

ELECTROCHEMICAL STUDIES ON SOME AZODISPERSE DYE STUFFS AZOCREATININE

IBRAHIM M.M. KENAWY

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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Polarographic behaviour of some azodisperse dye stuffs; 4,4'(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one) diphenyl (A); 3,3'-dimethoxy-4,4'-(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one) diphenyl (B); 4,4'(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one)-2,2'-stilbene disulphonic acid(C) and 2',3'-dimethyl-4-(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one)-benzidine (D) have been studied in universal buffer solution containing 10% (v/v) DMF over pH range 2-12. Millicoulometric method was employed for the determination of the total number of electrons in the reduction process, and the kinetic parameters $\propto k_{r,h}$ and ΔG^\ddagger were evaluated. The proposed reduction mechanism was based on the results obtained. The d.c polarography was used to develop an analytical method for azodisperse dye determination in the micro scale.

Key words: Azodisperse, Dyestuffs, Polarography, Electrochemistry.

Introduction

Azodisperse dyes have attracted considerable attention recently; azocreatinine derivatives are widely used in acetate fibers [1-3], woolen fabrics [4] and other synthetic polymer fibers [5]. Further, because of their substituted imidazoles, they have biochemical importance as imidazole plays important roles in living systems, in vitamin B₁₂, biotin and as chemotherapeutic agents [6].

Polarographic methods were used advantageously in determination of azobenzene and heterocyclic azo compounds [7-13]. From these facts and in continuation of our earlier work, we describe in the present paper the reduction behaviour of azo disperse dyes (azocreatinine A-D) and their determination in trace level by highly sensitive polarographic method.

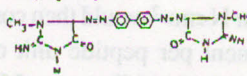
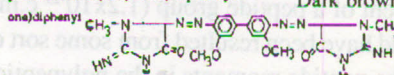
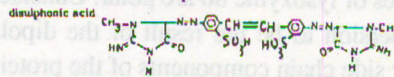
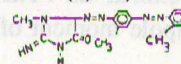
Experimental

Synthesis of azodisperses dye derivatives (A-D) was carried out as mentioned previously [1]. The purity of the samples was checked by TLC control, melting point, λ_{max} and molar absorptivity (Table 1). Analar grade samples were used for preparing the supporting electrolyte Britton-Robinson buffer [14], (pH 2-12) in bidistilled water. Stock solutions were prepared by dissolving the required amount of the dye in dimethyl formamide (DMF) and making up to volume with the supporting electrolytes to obtain the desired concentration. The test solution was purged with purified nitrogen for 15 mins. before the polarograms were recorded. All experiments were carried out at $25 \pm 0.1^\circ$. Polarograms were recorded with a polarographic analyzer Polarecord E506 Metrohm (Herisau/Switzerland) with polarographic stand E505A, 3 electrode system composed of DME (flow rate 1.6 mg/s, $t = 2.25$ s at a mercury pressure height of 50 cm), as a working electrode,

$Ag^\circ/AgCl_{(s)}$, $KCl_{(s)}$ as a reference electrode and a platinum wire auxiliary electrode. The Millicoulometric measurements at applied potentials were carried out using a Metrohm 612 VA Scanner coupled with a Metrohm 611 VA potentiostat and graphic WX 4421 XY recorder.

All the pH measurements were made using HANNA Instrument, (Italy) pH-meter. The spectra were recorded using a Perkin-Elmer Model Lambda 3B uv/vis spectrophotometer.

TABLE 1. AZODISPERSE DYESTUFFS, THEIR MELTING POINT, COLOUR OF CRYSTAL, WAVES LENGTHS IN DIFFERENT SOLVENTS AND LOG MOLAR ABSORPTIVITY.

Name of dye, structure	M.p., (°C) Colour of crystal	Wave length			
		Ethanol λ_{max} (nm)	log ϵ	DMF λ_{max} (nm)	log ϵ
Dye (A): 4,4'(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one)diphenyl	(225) Brown	Yellow 430	4.93	405	5.18
		295	3.72	283	5.13
Dye (B): 3,3'-dimethoxy-4,4'-(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one)diphenyl	(230) Dark brown	Yellow 420	4.71	415	5.01
		290	3.43	300	5.01
Dye (C): 4,4'-(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one) 2,2'-stilbene disulphonic acid	(235) Brown	Pale yellow 408	4.05	400	4.85
		275	3.40	295	4.10
Dye (D): 2',3'-dimethyl-4-(5-azo-2-imino-1,5-dihydro-1-methylimidazol-4(H)-one)-benzidine	(150) Yellowish brown	Yellow 400	4.82	430	4.73
		290	3.37	340	5.04

Results and Discussion

The polarographic behaviour of 0.05 mM of the compounds under investigation consists of a single welldefined wave over the entire pH range studied (Figs. 1 and 2). The height of the waves are practically pH-independent within the pH range 2-9.1. In solutions of pH > 9.1, the height of the wave increases with increasing the pH values for A and B dyes, while it remains constant in case of (C) and decreases in case of (D) (Table 2). The $E_{1/2}$ -pH curves for the azo dye compounds are illustrated in Fig. 3. The curves exhibit linear correlation constants with two segments. This behaviour may be attributed to the change in the nature of depolarizer species on increasing the pH values of the electrolytic medium and/or the transfer coefficient value (∞). From the slope (S_2) of these segments as well as the logarithmic analysis [15] (Slope S_1), the number of protons participating in rate determining step can be determined (Table 3).

$$Z_H^+ = \frac{(dE_{1/2} \cdot dpH)/(0.0591)}{\frac{\infty_{na}}{S_1}}$$

The number of protons (Z_H^+) for azo compound in question is found practically to be one within the pH range used.

The transfer coefficient (∞) was evaluated for the probable values of the ratio (Z_H^+/n_a) according to the following relationship [15].

TABLE 2. POLAROGRAPHIC DATA FOR THE REDUCTION WAVES OF 0.05 mM AZODISPERSE DYES IN UNIVERSAL BUFFER CONTAINING 10% (v/v) DMF.

pH	i_d	$-E_{1/2} V_2$ Ag, AgCl/KCl(s)	Slope (volt ⁻¹) (S_1)	∞	
				$n_a = 1$	$n_a = 2$
Dye A					
3.24	0.39	0.77	0.080	0.74	0.37
5.02	0.39	0.95	0.074	0.80	0.40
7.00	0.45	1.14	0.059	1.00	0.50
9.10	0.54	1.28	0.063	0.94	0.47
11.10	0.84	1.36	1.101	0.59	0.30
Dye B					
3.24	0.36	0.76	0.099	0.60	0.30
5.02	0.49	0.96	0.068	0.87	0.44
7.00	0.49	1.14	0.063	0.98	0.49
9.10	0.51	1.22	0.075	0.79	0.40
11.10	0.81	1.40	0.066	0.90	0.45
Dye C					
3.24	0.23	0.63	0.091	0.63	0.32
5.02	0.27	0.87	0.112	0.53	0.27
7.00	0.27	1.22	0.072	0.82	0.41
9.10	0.26	1.33	0.146	0.41	0.21
11.10	0.27	1.45	0.054	0.63	0.32
Dye D					
3.24	0.23	0.22	0.040	0.66	0.33
5.02	0.18	0.35	0.090	0.66	0.33
7.00	0.107	0.51	0.11	0.57	0.29
9.10	0.080	0.61	0.105	0.57	0.29
11.10	0.060	0.71	0.100	0.59	0.30

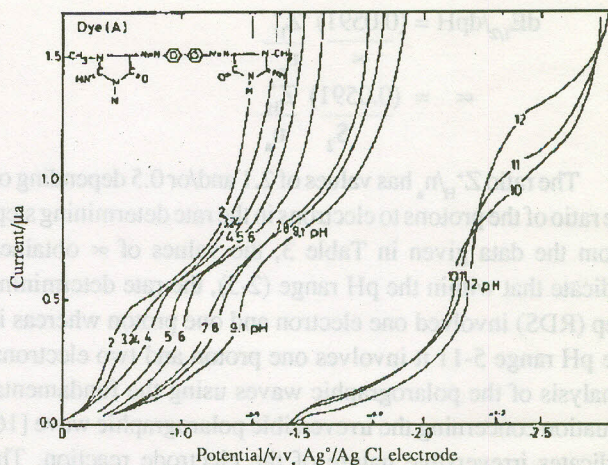


Fig. 1. Typical dc polarogram of 0.05 mM dye (A) in universal buffer pH 2-12, containing 10% DMF.

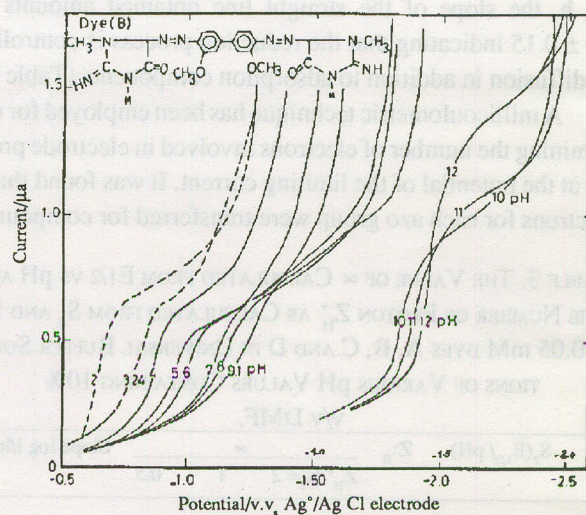


Fig. 2. Typical dc polarogram of 0.05 mM dye (B) in universal buffer pH 2-12, containing 10% DMF.

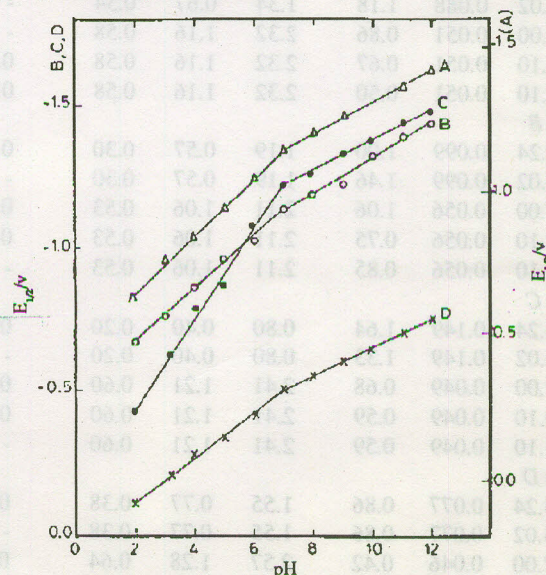


Fig. 3. ($E_{1/2}$)-pH plot, influence of pH on half wave potentials of dyes A, B, C and D.

$$dE_{1/2}/dpH = \frac{(0.0591) Z_H^+}{\alpha n_a}$$

$$\alpha = \frac{(0.0591) Z_H^+}{S_2 n_a}$$

The ratio Z_H^+/n_a has values of 2.1 and/or 0.5 depending on the ratio of the protons to electrons in the rate determining step. From the data given in Table 3, the values of α obtained indicate that within the pH range (2-5), the rate determining step (RDS) involved one electron and one proton whereas in the pH range 5-11 it involves one proton and two electrons. Analysis of the polarographic waves using the fundamental equation concerning the irreversible polarographic wave [16] indicates irreversible nature of the electrode reaction. The nature of the reduction waves was tested by plotting $\log i_1$ vs $\log h$, the slope of the straight line obtained amounts to 0.8 ± 0.15 indicating that the reduction process is controlled by diffusion in addition to adsorption components (Table 3).

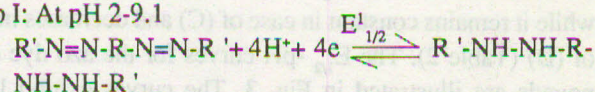
A millicoulometric technique has been employed for determining the number of electrons involved in electrode process at the potential of the limiting current. It was found that 4 electrons for each azo group were transferred for compounds

TABLE 3. THE VALUE OF α CALCULATED FROM $E_{1/2}$ VS pH AND THE NUMBER OF PROTON Z_H^+ AS CALCULATED FROM S_2 AND S_1 OF 0.05 mM DYES A, B, C AND D IN UNIVERSAL BUFFER SOLUTIONS OF VARIOUS pH VALUES CONTAINING 10% v/v DMF.

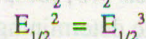
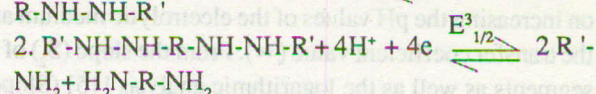
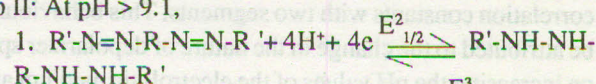
pH	$S_2(E_{1/2}/pH)$	Z_H^+	α			Slope $\log i/\log h$
			$Z_H^+/n_a=2$	1	0.5	
Dye A						
3.24	0.088	1.10	1.34	0.67	0.34	0.78
5.02	0.088	1.18	1.34	0.67	0.34	-
7.00	0.051	0.86	2.32	1.16	0.58	-
9.10	0.051	0.67	2.32	1.16	0.58	0.79
11.10	0.051	0.50	2.32	1.16	0.58	0.73
Dye B						
3.24	0.099	1.00	1.19	0.57	0.30	0.84
5.02	0.099	1.46	1.19	0.57	0.30	-
7.00	0.056	1.06	2.11	1.06	0.53	0.67
9.10	0.056	0.75	2.11	1.06	0.53	0.63
11.10	0.056	0.85	2.11	1.06	0.53	-
Dye C						
3.24	0.149	1.64	0.80	0.40	0.20	0.48
5.02	0.149	1.33	0.80	0.40	0.20	-
7.00	0.049	0.68	2.41	1.21	0.60	0.93
9.10	0.049	0.59	2.41	1.21	0.60	0.95
11.10	0.049	0.59	2.41	1.21	0.60	-
Dye D						
3.24	0.077	0.86	1.55	0.77	0.38	0.91
5.02	0.077	0.86	1.55	0.77	0.38	-
7.00	0.046	0.42	2.57	1.28	0.64	0.81
9.10	0.046	0.44	2.57	1.28	0.64	0.72
11.10	0.046	0.46	2.57	1.28	0.64	-

A and B whereas from compound C and D, 2 electrons from each azo group were obtained. Controlled potential electrolysis of azodisperse dyestuff indicates that the product was amino and hydrazo groups due to the change of colour of depolizer. Also, spot test for the products was carried out [17]. The general scheme suggested for the reduction of the azo center was as follows:

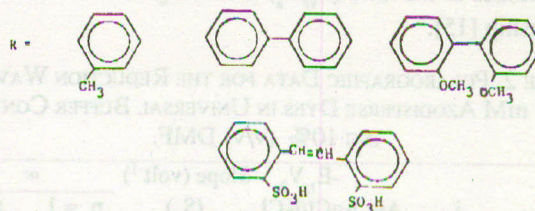
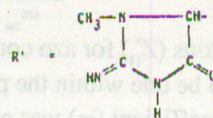
Step I: At pH 2-9.1



Step II: At pH > 9.1,



whereas for compound C and D, the reduction process can be expressed as step I only, where



For the dyes under consideration as evidenced by their polarographic behaviour; the reduction and cleavage of dye A and B occurs along the two N=N bands in alkaline solution (pH > 9.1), this accompanied by the increase in the limiting current, whereas for dye C and D the process of the reduction can be represented as shown in step (1). The variation in the reduction limiting current for dye C and D can be attributed to be difference in the structure between each compound.

In order to confirm the irreversibility of the reduction process, the kinetic parameter $n_a, \alpha, k_{f,h}^0$ and ΔG^* where α is the transfer coefficient, $k_{f,h}^0$ is rate constant at $E = 0$, Diffusion coefficient (D) and ΔG^* is the free energy of activation, were computed by aid of the Koutecky equation [18]. From Table 2, it is clear that the values of the heterogeneous forward rate constant $k_{f,h}^0$ decrease with increasing the pH where Z_H^+ decrease as shown in Table 4. This trend shows that the electrode reaction becomes more irreversible with increasing pH of the solution. Also, the activation energy values (ΔG^*) increase with pH values confirming the increase of irreversibility of the electrode reaction.

Analysis. In this study the dc polarography was em-

ployed as an absolute method of analysis by rearrangement of Ilkovic equation as follows:

$$I = \frac{I_d}{\text{cm}^{2/3} t^{1/6}}$$

where I is the so-called diffusion current constant. At pH 7, the lower detection limits from compound A and B were found to be $1 \times 10^{-6} \text{M}$ (Table 5). Regression analysis of the results gives the following equation:

$$\text{Dye A } C = 2.1 \times 10^{-2} + 8.65 i_d \text{ (0.99995)}$$

$$\text{Dye B } C = 4.6 \times 10^{-4} + 0.1 i_d \text{ (0.99987)}$$

TABLE 4. KINETIC PARAMETERS DATA FOR THE REDUCTION WAVES OF 0.05 mM AZODISPERSE DYES IN UNIVERSAL BUFFER CONTAINING 10% DMF.

pH	$K_{f,h}^\circ$ (ms^{-1})	$k_{f,h}^\circ D^{1/2}$ ($k = K_{f,h}^\circ$)	ΔG° (k cal mol^{-1})
Dye A			
3.24	7.03×10^{-14}	3.27×10^{-9}	105.5
5.04	3.29×10^{-16}	1.53×10^{-13}	118.9
7.00	1.14×10^{-22}	5.30×10^{-20}	156.3
11.10	9.93×10^{-24}	4.62×10^{-21}	162.4
Dye B			
3.24	3.40×10^{-11}	1.64×10^{-8}	90.0
5.02	8.36×10^{-17}	4.03×10^{-14}	122.4
7.00	8.95×10^{-25}	4.31×10^{-22}	168.4
11.10	6.95×10^{-24}	3.35×10^{-21}	163.3
Dye C			
3.24	1.71×10^{-10}	8.02×10^{-8}	85.9
5.02	2.83×10^{-11}	1.33×10^{-8}	90.4
7.00	1.96×10^{-20}	9.21×10^{-18}	143.3
11.10	4.70×10^{-19}	2.21×10^{-16}	135.4
Dye D			
3.24	4.58×10^{-6}	2.06×10^{-3}	60.3
5.02	5.38×10^{-7}	2.42×10^{-4}	65.7
7.00	6.62×10^{-9}	2.98×10^{-6}	76.7
11.10	5.90×10^{-10}	2.60×10^{-7}	82.7

TABLE 5. CORRELATION BETWEEN THE CONCENTRATION AND LIMITING CURRENT IN BOTH DYESTUFF A AND B AT pH 7.

Concen- tration mM	Dye A		Dye B	
	i_d (μA)	$I = i_d / c \cdot m_{2/3} \cdot t_{1/6}$	i_d (μA)	$I = i_d / c \cdot m_{2/3} \cdot t_{1/6}$
0.025	0.22	5.61	0.24	6.13
0.050	0.45	5.75	0.49	6.26
0.100	0.90	5.75	0.95	6.26
0.200	1.75	5.59	1.95	6.23
0.300	2.65	5.63	2.88	6.08
0.400	3.45	5.51	3.86	6.15
0.500	4.35	5.55	4.78	6.10
0.600	5.25	5.59	5.69	6.05
0.700	6.05	5.52	6.68	6.09
0.800	6.95	5.55	7.77	6.19
\bar{X}	—	5.61	—	6.15
SD	—	0.86	—	0.076
RSD	—	1.54(%)	—	1.24(%)

where r is the linear correlation coefficient of the calibrated data. Such linear dependence confirms the analytical determination of A and B within the concentration range 0.025-0.8 mM (Table 5). Also, good straight lines are obtained on plotting the i_d values against the depolarizer concentration at pH's 3.24, 7 and 9.1 of azocreatinines dyes C and D (Table 6).

TABLE 6. EFFECT OF AZOCREATININES (DYES C AND D) CONCENTRATION IN UNIVERSAL BUFFER SOLUTION ON LIMITING CURRENT.

Dye	pH	c(mM)	i_d (μA)	i_d/c	X average SD RSD(%)
Dye C	3.24	0.025	0.11	4.40	0.99993 r 4.495 X 0.072 SD 1.59 RSD%
		0.05	0.23	4.60	
		0.10	0.45	4.50	
		0.20	0.90	4.50	
		0.30	1.36	4.54	
		0.40	1.82	4.55	
	7.00	0.025	0.14	5.60	0.99986 5.571 0.137 2.47(%)
		0.05	0.27	5.80	
		0.10	0.54	5.70	
		0.20	1.13	5.65	
		0.30	1.65	5.50	
		0.40	2.17	5.43	
		0.50	2.70	5.44	
		0.60	3.27	5.45	
9.1	0.025	0.13	5.20	0.99997 5.223 0.025 0.48(%)	
	0.05	0.26	5.20		
	0.10	0.52	5.20		
	0.20	1.05	5.25		
	0.30	1.56	5.23		
	0.40	2.10	5.25		
Dye D	3.24	0.01	0.048	4.8	0.99986 4.703 0.097 2.07(%)
		0.025	0.12	4.8	
		0.050	0.23	4.8	
		0.08	0.37	4.63	
		0.10	0.47	4.70	
		0.12	0.55	4.59	
	7.00	0.010	0.021	2.10	0.99999 2.128 0.016 0.75(%)
		0.025	0.052	2.12	
		0.05	0.107	2.14	
		0.10	0.217	2.14	
		0.15	0.320	2.13	
		0.20	0.428	2.14	
		0.25	0.535	2.14	
		0.30	0.642	2.14	
9.10	0.010	0.016	1.60	0.99999 1.616 0.015 0.94(%)	
	0.025	0.040	1.60		
	0.050	0.080	1.60		
	0.100	0.162	1.62		
	0.150	0.245	1.63		
	0.200	0.325	1.63		
0.250	0.407	1.63			

r = linear correlation, X = average value, SD = standard deviation and RSD = relative standard deviation.

Thus, one can conclude that the limiting current is directly proportional to the concentrations of depolarizer which indicates an accurate application of Ilkovic equation in acidic, neutral and alkaline medium using universal buffer. These results are supported by constancy of the values of the current concentration coefficient (i_p/c) and good SD and relative standard deviation RSD (%) in Table 6.

In conclusion the method is more sensitive, accurate and precise and can be readily adopted for determination of azodisperse-dyes, azocreatinine AADMI.

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TABLE 6. CORRELATION BETWEEN THE CONCENTRATION AND LIMITING CURRENT IN BOTH DYE A AND B AT pH 7.

Concn. (mm)	Dye A		Dye B	
	i_p (mA)	i_p/c (mA/mM)	i_p (mA)	i_p/c (mA/mM)
0.000	0.02	0.02	0.13	0.13
0.100	0.02	0.02	0.26	0.26
0.200	0.02	0.02	0.52	0.52
0.300	0.02	0.02	0.78	0.78
0.400	0.02	0.02	1.04	1.04
0.500	0.02	0.02	1.30	1.30
0.600	0.02	0.02	1.56	1.56
0.700	0.02	0.02	1.82	1.82
0.800	0.02	0.02	2.08	2.08
0.900	0.02	0.02	2.34	2.34
1.000	0.02	0.02	2.60	2.60
1.100	0.02	0.02	2.86	2.86
1.200	0.02	0.02	3.12	3.12
1.300	0.02	0.02	3.38	3.38
1.400	0.02	0.02	3.64	3.64
1.500	0.02	0.02	3.90	3.90
1.600	0.02	0.02	4.16	4.16
1.700	0.02	0.02	4.42	4.42
1.800	0.02	0.02	4.68	4.68
1.900	0.02	0.02	4.94	4.94
2.000	0.02	0.02	5.20	5.20
2.100	0.02	0.02	5.46	5.46
2.200	0.02	0.02	5.72	5.72
2.300	0.02	0.02	5.98	5.98
2.400	0.02	0.02	6.24	6.24
2.500	0.02	0.02	6.50	6.50
2.600	0.02	0.02	6.76	6.76
2.700	0.02	0.02	7.02	7.02
2.800	0.02	0.02	7.28	7.28
2.900	0.02	0.02	7.54	7.54
3.000	0.02	0.02	7.80	7.80
3.100	0.02	0.02	8.06	8.06
3.200	0.02	0.02	8.32	8.32
3.300	0.02	0.02	8.58	8.58
3.400	0.02	0.02	8.84	8.84
3.500	0.02	0.02	9.10	9.10
3.600	0.02	0.02	9.36	9.36
3.700	0.02	0.02	9.62	9.62
3.800	0.02	0.02	9.88	9.88
3.900	0.02	0.02	10.14	10.14
4.000	0.02	0.02	10.40	10.40
4.100	0.02	0.02	10.66	10.66
4.200	0.02	0.02	10.92	10.92
4.300	0.02	0.02	11.18	11.18
4.400	0.02	0.02	11.44	11.44
4.500	0.02	0.02	11.70	11.70
4.600	0.02	0.02	11.96	11.96
4.700	0.02	0.02	12.22	12.22
4.800	0.02	0.02	12.48	12.48
4.900	0.02	0.02	12.74	12.74
5.000	0.02	0.02	13.00	13.00

TABLE 7. CORRELATION BETWEEN THE CONCENTRATION AND LIMITING CURRENT IN BOTH DYE A AND B AT pH 7.

Concn. (mm)	Dye A		Dye B	
	i_p (mA)	i_p/c (mA/mM)	i_p (mA)	i_p/c (mA/mM)
0.000	0.02	0.02	0.13	0.13
0.100	0.02	0.02	0.26	0.26
0.200	0.02	0.02	0.52	0.52
0.300	0.02	0.02	0.78	0.78
0.400	0.02	0.02	1.04	1.04
0.500	0.02	0.02	1.30	1.30
0.600	0.02	0.02	1.56	1.56
0.700	0.02	0.02	1.82	1.82
0.800	0.02	0.02	2.08	2.08
0.900	0.02	0.02	2.34	2.34
1.000	0.02	0.02	2.60	2.60
1.100	0.02	0.02	2.86	2.86
1.200	0.02	0.02	3.12	3.12
1.300	0.02	0.02	3.38	3.38
1.400	0.02	0.02	3.64	3.64
1.500	0.02	0.02	3.90	3.90
1.600	0.02	0.02	4.16	4.16
1.700	0.02	0.02	4.42	4.42
1.800	0.02	0.02	4.68	4.68
1.900	0.02	0.02	4.94	4.94
2.000	0.02	0.02	5.20	5.20
2.100	0.02	0.02	5.46	5.46
2.200	0.02	0.02	5.72	5.72
2.300	0.02	0.02	5.98	5.98
2.400	0.02	0.02	6.24	6.24
2.500	0.02	0.02	6.50	6.50
2.600	0.02	0.02	6.76	6.76
2.700	0.02	0.02	7.02	7.02
2.800	0.02	0.02	7.28	7.28
2.900	0.02	0.02	7.54	7.54
3.000	0.02	0.02	7.80	7.80
3.100	0.02	0.02	8.06	8.06
3.200	0.02	0.02	8.32	8.32
3.300	0.02	0.02	8.58	8.58
3.400	0.02	0.02	8.84	8.84
3.500	0.02	0.02	9.10	9.10
3.600	0.02	0.02	9.36	9.36
3.700	0.02	0.02	9.62	9.62
3.800	0.02	0.02	9.88	9.88
3.900	0.02	0.02	10.14	10.14
4.000	0.02	0.02	10.40	10.40
4.100	0.02	0.02	10.66	10.66
4.200	0.02	0.02	10.92	10.92
4.300	0.02	0.02	11.18	11.18
4.400	0.02	0.02	11.44	11.44
4.500	0.02	0.02	11.70	11.70
4.600	0.02	0.02	11.96	11.96
4.700	0.02	0.02	12.22	12.22
4.800	0.02	0.02	12.48	12.48
4.900	0.02	0.02	12.74	12.74
5.000	0.02	0.02	13.00	13.00

RSD = relative standard deviation. \bar{X} = average value, SD = standard deviation and i_p = limiting current.

RSD = relative standard deviation. \bar{X} = average value, SD = standard deviation and i_p = limiting current.