Polarography of Pyridine-2-carbaldehyde 2-Pyridylhydrazone in Solutions of Varying pH at a Dropping-mercury Electrode: Effect of Surface-active Substance

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The polarographic behaviour of pyridine-2-carbaldehyde 2-pyridylhydrazone (PAPH) at a dropping-mercury electrode was studied in aqueous Britton–Robinson buffers containing 50% ethanol. The polarograms consist of one wave in the acidic and alkaline medium. Two electrons are consumed in the splitting of the N–N bond to give 2-aminopyridine and pyridine-2-carbaldehyde. The adsorption effects of cationic, anionic, and non-ionic surfactants on the polargraphic waves of PAPH have been investigated. The kinetic parameters for the electrode reaction at different pH values have been computed.

Recently, nitrogen-containing heterocyclic hydrazones have been widely studied as analytical reagents.[1–16] Generally, the polarographic behaviour of hydrazone compounds has been the subject of many investigations.[17–21] The authors found that the reduction of the hydrazone group takes place *via* the fission of the N–N bond and consumption of four electrons in substituted as well as unsubstituted compounds. However, a literature survey revealed the absence of polarographic data on pyridine-2-carbaldehyde 2-pyridylhydrazone (PAPH).

In this paper, the polarographic behaviour of PAPH has been investigated to throw some light on its reduction mechanism and show the similarities and differences in its electroreduction from that of other hydrazones. The effect of cationic, anionic, and non-ionic surface-active substances (SAS) on the polarographic waves is also studied.

Experimental

(a) *Solutions.*—A 10^{-2}M-pyridine-2-carbaldehyde 2-pyridylhydrazone (PAPH) solution was prepared by dissolution of an appropriate amount of solid in hot ethanol. As supporting electrolytes the universal buffer series of Britton and Robinson[22] was used. Solutions of surface-active substances (SAS) such as Triton X-100 (T.X-100), sodium laurylsulphate (SLS), and cetyltrimethylammonium bromide (CTAB) were prepared by dissolving the calculated amounts in redistilled water.

(b) *Apparatus.*—The average current–voltage curves were recorded with a 3001 polarograph (Sargent Welch). The electrode characteristics were m = 1.53 mg s^{-1} and t = 4.9 s at a mercury height of 57 cm.

(c) *Techniques.—Controlled-potential electrolysis and identification of products.* Mercury-pool electrolysis was carried out in buffer pH 3.41 (200 ml) containing 50% ethanol and PAPH (200 mg). The electrolysis cell was a 250 ml conical flask in which the reference, auxiliary electrodes, and the gas inlet were inserted through a cork. The potential was controlled at − 1.8 V *versus* s.c.e. (*i.e.* on the limiting-current plateau of the wave). The progress of electrolysis was followed by recording the decrease in current with time and the number of electrons involved in the electrode process was computed from the *i–t* curve following the procedure outlined by Lingane.[23] For PAPH compound the number of electrons was calculated and found to be 1.88 ($\simeq$ 2). After disconnecting the electrolysis cell from the circuit, pyridine-2-carbaldehyde was identified among the products of electrolysis by evaporating the ethanol and adding 4% HCl solution (*ca.* 5 ml) followed by extraction with ether several times. The ether layer was then evaporated and the i.r. spectrum of the remaining residue was recorded. The aqueous layer was treated with NaOH solution and, after work-up as above, 2-aminopyridine was obtained. The products of electrolysis in acid and alkaline medium are the same.

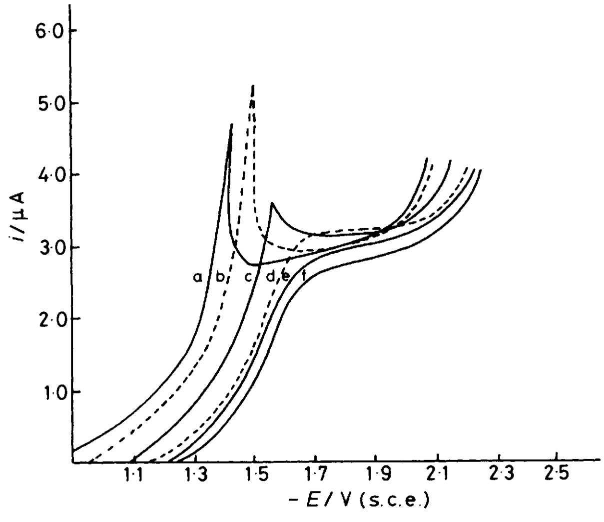

Figure 1. Effect of pH on 5 × 10^{-4}M-PAPH in 50% ethanol: a, pH 1.15; b, pH 1.89; c, pH 2.71; d, pH 5.66; e, pH 7.34; f, pH 11.8

Results and Discussion

The polarogram of 5 × 10^{-4}M-pyridine-2-carbaldehyde 2-pyridylhydrazone (PAPH) at the d.m.e. in 50% ethanolic buffers covering the pH range 1.15—11.8 revealed that this compound is reduced in a single irreversible step (Figure 1). The height of the wave was practically constant within the whole pH range. In buffer solutions of pH 1.15—4.05 the wave is accompanied by a maximum which can be eliminated by the addition of 9.7 × 10^{-4}—1.6 × 10^{-3}% Triton X-100.

The $\Delta E_{\frac{1}{2}}$–Δ pH relation is a straight line with a slope equal to 0.070 in the pH range 1.15—4.05 (Table 1). This slope indicates that 1H$^+$ ion per electron was consumed in the rate-determining step, because $\Delta E_{\frac{1}{2}}-\Delta\mathrm{pH} = X_{\mathrm{H}^+}(0.059/\alpha n_a)$ in which X_{H^+} and n_a represent the number of H$^+$ ions and electrons involved in the rate-determining step, respectively. Above pH

Table 1. Kinetic parameters of 5 × 10^{-4}M-PAPH in different buffer solutions containing 50% ethanol

pH	$\frac{0.059}{\alpha n_a}$	αn_a	α for n_a = 1	α for n_a = 2	$\Delta E_{\frac{1}{2}}$ − ΔpH pH range	 slope	Slope of log i–log h plot	K_o/Cm s^{-1}	$K_oD^{-\frac{1}{2}}$ ($K = K_o$)	ΔG^*/kcal mol^{-1}
3.41	0.31	0.19	0.19	0.10	1.15—4.05	0.070	0.60	2.63 × 10^{-7}	1.55 × 10^{-4}	67.48
7.34	0.24	0.24	0.24	0.12			0.56	6.61 × 10^{-8}	3.90 × 10^{-5}	70.95
11.80	0.20	0.29	0.29	0.15			0.56	1.05 × 10^{-10}	6.17 × 10^{-8}	87.13

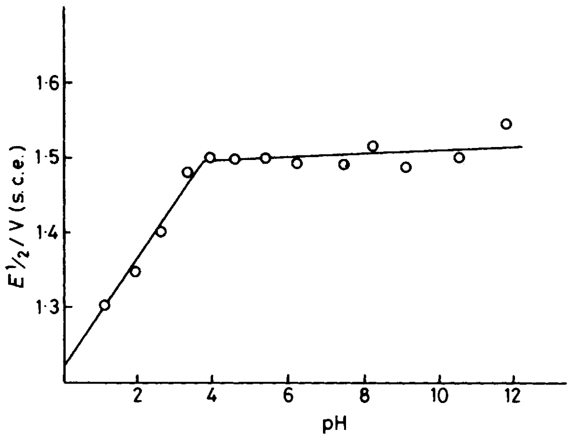

Figure 2. $E_{\frac{1}{2}}$-pH plot

4.05, the half-wave potential is practically pH-independent,[24] as shown in Figure 2.

The effect of mercury height h on the polarograms indicates that the wave mainly exhibits diffusion control with some adsorption component. This is obvious from the values of the exponent x in the relation $i_l = Kh^x$ which are in the range 0.56—0.60 at different pH values (Table 1). The values of i_l and h have been corrected for residual current and back pressure, respectively.

Plots of E *versus* log $(i/i_d - i)$ for the wave at different pH values are straight lines with varying slopes, values of the latter (Table 1) indicating that the reduction process proceeds irreversibly. The slopes of these plots give values for the transfer coefficient (α) which are less than unity (Table 1), confirming the irreversible nature of the waves.

Reduction Mechanism.—In order to throw some light on the mode of reduction of PAPH at the d.m.e., it was necessary to calculate the number of electrons in the electroreduction process by applying the Ilkovic equation. The value of the diffusion coefficient (D) is not available but can be calculated from equation (1)[25] where V_m is the apparent molar volume of

$$D = 3.32 \times 10^{-5}/(V_m)^{1/3}\ \text{cm}^2\ \text{s}^{-1} \qquad (1)$$

PAPH and is equal to molecular weight/density. The value of D thus obtained corresponds to that in aqueous solutions (D_{aq}). For use in 50% ethanol solutions, the effect of viscosity of the medium must be taken into account. The corrected value of D_{alc} can be obtained from equation (2) and equals 2.88 × 10^{-6} cm^2

$$\frac{\eta_{alc}}{\eta_{aq}} = \frac{D_{aq}}{D_{alc}} \qquad (2)$$

s^{-1}. Thus by substituting the values of i_l, D_{alc}, t, c, and m in the Ilkovic equation, it is evident that two electrons are consumed in the process of reduction in the whole pH range. Controlled-potential electrolysis applied at potentials on the plateau of the polarographic wave verified the consumption of two electrons per molecule.

It is evident that the reduction mechanism involves cleavage of the N–N bond similar to that proposed by Lund *et al.* for other hydrazones[19,26] and recently by Gomez *et al.*[17] The reduction of PAPH is carried out by two electrons in the whole pH range, while Lund[19] proposed a reduction of four electrons in acid medium and two electrons in alkaline medium for similar hydrazones. On the other hand, 2-C_5H_4N–NH–NH_2 is reduced polarographically in the available potential range confirming the splitting of the N–N bond.

The process of reduction of PAPH can be represented by equation (3) followed by hydrolysis (4) of compound (**II**) to the corresponding aldehyde. This process of hydrolysis is in accord with that obtained by Lund,[27] for similar compounds.

$$\underset{\textbf{(I)}}{2\text{-}C_5H_4N\text{-}HC{=}N\text{-}NH\text{-}NH_4C_5\text{-}2} + 2e + 2H^+ \longrightarrow \underset{\textbf{(II)}}{2\text{-}C_5H_4N\text{-}HC{=}NH} + \underset{\textbf{(III)}}{H_2N\text{-}NH_4C_5\text{-}2} \qquad (3)$$

$$2\text{-}C_5H_4N\text{-}HC{=}NH + H_2O \rightleftharpoons \underset{\textbf{(IV)}}{2\text{-}C_5H_4N\text{-}HC{=}O} + NH_3 \qquad (4)$$

Behaviour in the Presence of Surface-active Substances.—The three SAS, Triton X-100 (T.X-100), sodium laurylsulphate (SLS), and cetyltrimethylammonium bromide (CTAB), used have almost the same effect on the polarograms: (i) the elimination of the maximum at lower pH in the presence of small quantities of SAS, (ii) the shift of $E_{\frac{1}{2}}$ to more negative values with distortion of the wave, and (iii) the decrease of the limiting current. The waves obtained in the presence of Triton X-100 are more distorted and lie at more negative potentials than with cetyltrimethylammonium bromide and sodium laurylsulphate.

The effect of SAS on the different wave parameters is briefly discussed as follows.

A. *The half-wave potentials* ($E_{\frac{1}{2}}$). On increasing the concentration of SAS, $E_{\frac{1}{2}}$ shifts to more negative values and approaches a more or less constant value at relatively high concentration of SAS (Figure 3). The relations differ not only with pH but also with the nature of SAS. The effects observed are in the order of relative inhibiting power of the compounds, *i.e.* Triton X-100 > SLS > CTAB on the acid side and Triton X-100 > CTAB > SLS on the alkaline. The variable effects of CTAB and SLS in accordance with pH may be explained on the basis of the dissociation of the depolarizer to a cationic form at low pH and at the same time transformation of CTAB to the acid form, which appears to possess a lower surface activity than the anionic species. At higher pH, SLS is converted into the free base, and the depolarizer exists as an anion; thus the effect of SLS is lowered. This is in accord with the results obtained by Issa *et al.*[28]

B. *Nature of the wave.* (i) The effect of mercury pressure on the

Table 2. Effect of SAS on the kinetic parameters of 5 × 10^{-4}M-PAPH at pH 3.41 in the presence of 50% ethanol

SAS	$\frac{0.059}{\alpha n_a}$	αn_a	α for $n_a = 1$	α for $n_a = 2$	Slope of log *i*–log *h* plot	K_o/Cm s^{-1}	$K_oD^{-\frac{1}{2}}$ ($K = K_o$)	ΔG^*/kcal mol^{-1}
					Triton X-100			
4.0 × 10^{-3}	0.40	0.14	0.14	0.07	0.63	1.18 × 10^{-13}	6.92 × 10^{-11}	104.17
5.6 × 10^{-2}	0.43	0.13	0.13	0.07	0.68	8.13 × 10^{-15}	4.79 × 10^{-12}	110.88
					SLS			
4.0 × 10^{-3}	0.38	0.15	0.15	0.08	0.62	1.74 × 10^{-12}	1.03 × 10^{-9}	97.41
5.6 × 10^{-2}	0.42	0.14	0.14	0.07	0.64	9.34 × 10^{-13}	5.50 × 10^{-11}	104.75
					CTAB			
4.0 × 10^{-3}	0.34	0.17	0.17	0.09	0.60	1.10 × 10^{-10}	6.46 × 10^{-8}	87.01
5.6 × 10^{-2}	0.37	0.16	0.16	0.08	0.63	7.08 × 10^{-13}	4.17 × 10^{-10}	99.67

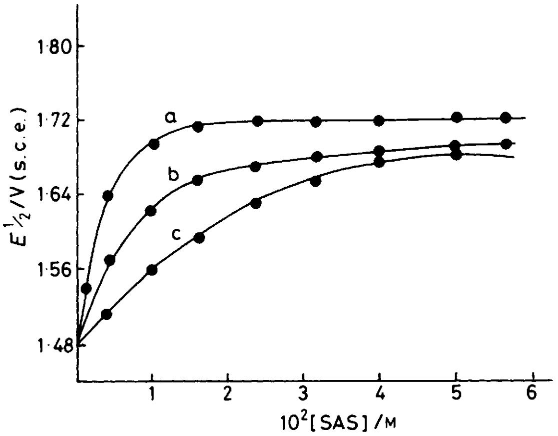

Figure 3. Effect of SAS concentration on $E_{\frac{1}{2}}$ at pH 3.41: a, T.X-100; b, SLS; c, CTAB

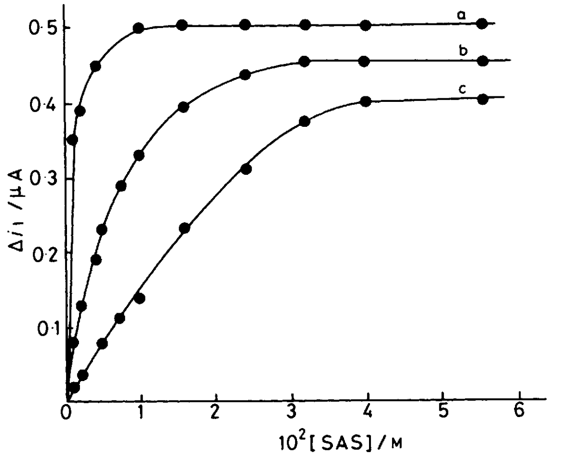

Figure 4. Effect of SAS concentration on Δi_l at pH 3.41: a, T.X-100; b, SLS; c, CTAB

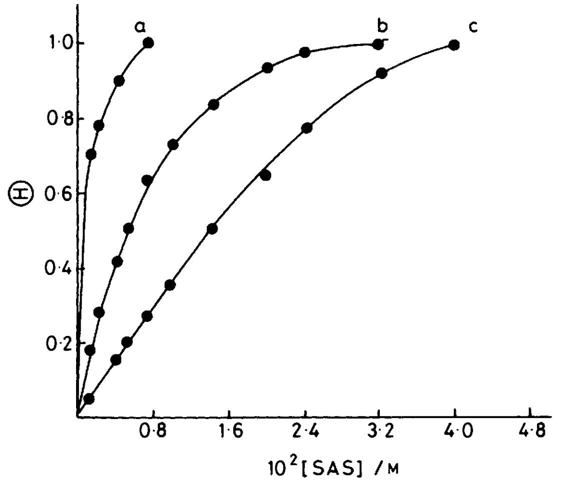

Figure 5. Dependence of surface coverage Θ on the bulk concentration of SAS at pH 3.41: a, T.X-100; b, SLS; c, CTAB

limiting current reveals that the presence of SAS increases the adsorption contribution on the reduction wave, as shown in Table 2. (ii) From the plots of *E versus* log ($i/i_d - i$) it was found that the values of the slope ($0.059/\alpha n_a$) in the presence of SAS (Table 2) are higher than in their absence and tend to increase with increasing concentration of SAS indicating that the reduction process in the presence of SAS becomes more irreversible.

C. *The limiting current*. Generally, the limiting current decreases with increasing concentration of the SAS. We can plot Δi_l, the decrease of the limiting current with respect to the i_l value in the absence of SAS, as a function of the concentration of the SAS. The resulting curves have the form of an adsorption isotherm, as shown in Figure 4.

To follow quantitatively the adsorption effect of SAS on the different wave parameters, the Δi_l value at a given concentration of SAS was determined and the degree of coverage Θ was evaluated by relation (5) where $(\Delta i_l)_m$ is the maxi-

$$\Theta = \Delta i_l/(\Delta i_l)_m \qquad (5)$$

mum decrease corresponding to full coverage. It has been found that the degree of coverage dependence on the concentration of SAS (Figure 5) fits well a Frumkin isotherm given by equation

$$\frac{\Theta}{1 - \Theta} \exp(-2a\,\Theta) = bc \qquad (6)$$

(6)[29] where Θ is the degree of coverage, *a* the interaction coefficient, *b* the adsorption coefficient, and *c* the concentration of SAS.

The interaction coefficient *a* was determined from the slope of the logarithmic plot of the Frumkin isotherm and the

Table 3. Adsorption parameters of T.X-100, SLS, and CTAB calculated from the polarographic result at pH 3.41

SAS	a	b/l mol^{-1}	$-\Delta G^\circ$/kcal mol^{-1}
T.X-100	0.83	1.0×10^3	6.44
SLS	1.03	2.0×10^2	5.49
CTAB	1.20	0.7×10^2	4.87

adsorption coefficient b from the values at half-coverage in the usual manner.[30] The free energy of adsorption ($-\Delta G^\circ$) was then calculated from the adsorption coefficient b according to equation (7). The calculated values of the adsorption parameters are given for the three SAS in Table 3. The various parameters indicate that the relative inhibiting power of the three SAS at pH 3.41 is in the order Triton X-100 > SLS > CTAB.

$$b = \frac{1}{55.5}\exp\left(\frac{-\Delta G^\circ}{RT}\right) \qquad (7)$$

Kinetic Parameters.—The kinetic parameters for the electrode reaction, in the absence and presence of SAS, were calculated using the Koutecky equation.[31] Tables 1 and 2 include representative values for αn_a (α is the transfer coefficient, n_a the number of electrons involved in the rate-determining step), K_o (the rate constant at $E = 0$), $K_oD^{-\frac{1}{2}}$ (D is the diffusion coefficient), and ΔG^* (free energy of activation).

In the absence of SAS, the various parameters indicate that the process of reduction is irreversible. This is shown by the fact that the value of α is less than unity when the rate-determining step involves the uptake of one or two electrons. In the mean, the ΔG^* values increase and K_o values decrease with increasing pH, confirming the increased irreversibility of the electrode reaction, as shown in Table 1.

The values of the parameters in the presence of SAS indicate that the degree of irreversibility increases as the concentration of the SAS is increased (Table 2). This effect of SAS is connected with the variation of the charge distribution in the double layer and the effect of this charge on the rate of electrochemical reactions.[32]

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