POLAROGRAPHIC REDUCTION OF PHENYLAZOCHROMOTROPIC ACID DYES IN AQUEOUS BUFFER SOLUTIONS

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The polarographic reduction of phenylazochromotropic acid, and some of its derivatives (o-,m-, p-Cl; 2, 4- dichloro; m-, p-COOH; m-, p-OCH_3 ; p-NH_2 SO_2 and p-SO_3Na) has been studied in aqueous Britton- Robinson buffer series (pH 2-12) at the dme. Over the entire pH range, the reduction process occurs by an irreversible four-electron step corresponding to the reduction of the -N=N- centre to the amine stage. The polarograms of some compounds (VI, VII, VIII, IX, X, XI) in alkaline media show a polarographic maxium which can be suppressed by the addition of 0.002% of Triton X-100, but the reduction wave splits into two waves of unequal heights while the total reduction current remains constant. The Kinetic parameters ($K^{\circ}_{f,h}$, ΔG^{*}, αn_{a},) are determined and discussed.

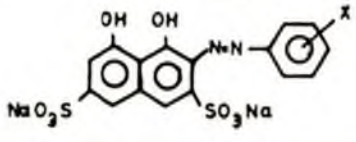
The reduction of several azo-compounds has been studied [1.5], but no study has been conducted on the reduction of chromotropic acids.

In present work, the current-voltage curves of eleven phenylazochromotropic dyes in aqueous buffer solutions at the dme are reported.

EXPERIMENTAL

Materials

Phenylazochromotropic acid dyes were either obtained from commercial sources (Schuchardt-Munchen) or prepared and purified by recommended procedures by coupling the diazotized amines with chromotropic acid in carbonate medium and recrystallizing the resulting crude product. Elemental analysis, and structural analysis confirm to the general formula:



X = H gives 2-phenylazo-chromotropic acid (I); o - Cl (II); p-Cl (III); m-CI (IV); o,p - dichloro (V); m-COOH (VI); p-COOH (VII); m-OCH_3 (VIII); p-OCH_3(IX); p-NH_2SO_2(X); p-SO_3Na (XI)

Stock solutions (1 mM) of each of these compounds were prepared by dissolving the accurate weight of the corresponding compound in the required volume of double-distilled water. Britton- Robinson buffers and maximum suppressor (Triton X-100), were prepard in twice distilled water.

The polarograms were recorded by using a pen recording radiometer polarograph (polariter PO4g type). The capillary characteristics at open circuit were, m= 2.4989 mg/sec and t= 3.5 sec/drop in deaeated 0.1 M KCl solution at a mercury height h=50 cm. All experiments were run at 25±0.5°C and the current values were corrected for the residual current. All the potentials were measured vs SCE. The solution was deareated with pure Argon. The pH was checked using a corning Research pH meter Model 12 with sensitivity ±0.05 pH units.

Number of electrons by controlled potential coulometry

The number of electrons involved in the overal reduction reaction of the depolarizer molecules at pH values 4 and 10, was computed with a Controlled Potential Coulometry (CPC) system Model 380 (Princton Applied Research corporation, PARC) which consists of a Model 173 Potentiostat, Model 179 Digital coulometer and cell system Model 377A. The cell system - a beaker with mercury pool (8 mL Hg) , platinum guaze counter electrode and saturated calomel reference eletrode - is designed to have a large electrode area to solution volume ratio along with provision for mechanically stirring the sample solution. The reference and counter eletrodes were well isolated from depolarizer

solution to prevent contamination and sample loss and to maintain proper cell current. A coulometric measurement is performed in deaerated solution by adding 10ml of Robinson buffer to the cell. The specified potential (at a point on the plateau of the polarographic wave) is applied to the cathode and electrolysis is continued until the background current attains a constant value. The residual depolarizer is thus eletrolysed and the display of the coulometer is now made to read zero. 0.5 ml of 0.0001 M of the depolarizer solution is then added and the electrolysis is allowed to completion. The charge passed (Q in coulombs) is read directly from the digital coulometer and the results are presented in Table 1. From these data, the number of electrons (n) involved in the overall reaction is computed using the relation: n= QM/FW, where Q is the charge (in coulombs) passed during electrolysis, M is the gram molecular weight of the depolaizer species, W is the weight of depolarizer species in grams present in the electrolysis cell and F is the faraday (.96487 coulombs/equivalent). The average number of electrons involved in the overall reduction process of each of the depolarizers species under investigation in acidic or alkaline medium is found to equal 4.0(Table 1).

TABLE 1

DATA OF CONTROLLED POTENTIAL COULOMETRY MEASUREMENTS OF SOME OF THE DEPOLARIZERS IN BRITTON-ROBINSON BUFFER SOLUTIONS

pH	Applied pot (V)	Depolarizer mg ml	Q Coulombs	No. of Electrons (n)	
				Calculated	Average
Parent Compound (I)			Mol. Wt = 468.38		
4.0 (a)	-0.60	0.2342	0.19185	3.98	3.92
10.0 (a)	-1.10	0.2342	0.18606	3.86	
Compound (III)	P-Cl		Mol. Wt = 502.83		
4.0 (a)	-0.60	0.2514	0.1879	3.89	3.86
10.0 (a)	-1.10	0.2514	0.185	3.83	
Compound (IX)	$P\text{-}OCH_3$		Mol. Wt = 498.41		
4.0 (a)	-0.60	0.2492	0.1919	3.98	3.91
10 (b)	-1.10	0.2492	0.1854	3.84	

n ≃ 4
(a) At the plateau of the single wave
(b) At the plateau of the second wave

RESULTS AND DISCUSSION

Effect of pH: The polarograms of 0.5 mM solutions of the above mentioned compounds were recorded in Britton-Robinson buffer solution (pH 2-12). This is found to consist of a single reduction wave of 4 electrons over the entire pH range (pH 2-12) (Fig. 1). The $E_{\frac{1}{2}}$ is pH-dependent and the limiting current is pH independent. The total reduction current indicates that the reduction of the N=N centre takes place to the amine stage [7]. In alkaline media (pH > 7), the polarograms of compounds VI,VII,VIII,IX,X and XI display a polarographic maximum of the first kind. This maximum is eliminated in presence of 0.002 %

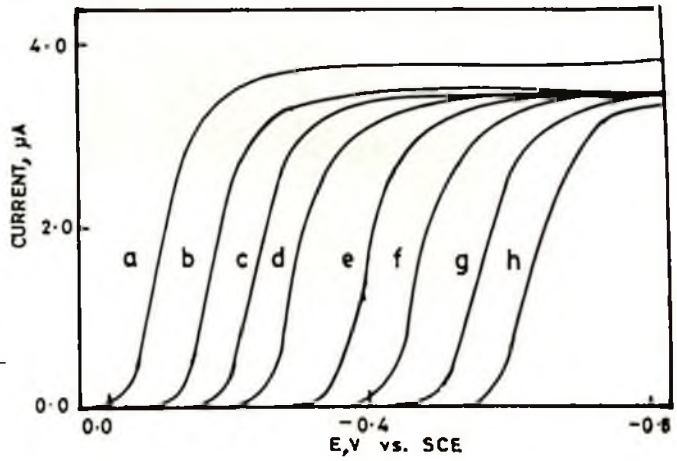


Fig.1 Phenylazochramotropic acid (I)

a) pH 2.4; b) pH 3.65; c) pH 5.25; d) pH d) pH 5.6; e)pH 7.27; f)pH 8.25; g)pH 10.65; h)pH 11.88

Triton X-100, but the reduction wave splits into two waves of unequal heights, but retaining the total reduction current practically constant and equal to that in acidic media (Fig.2). It is proable that the first wave represents a less hindered reduction of molecules that are on the uncovered part of the electrode surface whereas the shifted wave represents an inhibited reduction process taking place on the covered part.

The slight decrease of the total limiting current with increasing pH can be ascribed to the slower diffusion of the formed dye anions to the electrode surface or may be due to the increased viscosity of the medium.

Nature of the Waves

(a) The effect of pressure at mercury head on the limiting current reveals that value of the

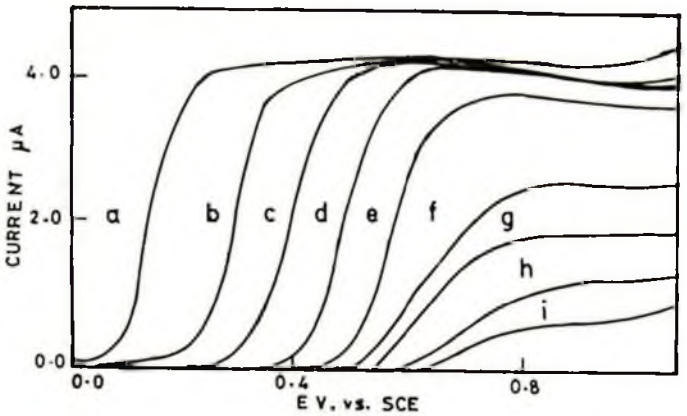


Fig. 2 p-COOH compound (VII)
a) pH 1.9; b) pH 3.5; c) pH 5.8; d) pH 6.19; e) pH 7.11; f) pH 7.67; g) pH 8.29; h) pH 10.55; i) pH 12.0

exponent x in the equation ($i_l = K\ h^x_{eff}$) between 0.4 and 0.75 indicating that the process of reduction of all the compounds under investigation is mainly diffusion-controlled with considerable kinetic adsorption components, both of which vary in magnitude according to the nature of substituent and the media applied.

(b) Anlysis of the reduction waves at the different pH values are made manually by measuring the reduction current point by point at different potential values (for every 0.01V) along the rising portion of the wave using Radiometer PO4g polarograph. The fundamental equation for irreversible polarographic waves [8] was applied :

$$E_{d.e} = E_{1/2} - \frac{0.0591}{\alpha n_a} \log [i/(i_d - i)]$$

The plots of E vs. log $[i/(i_d - i)]$ for the depolarizers under investigation at different pH values are straight lines (Fig.3) with slope (S_1) equal ($0.059/\alpha n_a$), Table 2. Values of the transfer coefficient (α) and αn_a indicate that the reduction process proceeds in an irreversable manner.

$E_{1/2}$ - pH curves

The plots of $E_{1/2}$ of the depolarizers under investigation as a function of pH consist of two segements (covering pH's 2-8 and 8-12) or three segements (covering pHs 2-5, 5-8, and 8-12), for different compounds (Fig.4). From

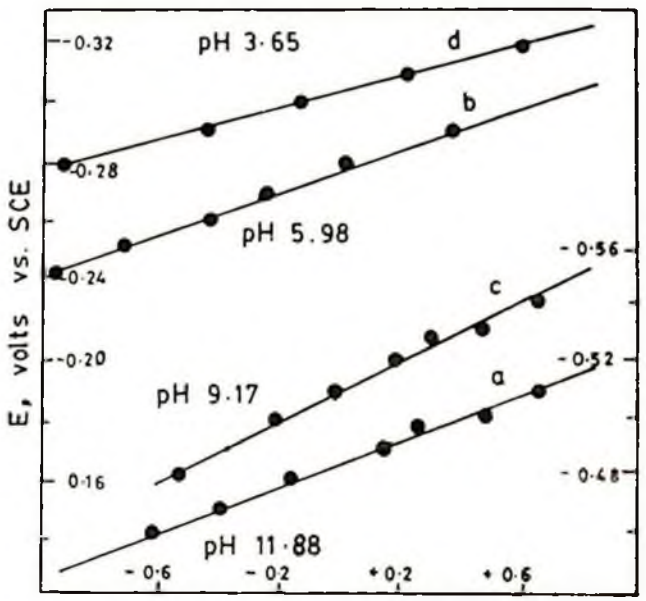


Fig. 3 Log [i/(i - i)] Compound (I)
a) pH 11.88;
b) pH 5.98;
c) pH 9.17;
d) pH 3.65;

the slopes (S_2) of $E_{1/2}$ - pH plots and the slopes (S_1) of E - log $[i/(i_d - i)]$ plots, the number of hydrogen ions (Z_{H^+}) participating in the rate-determining step is calculated using the relation :

$$Z_{H^+} = (\Delta E_{1/2} / \Delta \text{ pH}) \left(\frac{\alpha n_a}{0.059}\right) = S_2 / S_1$$

This is found to equal one (Table 2). The most probable values of α-parameter, given in Table 1, indicate that n = 2 and Z_{H^+} = 1.0. Accordingly, the rate-determining step of the electrode process would involve one proton (Z_{H^+} = 1.0) and two electrons (n_a = 2.0).

Reaction (2)

The total number of electron, involved in the electroreduction process of phenylazochromotropic acid compounds over the whole pH range (pH 2-12) has been calculated by the aid of Ilkovic equation [8] ($D^\circ = 1.4 \times 10^{-6}$ cm^2 /sec,

TABLE 2

POLAROGAPHIC DATA OBTAINED FOR THE REDUCTION OF PHENYLAZOCHROMOTROPIC ACID DYES IN DIFFERENT AQUEOUS BUFFER SOLUTION

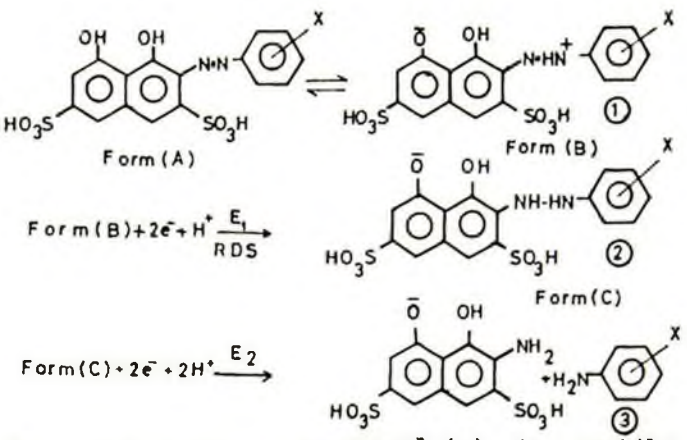
pH	$-E_{1/2}$ V	Slope, mV S_1	S_2	Z_H^+	αn_a	α $n_a=1$	$n_a=2$
	Phenylazochromotropic acid						
3.65	0.18	40	46	1.15	1.47	1.47	0.74
6.00	0.30	34	46	1.35	1.74	1.74	0.84
9.17	0.53	45	43	0.99	1.30	1.30	0.65
11.88	0.65	30	43	1.43	1.96	1.96	0.98
	m-chlorophenylazochromotropic acid						
3.54	0.32	76	100	1.32	0.78	0.78	0.39
6.31	0.57	63	67	1.06	0.94	0.94	0.47
9.21	0.69	38	34	0.89	1.56	1.56	0.78
	p-chorophenylazochromotropic acid						
3.52	0.33	96	125	1.3	0.61	0.61	0.31
6.20	0.56	57	75	1.3	1.03	1.03	0.51
9.40	0.72	47	28	0.6	1.26	1.26	0.63
11.98	0.80	40	28	0.7	1.47	1.47	0.74
	m-methoxyphenylazochromotropic acid						
3.55	0.32	106	113	1.06	0.56	0.56	0.28
6.32	0.55	79	69	0.87	0.74	0.74	0.37
	p-methoxyphenylazochromotropic acid						
3.64	0.32	150	150	1.00	0.39	0.39	0.20
6 63	0.56	59	60	1.06	1.00	1.00	0.50
9.38	0.76	66	69	1.04	0.90	0.90	0.45
	p-sulphonamidephenylazochromotropic acid						
3.59	0.34	92	107	1.16	0.64	0.64	0.32
6.27	0.55	47	60	1.17	1.26	1.26	0.63
9.13	0.70	28	20	0.71	2.11	2.11	1.05
	p-sulphonylphenylazochromotropic acid						
3.57	0.35	79	90	1.14	0.75	0.75	0.37
6.33	0.61	63	90	1.43	0.94	0.94	0.47

S_1 = slope of E ____ log $[i/(i_d - i)]$ plots

S_2 = slope of E 1/2 ____ pH plots

see Ref [9]) and is found to equal 4. This was confirmed by the controlled potential electrolysis measurements at mercury pool cathode. The data shown in Table (1) proved that in acidic or alkaline media, the number of electrons (n) involved in the reduction of a depolarizer species is found to equal 4, (Table 1).

According to the foregoing results, the reduction process can be represented as follows:



In acid media, reaction (1) is rapidly established and the depolarizer species are reduced at potentials E = E giving a single four-electron wave (steps 1-3). In alkaline media (pH 7) the polarograms of some of the depolarizers display a polarographic maximum which is eliminated by the addition of Triton X -100. The reduction wave splits into two waves.

Kinetic Parameters

The kinetics of the electrode reaction were determined by applying the equations due to Koutecky [8] and Delahay[10] and their simplified modification given by Issa et al [11]. These parameters include the rate constant ($k^\circ_{f,h}$), the energy of activation (ΔG^*) and $k^\circ_{f,h}\sqrt{D}$. The data shown in Table 3 indicate that the reduction takes place irreversibly and the degree of irreversibility increases as the pH of the medium increased. Values of ΔG^* increase with increasing pH indicating that the electron transfer becomes more difficult with the increasing pH.

Effect of Substituents on $E_{1/2}$

Substituent effects from polarographic study are based on shifts of half-wave potential with changed electronic character of the substituent.

The general trend observed in the present investigation is the shift of $E_{1/2}$ of phenylazochromotropic acid (I) to more negative values by introduction of different substituents in m- or p-position with respect to the N=N centre (however in case of the p- OCH_3 substituent, the shift is in the opposite direction). In addition to this, the formation of intermolecular hydrogen bond through the -N=N- centre and the o-hydroxy group [12,13] will play a part in the $E_{1/2}$ shift to less negative potentials.

TABLE 3

KINETIC PARAMETERS OF PHENYLAZOCHROMOTROPIC ACID DYES OF DIFFERENT AQUEOUCS BUFFER SOLUTIONS

The data is all for single waves

pH	k (Cm/sec)	K	$D^{\circ}_{1/2}$	ΔG° (k.cal/mol)
phenylazochromotropic acid				
3.65	5.75×10^{-2}	4.83×10^{-1}		36.6
6.00	8.13×10^{-5}	6.8×10^{-4}		53.1
9.17	8.13×10^{-10}	6.8×10^{-7}		82.0
11.88	2.29×10^{-17}	1.9×10^{-14}		125.6
m-chlorophenylazochromotropic acid				
3.54	1.53×10^{-4}	8.7×10^{-2}		51.5
6.31	1.99×10^{-8}	1.1×10^{-5}		73.9
9.21	1.77×10^{-15}	6.7×10^{-13}		115.7
11.84	2.39×10^{-25}	1.5×10^{-22}		171.4
p-chlorophenylazochromotropic acid				
3.52	2.45×10^{-4}	1.4×10^{-1}		50.3
6.20	4.45×10^{-9}	2.5×10^{-6}		77.7
9.40	7.76×10^{-14}	4.4×10^{-11}		105.2
11.98	1.70×10^{-17}	9.7×10^{-15}		126.4
p-carboxyphenylazochromotropic acid				
3.54	1.36×10^{-4}	9.6×10^{-2}		51.3
6.29	6.16×10^{-8}	4.3×10^{-5}		71.1
m-methoxyphenylazochromotropic acid				
3.55	1.66×10^{-4}	1.5×10^{-1}		51.3
6.32	1.32×10^{-7}	1.2×10^{-4}		69.2
p-methoxyphenylazochromotropic acid				
3.64	4.57×10^{-4}	3.9×10^{-1}		48.7
6.63	2.24×10^{-10}	1.9×10^{-7}		85.2
p-sulphonamidephenylazochromotropic acid				
3.59	1.99×10^{-4}	1.2×10^{-1}		50.8
6.30	1.86×10^{-9}	1.1×10^{-6}		79.9
9.13	5.89×10^{-19}	3.5×10^{-16}		134.8
p-sulphonylphenylazochromotropic acid				
3.57	1.1×10^{-4}	6.6×10^{-1}		52.3
6.33	3.8×10^{-9}	2.9×10^{-6}		78.1

According to Zuman [14] the shift of $E_{1/2}$ relative to that of parent compound is due to the additive polar (p), steric (S) and mesomeric (M) effects of the various substituents. Modified Hammet equation [8,15] in the most generally used form for the above expression is as

$$E_{1/2}(x) - E_{1/2}(H) = \rho_{\pi R}\sigma_x$$

This equation is used for benzenoid compounds bearing a polarographically active group (R) in the side chain and a substituent (X) in the m- or p-position. ρ is the reaction constant expressed in volts, characterizing the reducible group (R) σ_x is the Hammet total polar substituent constant depending only on the type and position of (X).

The plot of $E_{1/2}$ of phenylazochromotropic acid

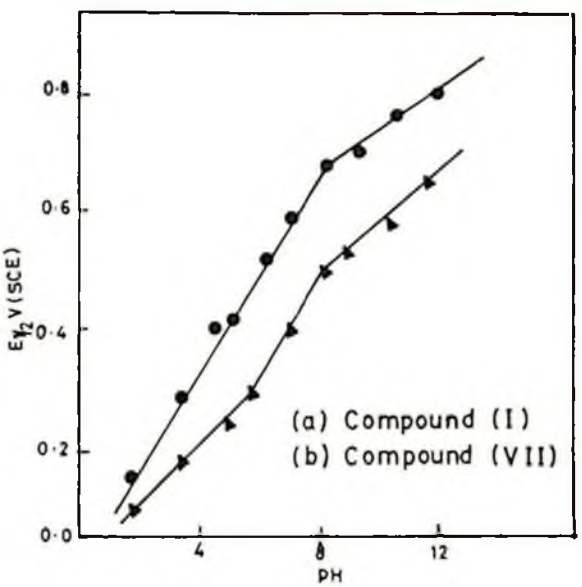


Fig. 4 $E_{1/2}$ vs. pH plots for compounds I & VII

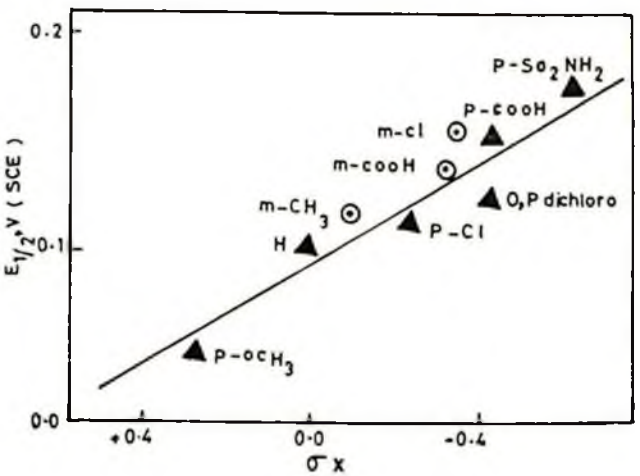


Fig. 5 Hemmet plots of phenyl azochromotropic acids

and its derivatives, at acidic or alkaline pH values, as a function of σx yields a satisfactory linear relationship with negative slope ($\rho_{\pi,R}$) amounting to 0.1 volts (Fig. 5) Negative value of $\rho_{\pi,R}$ indicates that the electroreduction of -N=N-centre is hindered by the present substituents and corresponds to electrophilic atack [11] in the potential - determining step.

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