

DC-polarography and cyclic voltammetric studies of some mono and bis azo compounds derived from aromatic primary amines and 2,3-dihydroxynaphthalene in aqueous solutions

R. EL-SAYED, ABDALLAH A. MOHAMED and E.M. MABROUK*

Department of Chemistry, Faculty of Applied Science, Umm Al-Qura University,
Makkah Al-Mukarramah (Saudi Arabia).
E-mail: drsayedmabrouk@yahoo.com

(Received: September 02, 2010; Accepted: December 11, 2010)

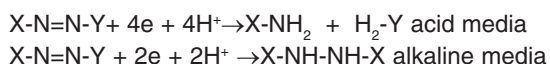
ABSTRACT

The DC and CV behavior of some mono and bis azo compounds based on aromatic primary amines and 2,3-dihydroxynaphthalene was investigated in Britton-Robinson buffer series. The obtained results indicated that these compounds undergo an irreversible reduction leading to cleavage of the N=N center with the formation of amine compounds. However, for the derivative m-CH₃ on the aniline ring in alkaline solutions, the reduction stops at the stage for saturation of the N=N center. The E_{1/2} and E_p shifted to more negative potentials with rise of pH and the values of i_i are not much influenced except for the m-CH₃ derivative. The total number of electrons involved in the reduction process was determined by controlled potential coulometry and calculated from Ilkovic equation. The effect of substituents on the electrode pathway was discussed. Based on the data obtained the electroreduction mechanism was suggested and discussed.

Key words: Azo compounds, Aromatic primary amines, DC polarography, Cyclic voltammetry.

INTRODUCTION

The electroreduction of azo compounds was the subject of some interesting studies¹⁻¹⁷. These investigations showed that azo compounds undergo a reduction in acid solutions involving the uptake of 4 electrons for each N=N linkage, while in alkaline media only 2 electrons are consumed:



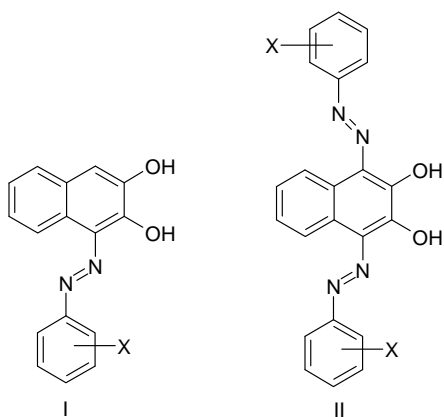
However, if the azo compound contained OH group in o-position to the N=N linkage, the reduction in alkaline media involved also four electrons giving the amino compounds. A mechanism based on the formation of hydrazone derivative, which undergoes easily reduction to amino compounds was suggested. The present study deals with dc-polarography and cyclic voltammetric investigation of some mono and bis

azo compounds based on aromatic primary amines and 2,3-dihydroxynaphthalene in which the azo linkage is in the o-position to the OH group of the dihydroxynaphthalene linkage. It is aimed to through light on the electrode reaction pathway of these azo compounds and effect of substituents in the phenyl ring on the reduction mechanism.

EXPERIMENTAL

All azo compounds used in the present investigation were pure chemicals from BDH or Aldrich. The azo compounds were prepared by diazotizing the aromatic amines then coupling with 2,3-dihydroxynaphthalene. For mono azo compounds, one equivalent of the diazonium salt was added slowly to the solution of 2,3-dihydroxynaphthalene. For bis-azo compounds, two equivalent of the diazonium salt were added to the solution of dihydroxynaphthalene. The purity of the compounds was tested by elemental analysis,

IR, ¹HNMR and UV/V is spectroscopy. The compounds obtained have the following structural formula:



X = p-COOH, p-OCH₃, p-OH, m-CH₃

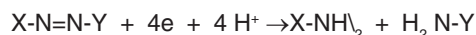
5×10⁻³ M stock solutions of the azo dyes in consideration were prepared by dissolving the accurate weighed required amount in ethanol then completed to the volume in a calibrated measuring flask. Buffer solutions used for control of pH were the components of the Britton-Robinson¹⁸ universal series containing 50% by volume ethanol to affect complete dissolution of the organic compounds.

DC-polarograms were recorded on an ink recording Sargent Welch polarograph using a dropping mercury electrode (DME) with $m = 1.7 \text{ mgs}^{-1}$ at mercury height (h) = 50 cm. The mercury used was purified according to the recommended method [19]. Cyclic voltammetry measurements were done by the aid of polarographic analyzer model 264A-PAR from (EG&G) provided with the electrode assembly 303A with a hanging mercury drop as working electrode (HMDE), a Pt wire as counter electrode and Ag/AgCl reference electrode. X-Y recorder model RE 0091 (Houston Instrument Division, EG&G) was used for recording the voltammograms.

RESULTS AND DISCUSSION

DC Polarography: The polarographic behavior of the mono- and bis- azo compounds under study was investigated in buffer solutions of pH 2-11 containing 50% ethanol. The addition of

ethanol to the buffer solutions was necessary to affect good solubility of the azo compounds. The reduction of the mono- and bis- azo compounds (I & II) at the dropping mercury electrode gave a single reduction wave (Fig.1). The limiting current (i_l) for the bis azo compounds is almost twice as that of the mono azo ones. The value of the current in strong acid media (pH 2) corresponds to the reduction of the N=N centers by the uptake of 4 electrons giving two amine molecules:



The reduction current was slightly influenced by rise of pH for both series I&II (5-10% decrease from pH 2 to pH 11) which can be attributed to decreased diffusion coefficient of the reducible species with rise of pH. This results from the ionization of the OH groups leading to anionic form which exert repulsive action with the electrode surface. Also, the decreased participation of adsorption to the electrode reaction can contributed to this decrease in i_l at higher pH. The effect of mercury pressure on the limiting current revealed that the reduction process is mainly controlled by diffusion with some adsorption or kinetic contribution. The value of the of the exponent x in the relation²⁰:

$$i_l = kh^x$$

amounts to (0.65-0.43), the value in general decreases with rise of pH.

Analysis of the reduction waves using the fundamental equation for the polarographic waves¹⁸ showed that the electrode reaction is irreversible. The transfer coefficient (α) and the number of electrons participating in the rate-determining step (n_a) were determined from the reciprocal slope of logarithmic analysis (S_1) and given in Table 1. The most probable α values were obtained for $n_a = 1$, which denoted that the rate- determining step should involve one electron. The half-wave potential ($E_{1/2}$) of the reduction waves shifted to more negative values with rise of pH indicating the contribution of H⁺ to the electrode reaction and that the proton uptake should precede the electron transfer¹⁶. The $E_{1/2} - \text{pH}$ curves comprised two segments with inflection point at pH 6-7. The number of protons

Table 1: DC-Polarographic data of 1×10^{-4} M of mono- (I) and bis- (II) azo compounds in buffer solutions of different pH values, at 25°C

Compd.	pH	i_l	$-E_{1/2}, V$	S_1, mV	$\alpha n_a = 1$	S_2, mV	Z_H^+
Ia	3.1	0.80	0.28	145	0.41	111	0.76
	7.1	0.80	0.68	160	0.37	111	0.70
	10.1	0.75	0.99	185	0.32	111	0.70
Ib	3.2	0.7	0.28	130	0.45	65	0.50
	7.0	0.64	0.52	113	0.52	65	0.58
	10.1	0.64	0.67	100	0.59	65	0.50
Ic	3.3	0.80	0.46	90	0.66	52	0.57
	7.4	0.67	0.64	90	0.66	52	0.57
	10.1	0.71	0.73	95	0.62	52	0.55
Id	3.3	0.74	0.31	190	0.31	150	0.79
	7.4	0.56	0.64	100	0.59	65	0.56
	10.2	0.40	0.79	100	0.61	65	0.65
IIa	3.2	1.70	0.18	97	0.61	105	1.10
	7.1	1.70	0.69	94	0.63	105	1.12
	10.1	1.65	0.90	100	0.59	56	0.56
IIb	3.3	1.6	0.30	89	0.66	82	0.92
	7.1	1.58	0.62	97	0.61	82	0.85
	10.1	1.55	0.72	87	0.68	45	0.52
IIc	3.3	1.65	0.27	110	0.54	87	0.79
	7.0	1.60	0.48	110	0.53	55	0.50
	10.2	1.55	0.62	110	0.53	55	0.50
IId	3.3	1.60	0.26	92	0.64	105	1.14
	7.1	1.30	0.52	80	0.66	50	0.56
	10.1	0.85	0.68	100	0.59	50	0.50

$$S_1 = 0.0591 / \alpha n_a$$

$$S_2 = dE_{1/2} / dpH$$

Table 2: Cyclic voltammetric data of 1×10^{-4} M of mono- (I) and bis- (II) azo compounds in buffer solutions of different pH values, at 25°C

Compd.	pH	S_3	αn_a	Compd	pH	S_3	αn_a
Ia	3.3	0.043	0.30	IIa	3.3	0.043	0.30
	7.2	0.033	0.38		7.0	0.040	0.32
	10.2	0.030	0.43		10.2	0.035	0.37
Ib	3.3	0.042	0.30	IIb	3.3	0.042	0.30
	7.0	0.033	0.38		7.0	0.035	0.37
	10.2	0.035	0.37		10.2	0.040	0.32
Ic	3.3	0.030	0.43	IIc	3.3	0.037	0.34
	7.0	0.033	0.38		7.0	0.032	0.40
	10.2	0.041	0.31		10.2	0.035	0.37
Id	3.3	0.030	0.43	IId	3.3	0.042	0.30
	7.0	0.033	0.38		7.0	0.038	0.34
	10.2	0.041	0.31		10.2	0.035	0.37

$$S_3 = d \ln E_p / d \ln v$$

involved in the rate-determining (p) was determined from the slopes of $E_{1/2} - \text{pH}$ plots (S_2) and the plots of logarithmic analysis (S_1) using the relation²¹:

$$E_{1/2} / \text{pH} = (0.0591 / \alpha n_a) = S_2 / S_1$$

The value of (p) as determined for all azo compounds under study was found to be unity Table 1.

Cyclic voltammetry

The mono- and bis- azo compounds (I & II) were studied by cyclic voltammetry at the HMDE in buffer solutions containing 50% by volume ethanol. Three pH media (pH 3, 7,9) were chosen for this study. The voltammograms were recorded at different sweep rates from 20-500 mV/s. As shown in Fig.2, the voltammograms consist of a single cathodic peak but not anodic peaks were appeared in the reverse scan. This denoted the irreversible nature of the electrode reaction. On increasing the sweep rate (ν) the peak potential (E_p) shifted to more negative values confirming the irreversibility of the reduction process. The values of the transfer coefficient (α) were determined by making use of

the Galus equation²² which relates the E_p and the αn_a .

$$E_p = -1.14 (RT / \alpha n_a F) + (RT / \alpha n_a F) \ln k_{ph}^0 / D^{1/2} - RT / \alpha n_a F \ln(\alpha n_a \nu)$$

The plots of E_p versus logarithm of sweep rate ($\ln \nu$) yielded straight lines of slopes (S_3), from these slope values αn_a were calculated and given in Table 2. The most probable values of α were obtained at $n_a = 1$. This indicated that the rate-determining step of the electrode reaction should involve one electron as confirmed before from DC polarography.

On plotting the peak current (i_p) as a function of the square root of sweep rate ($\nu^{1/2}$) linear relations passing through the origin were obtained which indicated that the electrode reaction is mainly governed by the diffusion of the reducible species²³.

Effect of substituents

From dc-polarography, the half-wave potential ($E_{1/2}$) values were found to be influenced by the nature of the substituent in the phenyl ring.

Table 3: Diffusion coefficients of mono- (I) and bis- (II) azo compounds and total number of electrons (n) calculated from Ilkovic equation and controlled potential electrolysis measurement*

Compd.	pH	$D^\circ \text{cm}^2 / \text{s}$	(n)	Compd	pH	$D^\circ \text{cm}^2 / \text{s}$	(n)
Ia	3.0	1.6×10^{-6}	4.23 ~ 4 3.85 ~ 4*	IIa	3.0	1.1×10^{-6}	8.14 ~ 8. 7.90 ~ 8*
	10	1.4×10^{-6}	3.87 ~ 4 3.75 ~ 4*		10	9×10^{-7}	7.11 ~ 8 8.05 ~ 8*
Ib	3.0	8.1×10^{-7}	3.75 ~ 4 3.85 ~ 4*	IIb	3.0	9×10^{-7}	7.62 ~ 8 7.75 ~ 8*
	10	6.5×10^{-7}	3.82 ~ 4 3.75 ~ 4*		10	7.8×10^{-7}	7.91 ~ 8 7.85 ~ 8*
Ic	3.0	1.3×10^{-6}	4.22 ~ 4 4.05 ~ 4*	IIc	3.0	1.1×10^{-6}	7.58 ~ 8 7.85 ~ 8*
	10	1.1×10^{-6}	3.63 ~ 4 3.75 ~ 4*				9.5×10^{-7}
Id	3.0	8.9×10^{-7}	3.78 ~ 4 3.95 ~ 4*	IIId	3.0	8.5×10^{-7}	7.84 ~ 8 7.65 ~ 8*
	10	8.2×10^{-7}	2.12 ~ 2 2.05 ~ 2*		10	8.0×10^{-7}	4.31 ~ 4 3.70 ~ 4*

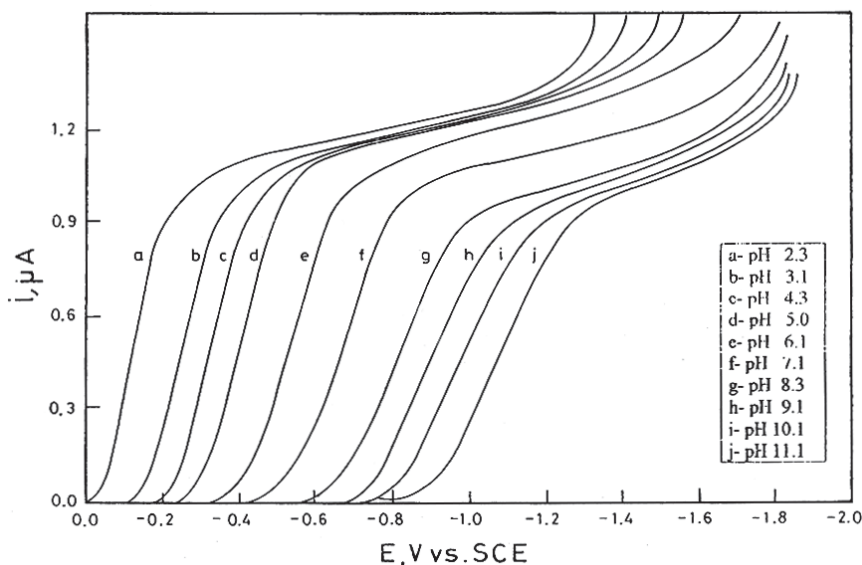


Fig. 1: DC-Polarogram of 1×10^{-4} of azo compound Ia in solutions of different pH values as typical example

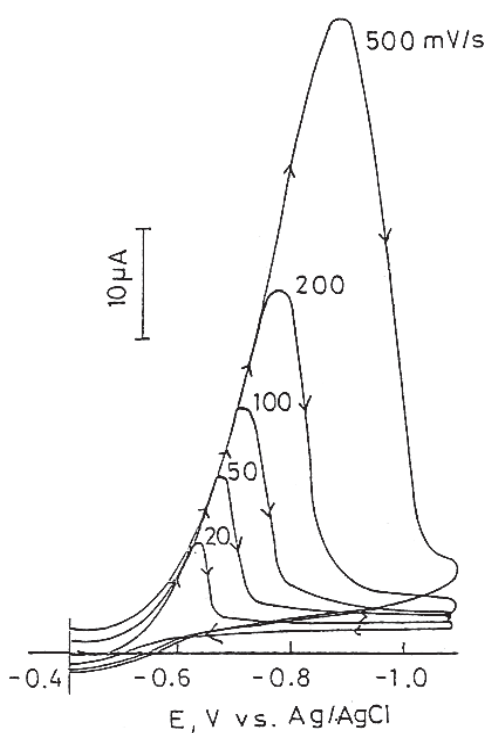


Fig. 2: Cyclic voltammograms of 1×10^{-4} of azo compound Ia at different scan rates in solution of pH 3 as typical example

Generally, it was found that $E_{1/2}$ shifted to more negative potential with decreased electron acceptor character of the substituent or when its electron donor character increased. Thus, the plots of $E_{1/2}$ as a function of Hammett constants (σ_x) gave linear relation (Fig. 3) indicating the validity of the Hammett free energy relationship in the form ²⁴:

$$E_{1/2}(S) = E_{1/2}(H) + \rho(\sigma_x)$$

From the value of the slope, ρ , amounting to 0.10 at pH 3. The positive slope of $E_{1/2} - \sigma_x$ plots indicates that the reduction process is influenced by nucleophilic attack in the potential determining

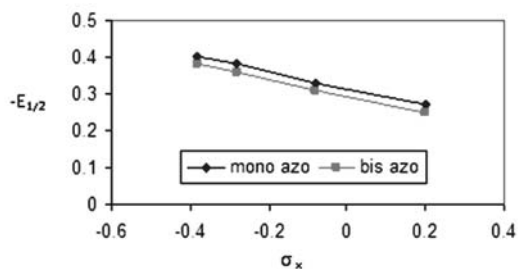


Fig. 3: $E_{1/2} - \sigma_x$ plots of mono and bis azo compounds at pH 3.0

step. The shift of $E_{1/2}$ to more negative potentials with increased electron donor property of the substituent can be explained in the light of increased electron density on the N=N centers. This in turn will increase the energy of the electron acquisition, leading to retardation of the reduction process.

Determination of the total number of electrons:

i- using Ilkovic equation:

The total number of electrons (n) involved in the overall electrode reaction was determined by two methods: i) using the Ilkovic equation:

$$i_d = 607 n D^{1/2} m^{2/3} t^{1/6} C$$

In this method, the values of the diffusion coefficient of the depolarizers (D°) were calculated using the Stock-Einstein equation [25]:

$$D^\circ = 3.22 \times 10^{-5} / (V_m) (M / D)$$

In which V_m and M are molar volume and molecular weight of the depolarizer, d is the density of the solid compounds. The densities of the solid azo compounds under study were determined using the simple density bottle method. The values obtained were corrected of medium effect and given in Table (3). The values of n determined by Ilkovic equation were found to be approximately 4 electrons in case of compounds I_{a-c} and 8 electrons for compounds II_{a-c} . For azo compounds I_d and II_d the values of n in acid solutions were 4 and 8 electrons, respectively, while in alkaline media they amounted to 2 and 4 electrons (Table 3).

ii - Using controlled potential electrolysis (cpe):

In this method, the background current was measured for the supporting electrolyte (buffer), then the desired potential was applied to the working electrode and the depolarizer solution (1×10^{-3} M) was introduced into the electrolysis cell. The electrolysis process allowed to proceed till completion of the reduction process and the accumulated charge (Q) was read directly from the digital coulometer. The average number of electrons

n involved in the overall electrode reaction was then calculated using the well known relation:

$$Q = nF (w / M)$$

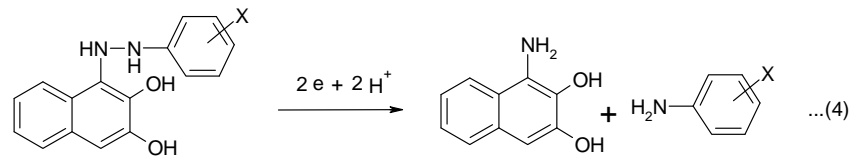
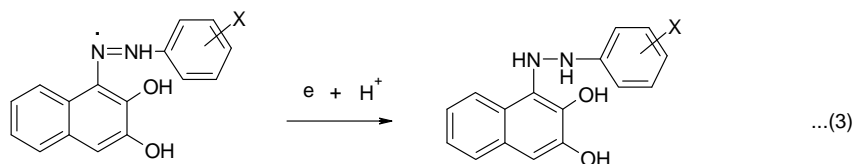
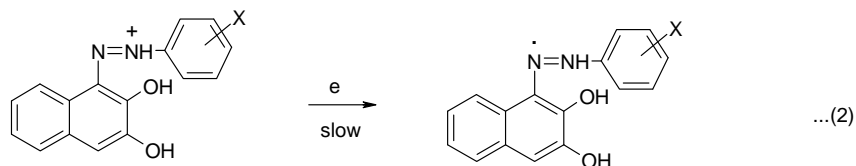
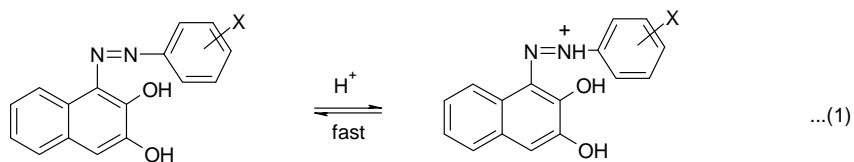
in which F is the Faraday constant (96487 coulombs), w is the weight of depolarizer in gram, M its molecular weight. The data obtained of cpe measurements were collected in Table (3). It was found that the values of n obtained by cpe were in satisfactory agreement with those of the Ilkovic equation. These data indicated the cleavage of the N=N centers for all azo compounds with the consumption of 4 electrons for each azo group (steps 1-4) in acidic solutions and (steps 5-8) in alkaline ones. For $m\text{-CH}_3$ derivatives in alkaline solutions, the reduction of the N=N center only occurs with the consumption of 2 electrons (steps 5-7).

The products of electrolysis of azo compounds I_a , II_a , I_d and II_d were concentrated by extraction with diethyl ether then subjected to TLC test. The TLC extract of the four azo compounds showed two spots in acid solutions (pH 3), while in alkaline solutions (pH 9), azo compounds I_d and II_d gave only one spot. These results denoted that for azo compounds I_d and II_d , the reduction process in alkaline solutions led only to saturation of the N=N centers, and the hydrazo compound is obtained, while in acid solutions the cleavage of the N=N bond occurs giving the aniline derivative and the aminodihydroxynaphthalein.

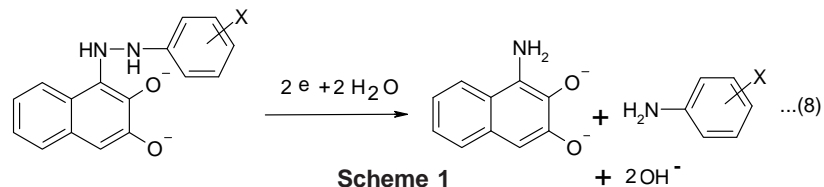
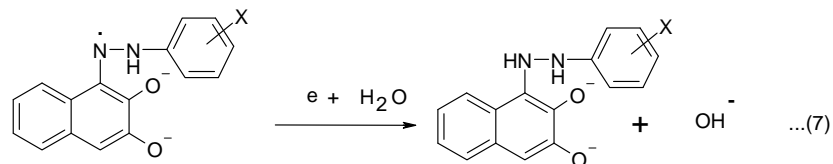
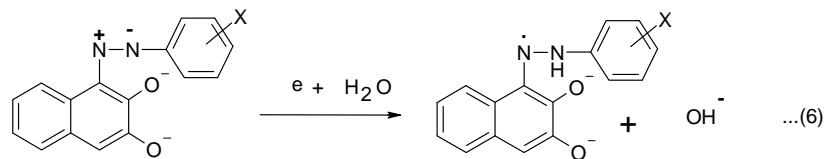
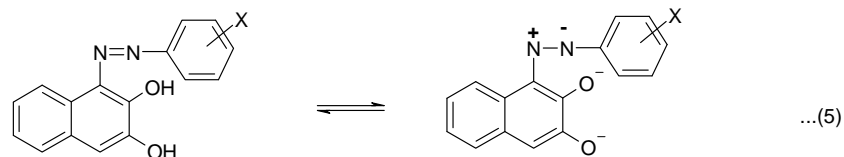
Sequence of the electrode reaction

The data obtained from dc-polarography, cyclic voltammetry and controlled potential electrolysis of mono- and bis- azo compounds under study revealed that the rate-determining step of the electrode reaction involved one electron and one proton and the protonation of the depolarizer should precede the electron transfer. In the light of the explanation of Zuman²¹ and the data gained in the present study, the sequence of electrode reaction would be H^+ , e, e, H^+ according to Scheme 1.

in acidic solutions



in alkaline solutions



Scheme 1

+ 2OH⁻

REFERENCES

1. M. Issa, Y.M. Issa, R.M. Issa and M.M. Ghoneim; *Z. Phys. Chem. (Leipzig)*, **2**: 257 (1976)
2. M.M. Ghoneim, Y.M. Issa, E.M. Mabrouk and T. Amerah; *J. Electrochemical Soc., India*, **35**: 267 (1986).
3. I.M. Issa, R.M. Issa, Y.M. Temerk and M.R. Mahmoud; *Electrochim. Acta*, **18**: 139 (1973).
4. E.M. Mabrouk, Y.M. Issa, M.M. Ghoneim and T. Amerah; *Bull. Electrochem.*, **3**: 321 (1987).
5. E.M. Mabrouk, M.M. Ghoneim, Y.M. Issa and A.M. Hassanein; *Egypt J. Chem.*, **36**: 225 (1993).
6. H.M. Killa, E.M. Mabrouk, A.A. Abd El-Fattah and S.A. Yasen; *Analytical Letters*, **24**: 275 (1991).
7. E.H. El-Mossaly and E.M. Mabrouk; *Bull. Electrochem.*, **11**: 202 (1995).
8. E.M. Mabrouk, H.M. Killa, A.A. Abd El-Fattah and S.A. Yasen; *Collect. Czech. Chem. Communication*, **57**: 268 (1992).
9. Y.I. Moharram, A.M. Hassanein and M.M. Ghoneim; *Bull. Electrochem.*, **14**: 180 (1998).
10. A. Eriksson and L. Nyholm; *Electrochim. Acta*, **44**: 4029 (1999).
11. R. Jain, P. Pandmaja and S. Gupta; *Can. J. Chem.* **75**: 567 (1997).
12. M.T. Mohamed, E.M. Mabrouk and E. H. El-Mossalamy; *Material. Sci. Res. India*, **3**: 155 (2006).
13. M.M. Ghoneim, H.S. El-Desoky, S.A Amer and A.D.Habazy, *Dyes and Pigments*,
14. E. Ungureanua, A.C. Razusb L. Birzanb, M.Cretua and G. Buicaa, *Electrochimica Acta*, **53**: 7089 (2008).
15. D. Yang, L. Zhu, X. Jiang, *J. Electroanal. Chem.*, **640**: 17 (2010).
16. S. Semiha, M. Odabasoglu, E. Bicer, and Z. Yazar, **918**: 81 (2009).
17. N. Menek and Y. Karaman, *Dyes and Pigments*, **68**: 101 (2006).
18. H.T.S. Britton; "Hydrogen Ions", Chapman and Hall, London, 4 th Ed., (1952).
19. L. Meites; "Polarographic Techniques", Interscience Publishers, New York, 2 nd Ed., 240 (1965).
20. J. Heyrovesky and J. Kuta; "Principles of Polarography", Academia, Prague, 61 (1965).
21. P. Zuman; "The Elucidation of Organic Electrode Process", Academic Press, New York, 28 (1969).
22. Z. Galus; "Fundamentals of Electrochemical Analysis", Ellis Harwood (1976).
23. A.J. Bard and L.R. Faulkner; "Electrochemical Methods", Wiley, New York, 218 (1980).
24. L.P. Hammett; "Physical Organic Chemistry", McGraw-Hill, New York (1940).
25. I.M. Kolthoff and J. Lingane; "Polarography, Theoretical Principle, Instrumentation and Technique", **1**: 58 (1965).