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Polarographic Behaviour of Salicylaldehyde-2-Pyridylhydrazone and Its Copper(II) Complex*

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Abstract. The polarographic behaviour of salicylaldehyde-2-pyridylhydrazone (SAPH) has been studied in aqueous buffer solution containing 40% ethanol using DC and DP polarographic methods. In the pH range 1.8—7.5 the observed single irreversible reduction wave is assigned to the splitting of the N—N bond and reduction of C=N centre. In alkaline medium, a second wave appears at a more negative potential due to the reduction of the salicylaldehyde which is formed by hydrolytic decomposition of the SAPH molecule. The effect of pH on the limiting current and $E_{1/2}$ as well as the reduction mechanism are discussed and compared with similar compounds. The kinetic parameters of the electrode reaction have been calculated.

The analytical properties of the copper(II)-SAPH system is described. The complex gave rise to a single irreversible well-defined wave ($E_{1/2} = -0.58$ V at pH = 5.2). The reaction process is diffusion controlled. A method is suggested for the determination of Cu(II) in presence of different metal ions as the difference in their $E_{1/2}$ values is sufficient for the purpose.

Key words: polarography, salicylaldehyde-2-pyridylhydrazone, Cu(II) complex.

The nitrogen-containing heterocyclic hydrazones were studied as analytical reagents [1—11]. The metal-complexing properties of salicylaldehyde-2-pyridylhydrazone (SAPH) were described, where the heterocyclic nitrogen atom plays an important part [11].

On the other hand, the polarographic behaviour of hydrazone compounds were the subject of many investigations [12—15], but those

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related to nitrogen-containing heterocyclic hydrazones are scarce [16—18]. So, the polarographic behaviour of SAPH was investigated to throw some light on its reduction mechanism and shows similarities and differences in its electroreduction from that of other hydrazones.

In this work the polarographic characteristics of copper(II) using SAPH as a complexing agent were investigated and suitable conditions are suggested for the determination of Cu(II) in the presence of different metal ions.

Experimental

Solutions

Salicylaldehyde-2-pyridylhydrazone (SAPH) was prepared as reported by Anderson and Nickless [11]. 10^{-2} *M* SAPH solution was prepared by dissolution of an appropriate amount of solid in hot ethanol. As supporting electrolyte the acetate buffer (pH 3—3.5) and the universal buffer series of Britton and Robinson [19] (pH 1.9—7.5) were used. Copper(II) standard solution, $1 \times 10^{-2} M$, prepared from analytical-reagent grade copper sulfate pentahydrate and then standardized titrimetrically [20].

Apparatus

DC polarography. The average current-voltage curves were recorded by a polarograph model a 3001 (Sargent-Welch). The electrode characteristics were $m = 1.7$ mg s^{-1} and $t = 4.5$ s at a mercury height of 57 cm.

DP polarography. A PAR, model 174, polarograph was fitted with a drop timer, model 172, and a Hewlett-Packard 7005 B X-Y recorder was attached. All experiments were carried out in a three-electrode configuration, employing a dropping-mercury electrode as the working electrode and a platinum wire as the counter electrode. The potentials were measured and reported versus S.C.E. The pH values of the solutions were measured with a Corning Model 12 pH-meter.

Results and Discussion

Effect of pH

The DC polarogram of 5×10^{-4} *M* SAPH at the dme consists of one or two waves depending on the pH of the supporting electrolyte. In buffer solutions of pH 1.8—7.5, the polarograms exhibit a single wave. At pH's 8.1, 8.5 and 9.2 the polarogram consists of two waves. On increasing the pH above 7.5, the first wave decreases gradually till it disappears almost completely at pH 10.2. The second wave, on the other hand, becomes developed with rise of pH and its height assumes a constant value at pH > 10.2.

When the DP technique is used, a single sharp peak is obtained in acidic medium (Fig. 1) and its height decreases on increasing the pH. Above pH 7.5, another peak is obtained whose height increases on increasing of

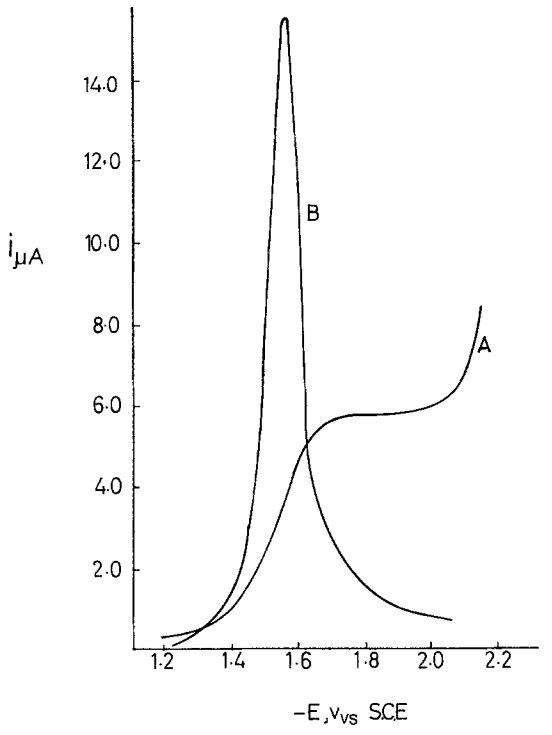


Fig. 1. Polarograms of SAPH at pH 3.5; *A:* DC polarogram of 5.0×10^{-4} *M* SAPH and *B:* DP polarogram of 5.0×10^{-6} *M* SAPH (scan rate = 2 mV/s, amplitude = 50 mV, $t = 0.5$ s)

pH. At pH 10.2 the first peak disappears completely and the height of the second peak almost pH-independent.

The $E_{1/2}$ and E_p of the reduction waves shift to more negative potentials with increasing pH, indicating that H^+ ions are involved in the electrode reaction.

Analysis of the first wave by applying the fundamental equation for the polarographic waves [21] showed that this wave is irreversible in nature as is evident from the values of kinetics parameters (αn_a, k_0 and ΔG^*) as shown in Table 1. We did not analyze the second wave because it was not attributed to the reduction of the SAPH molecule, and owing to the reduction of the hydrolysis product.

Table 1. Polarographic data obtained for the reduction of SAPH at dme in different buffer solution containing 40% ethanol

pH	$-E_{1/2}$ (V)	$-E_p$ (V)	$\frac{0.059}{\alpha n_a}$	αn_a	α ($n_a=1$)	α ($n_a=2$)	I^a	Slope of log i—log h plot	k_0 cm s^{-1}	ΔG^* kcal mol^{-1}
1.8	1.44	1.48	0.09	0.65	0.65	0.33	6.17	0.49	2.34×10^{-11}	90.8
3.5	1.56	1.52	0.11	0.53	0.53	0.27	6.03	0.53	1.68×10^{-14}	108.8
6.4	1.70	1.68	0.09	0.65	0.65	0.33	6.10	0.51	5.0×10^{-18}	129.4

[a] $I = i_d/cm^{2/3} t^{1/6}$, where I = diffusion current constant, i_d = diffusion current (μA), c = concentration of electrolyzed substance (mmol/l), m = flow-rate of mercury (mg s^{-1}), and t = drop time of the DME (s)

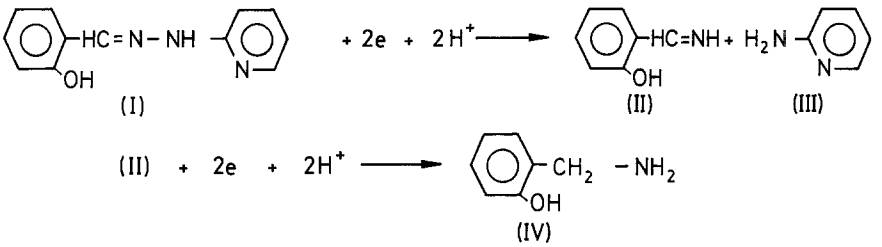
The effect of mercury height (h) on the polarogram indicated that the reduction process of SAPH is diffusion controlled. This is obvious from the values of the exponent X in the relation ($i_l = kh^X$) ranging between 0.49—0.54 and the perfect linearity of the i_d versus $\sqrt{h}$ plot.

Reduction Mechanism

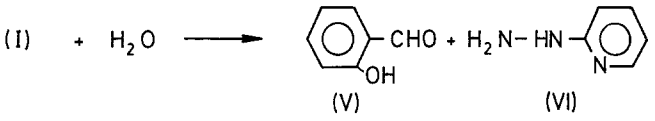
In order to elucidate the mechanism for the electrode reduction process, the number of electrons involved in the reduction waves at various pH's has been calculated. This can be done by the aid of the Ilkovic equation, provided that D, the diffusion coefficient of SAPH, may be calculated using the method previously described by us [17].

The process of reduction of SAPH can be represented as:

(a) In acidic solution. The number of electrons involved in the process of reduction of SAPH in acidic medium is 4 electrons. It is evident that the reduction involves cleavage of the N—N bond similar to the one proposed by Lund [13], Gomez et al. [16] and recently by us [17]:



(b) In alkaline medium. The height of the second wave corresponds to 2 electrons and this wave is attributed to the reduction of salicylaldehyde formed by the hydrolysis of the SAPH compound.



This process of hydrolysis is in accordance to that obtained by Temerk et al. [22, 23] for similar compounds.

The above mechanism is substantiated by the following:

(1) After disconnecting the electrolysis cell from the circuit, in acidic medium (pH 3.5), 2-aminopyridine was identified among the products of electrolysis by evaporating the ethanol and adding 4% HCl solution (ca. 5 ml) followed by extraction of organic compounds with diethylether several times. The aqueous layer was treated with NaOH solution and the presence of 2-aminopyridine was confirmed using IR measurements.

(2) Py—NH—NH_2 is reduced polarographically in acidic medium via the fission of N—N bond, and did not reduce in alkaline medium. This behaviour, in acidic medium, confirms the splitting of N—N bond in SAPH molecule (I) to give the products (II) and (III). On the other hand, the

N—N bond in SAPH (I) is not reduced in alkaline medium and (I) then hydrolyzed to give the corresponding aldehyde (V) and amine (VI).

(3) Coincidence of $E_{1/2}$ of the second wave (−1.70 V) with that of salicylaldehyde determined experimentally under the same conditions (− 1.68 V).

(4) Increase of the second wave height with rise of pH, while the first wave is decreasing. This decrease occurs as a result of hydrolysis.

(5) Identification of salicylaldehyde and 2-hydrazinopyridine in the hydrolysis product in alkaline medium.

SAPH was found to be reduced in aqueous alcoholic medium in a 4-electron reduction with cleavage of the N—N bond. These polarographic characteristics are similar to those previously reported by Lund [13] for classic hydrazones. On the other hand, the reduction of SAPH differs from that proposed for the reduction of pyridine-2-carbaldehyde-2-pyridylhydrazone (PAPH) [17], where the latter reduced by a two electron mechanism with cleavage of N—N bond. It is evident that the $E_{1/2}$ of the reduction wave for SAPH (−1.56 V at pH 3.5) has a more negative value than that for PAPH (−1.48 V at pH 3.5). This may be due to the electron attracting character of the two pyridine groups in PAPH, which decreases the electron density of the N-atom causing the reduction of PAPH to takes place at a somewhat less negative potential in comparison to SAPH.

Effect of Concentration of SAPH

It was found that the *dc* wave could have been used for analytical purposes, but the *dp* peak is much better resolved and of higher sensitivity. The i_d and i_p are plotted as functions of the concentration of the [SAPH] at pH 3.5 in presence of 40% ethanol; at this value of pH a single well-defined wave is obtained using *dc* and *dp* methods. Satisfactory linear relations passing through the origin are obtained. At higher concentration, a slight negative

Table 2. Effect of concentration of SAPH on i_d and i_p at pH 3.5 in 40% ethanol

DC method		DP method	
C(mM)	i_d/c (μA/mM)	C(mM)	i_p/c (μA/mM)
0.05	13.0	0.30	6.0
0.10	12.5	0.58	5.8
0.15	13.0	1.20	6.0
0.20	12.4	2.50	6.2
0.25	12.3	3.00	6.0
0.35	11.7	6.00	6.0
0.50	11.2	11.70	5.9
0.75	11.0	17.35	5.8
		24.00	6.0

deviation is obtained; this may be due to the adsorption of the depolarizer or its reduction product at higher concentration. The sensitivity of the DPP technique is demonstrated by the variation of the detection limit, which is amplified from 5×10^{-5} *M* for the classic technique to 5×10^{-8} *M* for DPP.

On the other hand, the applicability of the DPP method for the analysis is also supported by the constancy of the i_p/c values. This constancy is more apparent in the DPP than the DC method, as shown in Table 2. Hence, the DPP technique has been used successfully in the determination of SAPH.

It is evident that, when the concentration of SAPH increases, the $E_{1/2}$ and E_p change to more negative values. This phenomenon has been observed in the reduction of organic compounds [24—26] and is characteristic of irreversible processes.

Polarographic Behaviour of Copper(II)-SAPH Complex

Effect of pH. Polarograms were recorded at various pH values keeping other factors (such as metal ion concentration—0.5 mM—and SAPH concentration—0.5 *M*) constant. A well-defined wave was obtained in the pH range 1.9—7.5 in presence of 40% ethanol. It was found that the wave shape of the complex was unchanged and the half-wave potential of the complex is −0.58 V at pH 5.2, whereas under the same conditions the half-wave potential of copper(II) and SAPH are −0.15 V and −1.65 V, respectively. It was observed that the negative shift of $E_{1/2}$ was a maximum in acetate buffer at pH equal to 5.2. Hence, this pH value was chosen to study the polarographic behaviour of the Cu(II)-SAPH complex.

Effect of SAPH concentration. The values of $E_{1/2}$ and the slope of plot $-E$ versus $\log i/i_d - i$ for various concentrations of SAPH are given in Table 3. It is evident that $E_{1/2}$ shifted to a more negative value with increasing concentration of SAPH. The values of kinetic parameters such as αn_a (charge transfer coefficient), k_0 (rate constant) and ΔG^* (free energy change) were calculated using Koutecky's equation [27] and are reported in Table 3. It was found that the values of k_0 decrease and of ΔG^* increase with increasing concentration of SAPH indicating the tendency of the wave to move toward irreversibility.

Table 3. Polarographic data for Cu(II)-SAPH complex ($[Cu^{2+}] = 5 \times 10^{-4}$ *M*, pH = 5.2)

[SAPH], *M*	$-E_{1/2}$, V versus S.C.E.	αn_a	α ($n_a = 1$)	α ($n_a = 2$)	k_0 cm s^{-1}	ΔG^* kcal mol^{-1}
5.0×10^{-5}	0.30	0.95	0.95	0.47	4.49×10^{-7}	66.14
1.0×10^{-4}	0.32	0.88	0.88	0.44	4.09×10^{-8}	72.15
2.5×10^{-4}	0.40	0.76	0.76	0.38	1.26×10^{-8}	75.10
3.5×10^{-4}	0.52	0.65	0.65	0.32	1.18×10^{-9}	81.06
5.0×10^{-4}	0.58	0.59	0.59	0.29	1.67×10^{-10}	85.96
7.5×10^{-4}	0.58	0.51	0.51	0.25	8.75×10^{-11}	87.58
1.0×10^{-3}	0.58	0.43	0.43	0.21	4.29×10^{-12}	95.15

Effect of Cu(II) ions concentration. A calibration graph was constructed for the copper ion concentration versus diffusion current using 5×10^{-4} *M* SAPH at pH 5.2 in presence of 40% ethanol. The Cu(II)-SAPH ratio was determined by Yoe and Jones' method. The stoichiometry was found to be 1 : 1 as in the spectrophotometric study [11]. The polarographic results can be used for quantitative determination of Cu(II) ions. Good precision and accuracy were obtained in the analysis, as shown in Table 5.

Effect of ethanol concentration. The polarographic behaviour of Cu(II)-SAPH complex at pH 5.2 was tested in presence of different ethanol percentages (30—70%), where below 30% the ligand precipitated. It was found that the limiting current decreased and a large maximum appears with increasing ethanol percentage. This behaviour may be attributed to the surface activity of ethanol at the electrode-solution interface by an increase of the medium viscosity and by solvation [28].

Effect of foreign ions. The effect of various anions and metal ions on the polarogram of the Cu(II)-SAPH complex at pH 5.2 has been investigated. It was found that the $E_{1/2}$ value remained almost constant in the presence of acetate, phosphate, citrate, nitrate, borate and sulfate. Alkaline earth metals, Ca(II), Sr(II) and Ba(II) do not interfere. On the other hand, Co(II), Fe(II),

Table 4. Effect of diverse cations on the determination of copper (0.127 mg) using SAPH, pH 5.2, 40% ethanol

Metal ion	Amount of metal added (mg)	Amount of copper(II) found (mg)	Error, %
Co^{2+}	0.117	0.125	−1.57
	0.294	0.123	−3.15
	0.589	0.119	−6.30
Pb^{2+}	0.414	0.127	0.00
	1.036	0.128	+0.79
	2.072	0.135	+6.30
Zn^{2+}	0.130	0.127	0.00
	0.326	0.127	0.00
	0.653	0.127	0.00
La^{3+}	0.277	0.127	0.00
	0.694	0.127	0.00
	1.389	0.119	−6.30
Y^{3+}	0.177	0.127	0.00
	0.445	0.127	0.00
	0.889	0.123	−3.15
Ce^{3+}	0.280	0.127	0.00
	0.700	0.135	+6.30
	1.401	0.067	[a]
Fe^{2+}	0.111	0.138	+8.66
	0.279	0.146	+14.96
	0.558	[a]	[a]

[a] Higher error value

Cd(II), Pb(II), Ni(II) and Zn(II) undergo reduction at more negative potentials than Cu(II), thus they do not interfere. This advantage can be used to differentiate between Cu(II) ions and the above metal ions in SAPH solution because their $E_{1/2}$ potentials differ from that of Cu(II). The results obtained are presented in Table 4.

Mixed Polarograms of Copper and Cadmium

From the individual polarograms of copper and cadmium, it is possible to differentiate the two metals in SAPH solution, because their half-wave potentials differed by 0.3 V from each other. Consequently, a series of polarograms were recorded with synthetically mixed solutions of copper and cadmium and the i_d values referred to the respective calibration graph.

Table 5. Polarographic determination of copper(II) and cadmium(II) in a mixture, [SAPH] = 5.0×10^{-4} *M*, pH = 5.2

Sample	Amount added (mg)		Amount found[a] (mg)		Error, %	
	Copper	Cadmium	Copper	Cadmium	Copper	Cadmium
1	0.567	0.112	0.569	0.111	+0.35	−0.89
2	0.504	0.224	0.508	0.223	+0.79	−1.33
3	0.378	0.448	0.376	0.445	−0.53	−0.67
4	0.254	0.672	0.257	0.679	+1.10	+1.04
5	0.127	0.896	0.128	0.892	+0.78	−0.44
6	0.063	1.008	0.064	1.001	+1.58	−0.69

[a] Average of 5 determinations

The concentration of copper(II) and of cadmium(II) present in the mixed solution are given in Table 5. It was found that, in presence of excess cadmium ions, the minimum amount of copper(II) determined is 3.2 μg/ml.

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