. Coeff. of I %/deg	1.97	1.97	1.45		1.45	1.38	1.02	
r, A°	7.58	6.24	5.13	4.50	15.70	14.32	12.96	12.41
D x 10^6 (cm^2/sec)	7.54	9.50	11.71	14.15	7.54	9.50	11.71	14.15
$k^\circ_{f,h}$ x 10^{15} (cm/sec)								
Koutecky-Cizek	3.22	3.49	3.86	4.13	3.11	3.26	3.48	4.02
Meites-Isreal	3.76	3.97	4.31	4.62	3.57	3.83	4.25	4.52
Oldham-Parry	3.38	3.69	4.15	4.45	3.28	3.52	4.02	4.29
Gaur-Bhargava	5.73	6.04	6.56	7.02	5.44	5.84	6.47	6.91
ΔH_p (K Cals/mol)								
Koutecky-Cizek			1.66				1.72	
Meites-Isreal			1.38				1.58	
Oldham-Parry			1.84				1.79	
Gaur-Bhargava			1.36				1.60	
ΔH_v (K Cals/mol)								
Koutecky-Cizek	1.06	1.04	1.02	1.01	1.12	1.11	1.08	1.06
Meites-Isreal	0.78	0.76	0.74	0.72	0.98	0.96	0.94	0.92
Oldham-Parry	1.24	1.22	1.20	1.19	1.19	1.17	1.15	1.13
Gaur-Bhargava	0.76	0.74	0.72	0.70	1.00	0.98	0.96	0.94
$\Delta G^{\neq}$ (K Cals/mol)								
Koutecky-Cizek	27.17	28.03	28.89	29.75	29.96	30.94	31.90	32.82
Meites-Isreal	27.07	27.95	28.80	29.68	29.88	30.84	31.78	32.74
Oldham-Parry	27.14	28.00	28.84	29.70	29.93	30.89	31.82	32.78
Gaur-Bhargava	26.82	27.69	28.55	29.40	29.62	30.58	31.51	32.46
$\Delta S^{\neq}$ (e.u)								
Koutecky-Cizek	-86.17	-85.23	-86.28	-86.31	-95.18	-95.30	-95.42	-95.38
Meites-Isreal	-86.77	-86.87	-86.90	-86.97	-95.30	-95.46	-95.48	-95.56
Oldham-Parry	-85.48	-82.36	-85.57	-85.65	-94.85	-94.95	-94.96	-95.05
Gaur-Bhargava	-86.01	-86.10	-86.16	-80.18	-94.46	-94.56	-94.58	-94.65

The enthalpy of activation (ΔH_p) is calculated from the slope of the plots of log $k^\circ_{f,h}$ vs 1/T. The heat of activation at constant volume (ΔH_v) is evaluated using the relation.

$$\Delta H_p = \Delta H_v + RT \quad .....(1)$$

The activation free energy change, $\Delta G^{\neq}$ is determined using the relationship [12]

$$k^\circ_{f,h} = (kT/h)\ r_o\ \exp(-\Delta G^{\neq}/RT) \quad ...(2)$$

where

k = Boltzman constant
h = Planck's constant
r_o = mean distance between two depolariser ions in the bulk solutions.

In general the value of r_o is taken as 2×10^{-8} cm [13]

The thermodynamic functions viz , ΔH_p , ΔH_v , $\Delta G^{\neq}$ and ΔS follow the same trend as that of $k^\circ_{f,h}$ with respect to the mode of reduction of reducible species and are tabulated in table 1.

The positive values of $\Delta G^{\neq}$ for all the systems suggest the non-spontaneous nature of the electrode process. A small positive increase in the value of $\Delta G^{\neq}$ in all the systems with the increase in temperature may be becuase of the inconsistancy in the vlaue of r_o with the change in temperature [14].

The activation entropy (ΔS) is calculated using Helmholtz relation:

$$\Delta S = \frac{\Delta H_v - \Delta G^{\neq}}{T}$$

The negative values of ΔS obtained in each system suggest that the activated state has more rigid structure than the initial state [14].

The approximate radius of the reduced species (r) has been calculated for various systems, and are given in Table 1. The values of r_o and diffusion coefficient D are in reverse order, obeying Stokes-Einstein relation [10]. The decrease in the value of r_o with the increase in temperature may indicate that the reduced species are solvated; the extent of decrease in the value of r_o is different at different pH values. This may be because of the difference in the extent of solvation [15]

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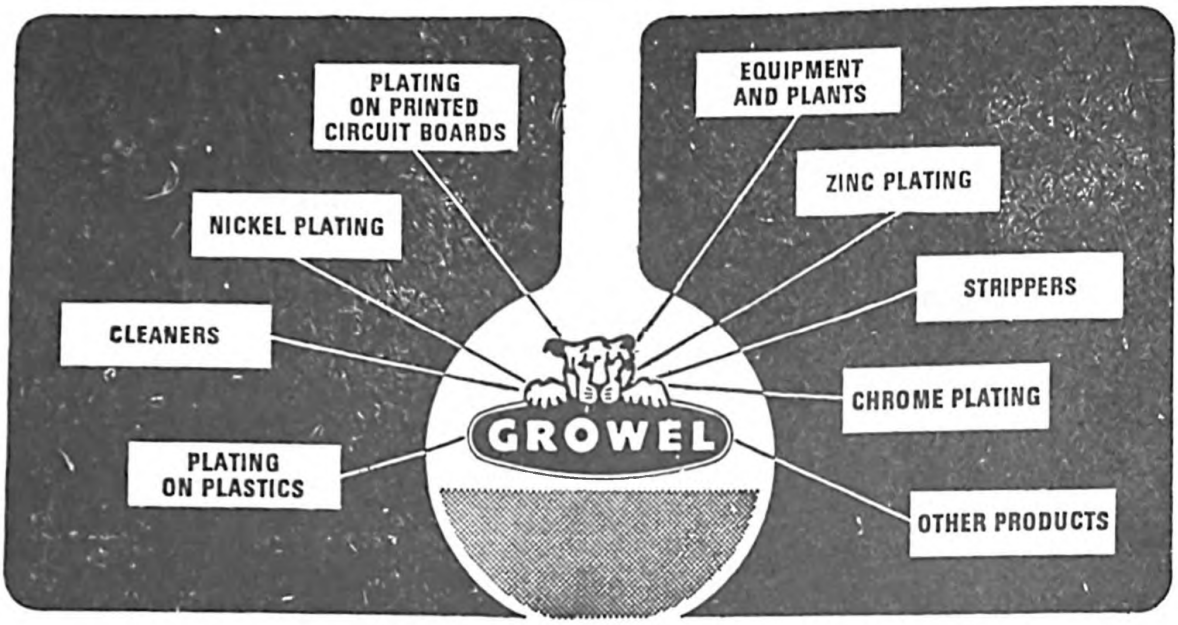
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