Polarography of Salicylidenebenzohydrazide in Solutions of Varying pH at a Dropping-mercury Electrode: Effect of Hydrogen Bonding

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The polarographic behaviour of salicylidenebenzohydrazide (SBH) at a dropping-mercury electrode was studied in aqueous Britton–Robinson buffers containing 40% ethanol. The polarograms consist each of one wave in acidic medium. The height of the wave decreases and its $E_{\frac{1}{2}}$ shifts to more negative potentials with increasing pH until it diminishes completely at pH >10.7. At pH values >7.2 a second wave appears, the height of which increases with pH and becomes developed at pH values >10.7. In acid solutions 4-electrons are consumed in the reduction of C=N. The second wave is attributed to the reduction of salicylaldehyde which is formed from the hydrolysis of the hydrazide. The effect of pH on the limiting current and $E_{\frac{1}{2}}$ as well as the reduction mechanism are discussed. The kinetic parameters of the electrode reaction are also determined.

THE polarographic behaviour of compounds containing either a C=N– or a C=O group have been investigated, but few studies were made on compounds containing both. Tirouflet[1] observed a 4-electron reduction of benzaldehyde thiosemicarbazone to benzylamine plus thiourea in acid solutions. The polarographic reduction of benzaldehyde, benzophenone, and *p*-aminoacetophenone semicarbazones showed a single pH-dependent wave in acid solution, the height of which diminished with increasing pH;[2] the reaction consumed 4 electrons in acidic media.

The present work represents an investigation of the polarographic behaviour of salicylidenebenzohydrazide (SBH) in buffer solutions of varying pH containing 40% ethanol in order to throw some light on the reduction mechanism.

EXPERIMENTAL

A 10^{-2}M-salicylidenebenzohydrazide (SBH) 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[3] was used. The average current–voltage curves were recorded by polarograph model LP 60. The electrode characteristics were $m = 1.50$ mg s^{-1} and $t = 4.5$ s at a mercury height of 45 cm. The coulometric method of De Vries and Kroon[4] using a mercury pool cathode was used for determining the value of n, the number of electrons involved in the reduction process.

RESULTS AND DISCUSSION

The polarograms of 5×10^{-4}M-salicylidenebenzohydrazide (SBH) at the dropping-mercury electrode (d.m.e.) each consist of one or two waves depending on the pH of the solution (see Figure 1). In buffer solutions of pH 3.7—6.2 the polarogram consists of one wave which is accompanied by an apparent minimum which can be eliminated by the addition of 9.7×10^{-4}—1.6×10^{-3}% gelatin. This phenomenon may be attributed to the adsorption of the depolarizer on the electrode surface, as is evident from the decrease of drop time and shift of the electrocapillary maximum on increasing the concentration of the depolarizer. Another smaller second wave appears at pH 7.2. On increasing the pH, the first wave decreases gradually until it disappears almost completely at pH 10.7, while the second wave becomes developed and constitutes the whole polarogram. The reduction waves shift to more negative potentials, with rise of pH indicating that hydrogen ions are consumed in the reduction process.

The $\Delta E_{\frac{1}{2}}/\Delta$pH relation of the first wave (Figure 2), is a straight line with a slope equal to 0.104 in the pH range 3.7—7.2. Also, the $\Delta E_{\frac{1}{2}}/\Delta$pH relation of the second wave has a slope of 0.057 and covers the pH range 7.2—11.6. These slopes indicate that 2 H^+ ions per electron are consumed along the first wave and one only along the second wave in the rate-determining step, because $\Delta E_{\frac{1}{2}}/\Delta\text{pH} = x_{H^+}(0.059/\alpha n_a)$ in which x_{H^+} and n_a represent the number of H^+ ions and electrons involved in the rate-determining step respectively.

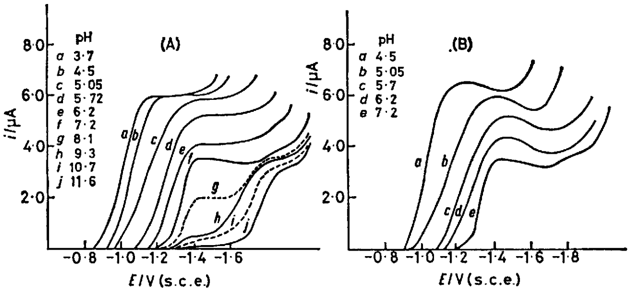

FIGURE 1 Effect of pH on 5×10^{-4}M-SBH in 40% ethanol in the presence of gelatin (A) and in the absence of gelatin (B)

TABLE 1

Effect of concentration of SBH on i_l in 40% ethanol

pH	$c \times 10^{-4}$/ M	i_d/c μA/mmol^{-1}
5.05	1	10.50
	3	10.55
	5	10.40
	7	10.30
	10	10.20
8.1	1	5.50
	3	5.63
	5	5.60
	7	5.50
	10	5.50
11.6	1	4.90
	3	4.83
	5	4.76
	7	4.64
	10	4.62

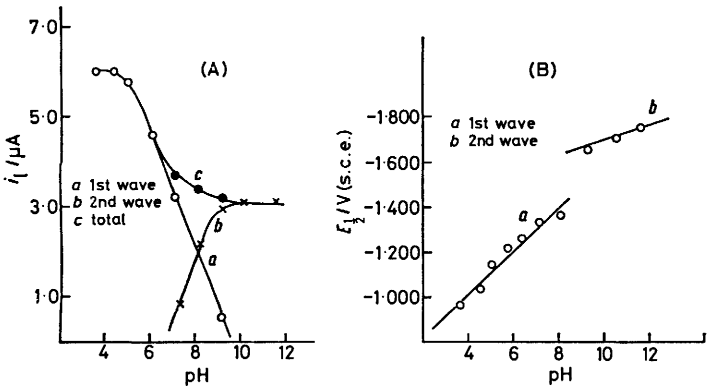

FIGURE 2 (A) i_l *vs.* pH plot. (B) $E_{\frac{1}{2}}$ *vs.* pH plot

The validity of the Ilkovic equation and the possibility of the polarographic determination of SBH were established by plotting the total limiting current *vs.* concentration of the depolarizer. Satisfactory linear relations passing through the origin are obtained at pH values 5.05 and 8.1. The applicability of the method for analysis is also supported by the constancy of the i_d/C values (see Table 1). This constancy is more apparent at lower than at higher pH values.

TABLE 2

Kinetic parameters of 5×10^{-4}M SBH in different buffer solutions containing 40% ethanol

pH	$-E_{\frac{1}{2}}$/V	$-E_{\frac{1}{2}}^{r}$/V	$0.059/\alpha n_a$ (S_1)	$\Delta E_{\frac{1}{2}}/\Delta$pH plot: pH range	$\Delta E_{\frac{1}{2}}/\Delta$pH plot: Slope ($S_2$)	αn_a	α for $n_a = 1$	α for $n_a = 2$	$Z_{H^+} = S_2/S_1$	i_d/μA	Apparent n_a ($\alpha = 0.5$)	Slope of log i_l — log h plot
5.05	1.14	1.005	0.11	3.7—7.2	0.104	0.53	0.53	0.27	0.94	6.00	1.06	0.66
7.2	1.33	1.292	0.053	7.2—11.6	0.057 *	1.13	1.13	0.57	1.07	3.8	2.26	0.61
8.1	1.34	1.304	0.071			0.84	0.84	0.42	0.80	1.80	1.68	0.54
	1.64 *	1.542 *	0.120 *			0.50 *	0.50 *	0.25 *	0.48 *	1.85 *	1.08 *	0.61 *
11.6	1.78 *	1.703 *	0.095 *			0.63 *	0.63 *	0.32 *	0.60 *	3.00 *	1.06 *	0.60 *

* Second wave. S_1 = slope of log $i(i_d - i)$ *vs.* E plot. S_2 = slope of $E_{\frac{1}{2}}$ *vs.* pH plot.

The effect of mercury height h on the polarograms indicates that the first and the second waves mainly exhibit 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 0.54—0.66 at different pH values for the two waves.

The waves were analysed by applying equation (1).

$$\Delta E/\Delta \log (i/i_d - i) = 0.059/n \text{ at } 25\ ^\circ\text{C} \qquad (1)$$

Plots of E *vs.* log (i/i_d — i) for the waves are straight lines with varying slopes, values of the latter (Table 2) indicating that the reduction process proceeds irreversibly. On applying equation (2) for irreversible waves[5]

$$\Delta E/\Delta \log (i/i_d - i) = 0.059/\alpha n_a \qquad (2)$$

the values of the transfer coefficient (α) obtained are less than unity (Table 2), confirming the irreversible nature of the waves.

Reduction Mechanism.—In order to throw light on the mode of reduction of salicylidenebenzohydrazide, it was necessary to calculate the number of electrons involved in the reaction by applying the Ilkovic equation. This necessitates a knowledge of the value of the diffusion coefficient D of SBH.

The value of D is not available, and may be calculated from (3), Stoke's relation, provided that the density of the compound is known.

$$D = \frac{3.22 \times 10^{-5}}{(V_m)^{1/3}} \text{ cm}^2 \text{ s}^{-1} \qquad (3)$$

V_m Is the apparent molar volume of the substance in the solid state, and is equal to molecular weight/density (240.25/1.11). The value of D thus obtained corresponds to that in aqueous solutions ($D_{aq} = 5.36 \times 10^{-6}$). For use in 40% ethanol solutions, the effect of viscosity of the medium must be accounted for. Thus, taking the relative viscosity of H_2O equal to 1, that of 40% ethanol is equal to 1.98, the corrected value of D_{alc} can be obtained from relation (4).

$$\frac{\eta_{alc}}{\eta_{aq}} = \frac{D_{aq}}{D_{alc}} \qquad (4)$$

The number of electrons involved in the electroreduction process can be evaluated by substituting the values of D_{alc}, c, t, and m in the Ilkovic equation to give $n = i_d/1.62$.

From Table 2 it is clear that the height of the first wave in acidic media (6.0 μA) corresponds to the uptake of 4 electrons. Further, the height of the second wave in alkaline media (3.0 μA) corresponds to 2 electrons.

The coulometric experiments (pH = 3.7) applied at potentials on the plateau of the polarographic curve verified a consumption of 4 electrons per molecule in acid media.

Although SBH contains two reducible centres, C=N and C=O, the latter is inactive towards reduction as a result of the mesomeric effect with the neighbouring imine group.[6,7] Thus the electrode reaction for SBH can be considered to take place as follows.

(*a*) In acidic media, the reduction of N=C proceeds along a single wave corresponding to 4 electrons [see equation (5)].

$$\text{BzNH·N=CH·}C_6H_4\text{OH-}o + 4e + 4H^+ \longrightarrow \text{BzNH·}NH_2 + \text{Me}C_6H_4\text{OH-}o \qquad (5)$$

$$\text{N=CH} + 2H^+ + e \longrightarrow [\text{NH–}CH_2]^+ + e \longrightarrow \text{NH–}CH_2 \qquad (6)$$

Since the rate-determining step involves one electron and two H^+ ions in acidic solutions, the reaction path may be given as in equation (6). Step (6) is followed by reaction (7).

$$\mathrm{NH{\cdot}CH_2 + 2H^+ + 2e \longrightarrow CH_3 + NH_2} \qquad (7)$$

(*b*) At pH values >7.2 a second wave appears, whose height increases gradually as the pH of the supporting electrolyte increases and attains a constant value at pH values >10.7; this corresponds to the uptake of 2 electrons.

The second wave may be attributed to the reduction of salicylaldehyde formed by the hydrolysis of the compound. The latter is brought about by the weakening of the double bond in C=N, a result of the localization of electrons on the nitrogen atom, caused by the inductive effect of the *ortho*-OH group as well as the strong intramolecular hydrogen bond formed between the OH group and azomethine nitrogen atom. This reasoning is supported by the following evidence. (i) Coincidence of $E_{\frac{1}{2}}$ of the second wave with that of salicylaldehyde at the same pH values (-1.32 and -1.63 V at pH 8.0 and 13 respectively).[8] (ii) Constancy of the limiting current of the wave with a change of pH from alkaline to acid solutions. (iii) An increase in the pH, results in a decrease in the C=N absorption ($\lambda = 290$ nm) and appearance of that corresponding to aldehyde. (iv) Increase of the second-wave height with rise of pH and concurrent decline of that for the first as a result of hydrolysis [Figure 2(A)].

Hydrolysis of the compound is both acid- and alkali-catalysed, the former occurring below pH 5.05 and increasing with decrease of pH, the latter occurring above pH 7.2 and increasing with pH. The range of stability of the compound lies between pH 5.05—7.2 in contradistinction to benzylidenebenzohydrazide [9] (BBH) (3.7—8.1) as a result of hydrogen bonding between the hydroxy-group and the π-bond of the azomethine nitrogen. Hydrogen bonding appears to increase the tendency of the compound to hydrolyse, by localising the electron density on the nitrogen atom. At the same time reduction of the hydrogen-bonded nitrogen atom appears to take place at somewhat more negative potentials as a result of localization of the electrons on the nitrogen atom in contradistinction to the BBH which occurs at less negative potentials. This is evidenced by increased value of ΔG^* and decreased value of K_0 relative to benzylidenebenzohydrazide.

Effect of Time on the Polarogram.—In strongly acid solutions, the limiting current decreases with time. This renders it difficult to carry out a detailed study of the effect of Hg height and analysis of the waves obtained in such solutions.

The decrease of current is ascribed to the hydrolysis of the compound to yield the benzohydrazide and the salicylaldehyde. In acid medium hydrolysis is more enhanced than at higher pH values as a result of the protonation of the nitrogen atom of the azomethine centre which increases the localization of electrons on the nitrogen and weakens the double bond. This idea is confirmed spectrophotometrically by recording the spectra after different periods of time. It was found that absorbance of the band with $\lambda_{\text{max.}} = 290$ nm, which is ascribed to C=N group decreases with time.

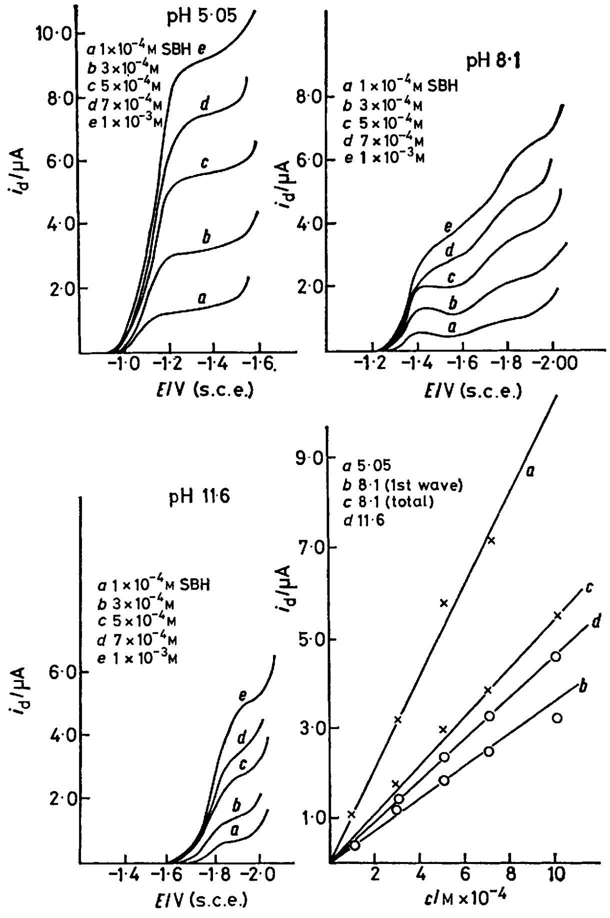

FIGURE 3 Effect of concentration of SBH at different pH values

The absorbance A (which is proportional to the con-

TABLE 3

Kinetic parameters of the electrode reaction 5×10^{-4}M SBH

pH	K_0/cm s^{-1} ($E = 0$)	$K_0D^{-\frac{1}{2}}$ ($K = K_0$)	ΔG_f^*/kcal mol^{-1}	K_f/cm s^{-1}	$K_fD^{-\frac{1}{2}}$ ($K = K_f$)	ΔG_f^*/ kcal mol^{-1}
5.0	7.53×10^{-16}	3.19×10^{-13}	116.85	2.17×10^{-4}	0.093	50.062
7.2	2.78×10^{-33}	1.18×10^{-30}	217.57	6.23×10^{-4}	0.282	47.86
8.1	3.12×1^{-27}	1.32×10^{-24}	182.62	7.1×10^{-4}	0.306	47.65
	1.04×10^{-31} †	4.40×10^{-29} †	200.49 †	6.48×10^{-4} †	0.280 †	47.88 †
11.6	1.22×10^{-23} †	5.17×10^{-21} †	161.87 †	1.02×10^{-3} †	0.441 †	46.72 †

† Second wave.

centration of SBH) was measured at $\lambda_{\mathrm{max.}} = 290$ nm after different time intervals. The plot of $\log A$ *vs.* time indicates that the reaction is first order and confirms the decomposition of SBH into its constituents.

Kinetic Parameters of the Electrode Reaction.—In order to confirm the irreversibility of the reduction process, the kinetic parameters for the electrode reaction at $E = 0$ were calculated using the Koutecky[10] equation and by plotting $\log(i/i_{\mathrm{d}} - i)$ *vs.* E.

The values of the formal constants at the reversible half-wave potential at a given pH have been also calculated. The reversible half-wave potentials $E_{\frac{1}{2}}^{\mathrm{r}}$ have been obtained by the method of Gellings.[11]

From Table 3, it is evident that ΔG^* values increase and the K_0 decreases with increasing pH thus confirming the increasing irreversibility of the electrode reaction. Furthermore the values of K_{f}, although higher than those of K_0, do not correspond to those of K_{s}, the standard rate constant. This is because the value of $E_{\frac{1}{2}}^{\mathrm{r}}$ does not coincide with $E_{\frac{1}{2}}$ due to shift of E_{s} to more negative potentials as a result of the adsorption of the reduction or the hydrolysis products on the electrode surface. This renders the reduction process more irreversible than expected for electrode reactions.

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