

A Cyclic Voltammetric Study of the Aqueous Electrochemistry of Some Anthraquinone Derivatives on Carbon Paste Electrode[✧]

Ojani, Reza; Raoof, Jahanbakhsh* and Ebrahimi, Manoochehr

Department of Chemistry, Faculty of Basic Science, Mazandaran University, P. O. Box 453, Babolsar, I. R. Iran

ABSTRACT: The aqueous electrochemistry of a number of anthraquinone derivatives was studied by using cyclic voltammetry at the surface of carbon paste electrode (CPE). From measurements of the half-wave potential as a function of pH, the potential - pH diagrams were constructed for each compound. The values of formal potentials and the pK'_a of some different redox and acid-base couples involved in each compound at various pHs were obtained.

KEY WORDS: Carbon paste electrode, Aqueous electrochemistry, Cyclic voltammetry, Anthraquinone -2- carboxylic acid, Anthraquinone -2- sulfonic acid sodium salt monohydrate.

INTRODUCTION

Quinones are a series of widespread compounds found in the living organisms performing a variety of biochemical and physiological functions and constitute a broad range of organic compounds with various interesting properties such as antitumor, antibacterial, antifungal and antibiotoxic activities [1-5]. The main activity of these compounds arise from their reversible electron transfer behaviour [6-8]. It is also found that, in many cases, the electron transfer process occurs through two one-electron steps via a semiquinone free radical production mechanism [9-10].

The reduced form of quinonic compounds produces ortho or para diphenols which can appear as undissociated (acid) or dissociated (mono or dibasic) forms depending on the pH. Therefore, determina-

tion of the formal potential of some different redox species produced during the variation in solution pH of the quinonic compounds and the pK'_a of their reduced forms are important, specially in aqueous media [7,11-14].

In previous works, we have studied the electrochemical properties of some 1,4-naphthoquinone derivatives as modifiers of the chemically modified carbon paste electrodes in aqueous buffered solutions [13]. These modified electrodes have also been used for the electrocatalysis of O_2 to hydrogen peroxide [15]. Moreover, the electrochemical behaviour of some naphthoquinones and anthraquinones have been studied in non-aqueous media at solid electrodes [10,16,17].

✧ Dedicated to Professor Mahdi Golabi on the occasion of his 67th birthday.

* To whom correspondence should be addressed.

1021-9986/01/2/75 7/8/2.70

In this paper, we report on the aqueous electrochemistry of some anthraquinone derivatives such as anthraquinone-2-carboxylic acid, anthraquinone-2-sulfonic acid sodium salt monohydrate and 1,2-dihydroxy-anthraquinone (alizarin) in various buffered solutions by using cyclic voltammetry. The potential-pH diagrams of these compounds are constructed and by using of these diagrams, the apparent standard potentials of various anthraquinones redox couples, together with the dissociation constant of intervening acid-base couples are estimated.

EXPERIMENTAL

Electrodes

The working electrodes were constructed in a way similar to that described elsewhere [13]. The graphite powder is mixed by diethylether with a mortar and pestle. The solvent was evaporated by stirring. A 1:1 (w/w) carbon powder and paraffin was blended by hand-mixing and the resulting paste was then inserted in the bottom of polypropylene tube. The electrical connection was implemented by a copper wire lead fitted into a polypropylene tube. Such an electrode was satisfactorily used in cyclic voltammetry. An aqueous saturated calomel electrode (CRL, Russel Co. Scotland) was used as a reference electrode and a platinum wire electrode constituted the auxiliary electrode.

Chemicals

Anthraquinone-2-carboxylic acid, anthraquinone-2-sulfonic acid sodium salt monohydrate and alizarin were obtained from Aldrich, and used without further purification. Spectrographically pure graphite rod (Grade II, from Johnson Matthey Chemical Limited), ground to a fine powder, was used as a working electrode substrate. High viscosity mineral oil ($d=0.88 \text{ g cm}^{-3}$), from Fluka (Buchs, Switzerland), constituted the pasting liquid of the carbon paste electrode. All solutions were prepared with twice distilled water. The buffers used at different pHs were: $\text{H}_2\text{SO}_4 + \text{NaOH}$ (for $\text{pH}=0.5-1.5$), $\text{H}_3\text{PO}_4 + \text{NaOH}$ ($\text{pH}=2-3$), sodium dihydrogen phosphate + NaOH ($\text{pH}=4-9$) and disodium hydrogen phosphate + NaOH ($\text{pH}=9-13$). All of the chemicals were of reagent grade from Fluka or Merck (Darmstadt, Germany) and were used as received. N_2 gas with a purity of 99.999% was used for

removing dioxygen from solution during the experiments.

Apparatus

Cyclic voltammetry was carried out in a thermostated system at $25.0 \pm 0.1^\circ\text{C}$ by using a potentiostat/galvanostat (model 78 BHP 2061007, Behpajoo Co. Iran) with a Pentium personal computer. A three-electrode cell configuration was employed.

RESULTS AND DISCUSSION

Anthraquinone-2-carboxylic acid (CAQ)

The electrochemical properties of 1 mM CAQ in aqueous buffered solutions were studied by cyclic voltammetry in the pH range between 0.5-13 in the absence of dioxygen at the carbon paste electrode. Over a potential range corresponding to the electroactivity domain of the solvent, cyclic voltammograms show a single reduction peak and a corresponding oxidation peak (Fig. 1a). In this range of the potential, anthraquinone-free solution shows no peaks (Fig. 1b). However in the presence of dioxygen, the limitation of negative potentials corresponds to the reduction of dioxygen (Fig. 1c). The half-wave potentials ($E_{1/2}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms ($(E_{pa} + E_{pc})/2$) [18], recorded at a

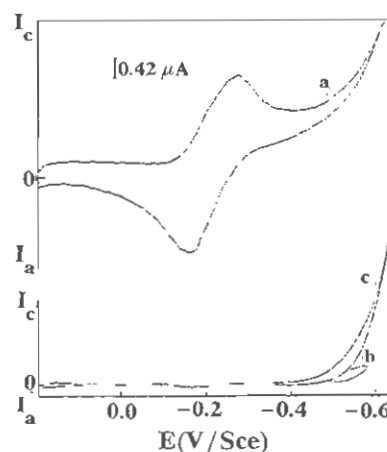


Fig. 1.: Cyclic voltammograms of a) 1mM CAQ in deaerated aqueous buffered solution ($\text{pH}=2.00$), b) as a) in anthraquinone-free solution and c) as a) at the surface of CPE in the presence of dioxygen. Scan rate is 50 mV/s and supporting electrolyte $\text{H}_3\text{PO}_4 + \text{NaOH}$ ($\text{pH}=2.00$).

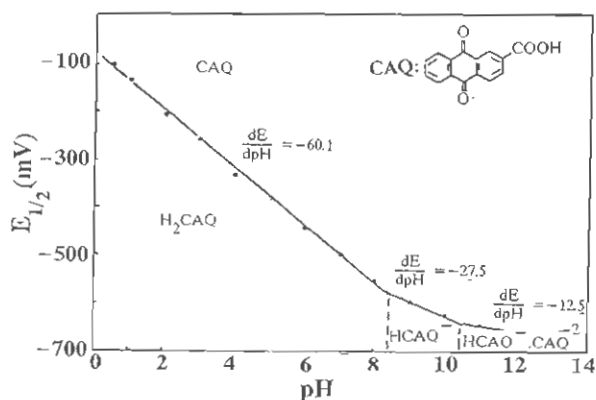


Fig. 2: The pH-Potential diagram for CAQ (anthraquinone-2-carboxylic acid).

potential scan rate of 50 mV/s and then they are plotted as a function the solution pH (Fig. 2). This $E_{1/2}$ -pH diagram comprises of three linear segments with different slopes: -60.1 mV (pH < 8.3), -27.5 mV (8.3 < pH < 10.5) and -12.5 mV (pH > 10.5) per unit of pH. This means that parallel to the variation of the solution pH and electrode potential, four different forms of CAQ can be produced, one of which is an oxidized form of CAQ, and the other three are the reduced forms of anthraquinone-2-carboxylic acid.

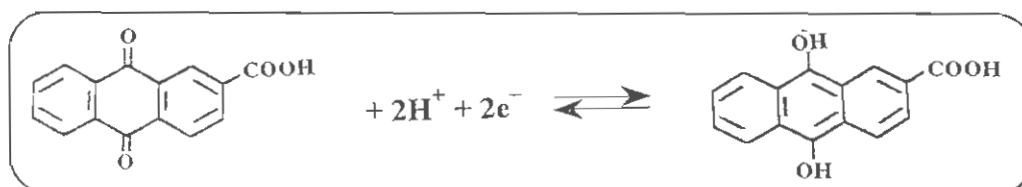
The electrochemical reaction occurring at a pH below 8.3 is a two-proton, two-electron process (Scheme 1). However, for the pH ranging from 8.3 to 10.5, CAQ undergoes a one-proton, two-electron reduction producing HCAQ^- , and vice versa (Scheme 2).

Finally, the electrochemical reaction at a pH higher than 10.5 is related to a four-electron, one-proton reduction (Scheme 3).

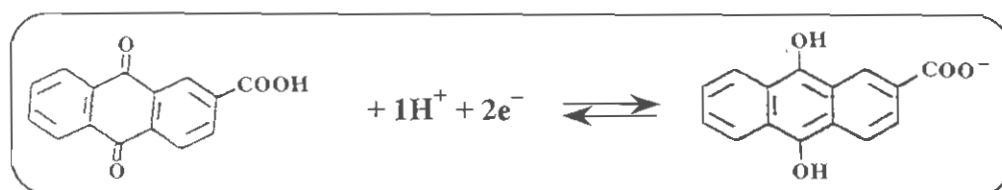
We assume the existence of such a dimerized species by analogy with the case of other quinonic compounds indicated in the literatures [7,13].

The values of E° and pK'_a for all possible equilibria between the conjugated forms of CAQ are quoted in Tables 1 and 2. The uncertainties involved in the estimation of each E° and pK'_a value were calculated from different linear segments of $E_{1/2}$ -pH diagrams by a common method described in the literature [19].

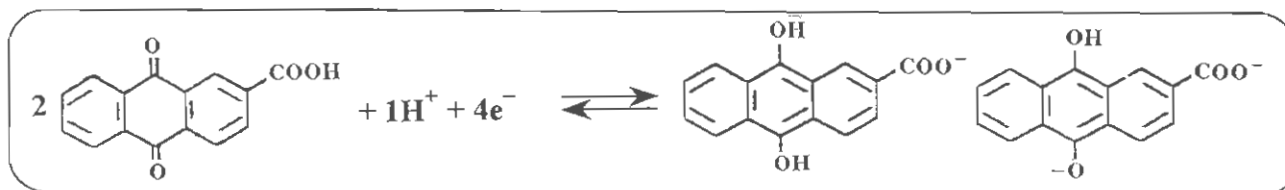
The effect of scan rates on the electrochemical behavior of all compounds under test have also been studied at CPE, in the scan rates range (20 mV/s - 400 mV/s). As an example, the cyclic voltammetric data obtained for 1mM of CAQ in aqueous buffered solution (pH=2) and in the absence of O_2 are listed in Table 3. The results show that the peak separa-



Scheme 1



Scheme 2



Scheme 3

Table 1 : Redox equilibria in the aqueous electrochemistry of some anthraquinone derivatives

compounds	Redox reaction	E° (V/SCE) ^a	E° (V/SHE)	E° (V/SHE) ^b	Reference
CAQ	$CAQ + 2H^+ + 2e^- \rightleftharpoons H_2CAQ$	-0.080 ± 0.006	$+0.161 \pm 0.006$		
	$CAQ + H^+ + 2e^- \rightleftharpoons HCAQ^-$	-0.350 ± 0.005	-0.109 ± 0.005		
	$2CAQ + H^+ + 4e^- \rightleftharpoons HCAQ^-, CAQ^{2-}$	-0.510 ± 0.004	-0.269 ± 0.004		
SAQ	$SAQ + 2H^+ + 2e^- \rightleftharpoons H_2SAQ$	-0.073 ± 0.009	0.168 ± 0.009	0.225	[12]
	$SAQ + H^+ + 2e^- \rightleftharpoons HSAQ^-$	-0.335 ± 0.015	-0.094 ± 0.015		
	$SAQ + H^+ + 4e^- \rightleftharpoons HSAQ^-, SAQ^{2-}$	-0.467 ± 0.018	-0.256 ± 0.018		
HAL	$HAL + 2H^+ + 2e^- \rightleftharpoons H_3AL$	-0.228 ± 0.008	0.013 ± 0.008		
	$HAL + 1H^+ + 2e^- \rightleftharpoons H_2AL^-$	-0.356 ± 0.007	-0.115 ± 0.007		
	$HAL.AL^- + 3H^+ + 4e^- \rightleftharpoons 2H_2AL^-$	-0.272 ± 0.006	-0.031 ± 0.006		
	$HAL.AL^- + 1H^+ + 4e^- \rightleftharpoons 2HAL^{2-}$	-0.613 ± 0.007	-0.373 ± 0.007		

a) E° , formal potential at 95% confidence limits, obtained from the intercept of each linear segment with Y axis in Figs. 2, 3 and 4 respectively.

b) Literature data.

Table 2 : Acid-base equilibria of some anthraquinone derivatives in various buffered media

compounds	acid-base reaction	pK'_a ^(b)	pK'_a ^(c)	Reference
CAQ	$H_2CAQ \rightleftharpoons H^+ + HCAQ^-$	8.30 ± 0.15		
	$2HCAQ^- \rightleftharpoons HCAQ^-.CAQ^{2-} + H^+$	10.50 ± 0.05		
SAQ	$H_2SAQ \rightleftharpoons HSAQ^- + H^+$	8.22 ± 0.08	8.30	[12]
	$2HSAQ^- \rightleftharpoons HSAQ^-.SAQ^{2-} + H^+$	10.53 ± 0.10		
HAL	$H_3AL \rightleftharpoons H_2AL^- + H^+$	4.00 ± 0.08		
	$2HAL \rightleftharpoons HAL.AL^{1-} + H^+$	6.00 ± 0.06		
	$H_2AL^- \rightleftharpoons HAL^{2-} + H^+$	10.90 ± 0.05		

b) The values indicate the apparent acidity constant at 95% confidence limits, and each pK'_a value was obtained from corresponding pH value of intersection point of two neighbour linear segment.

c) Literature data.

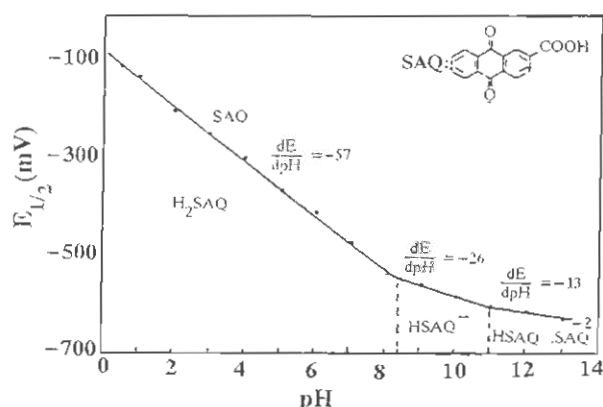


Fig. 3 : The pH- Potential diagram for SAQ (anthraquinone-2-sulfonic acid sodium salt monohydrate).

tions ($\Delta E = E_{pa} - E_{pc}$) are higher than 59 mV and are increased by increasing the scan rate, which signifies the quasi-reversible behavior of electron transfer process for CAQ.

Anthraquinone-2-sulfonic acid, sodium salt monohydrate (SAQ)

The electrochemical behaviour of 1mM SAQ was studied in aqueous buffered solution in the pH range of 0.5 to 13 in the absence of O_2 by cyclic voltammetry at CPE. An $E_{1/2}$ -pH diagram of this compound is shown in Fig. 3; which is similar to $E_{1/2}$ diagram of CAQ. The slopes of this diagram at various regions of pH are as follows: -57 mV (for pH < 8.22),

-26mV (for $8.22 < \text{pH} < 10.53$) and -13mV (for $10.53 < \text{pH} < 13$) per pH unit.

The data given in Tables 1 and 2 are the apparent standard redox potentials (E°) and the pK'_a values of different forms, which are reduced at various pHs.

1,2-Dihydroxy-anthraquinone or Alizarin (HAL)

The electrochemical properties of 1mM HAL has also been studied in aqueous buffered solution in the pH range 0.5-13 in the absence of O_2 by cyclic voltammetry. The half-wave potentials ($E_{1/2}$) are plotted as a function of the solution pH in Fig. 4. As shown in this figure, five different forms of HAL can exist in various solution pH, three of which are reduced forms and two others are oxidized forms. The slopes of four linear segments are as follows: -64.1 mV (for $\text{pH} < 4.0$), -32.5 mV (for $4.0 < \text{pH} < 6.0$), -48.5 mV (for $6.0 < \text{pH} < 10.9$) and -17.5 mV (for $10.9 < \text{pH} < 13$) per unit of pH. A slope of -48.5 mV per pH unit, in $6.0 < \text{pH} < 10.9$, refers to a redox process with a proton/ electron ratio of 3:4. This can be explained by the formation of dimers, similar to the case of plumbagin and juglone [13]. The electrochemical reaction of redox couple in this pH region can be shown by Scheme 4.

However, at $\text{pH} > 10.9$, the oxidized form exists as a dimer, and the -17.5 mV/pH unit refers to a four-electron, one-proton redox process (Scheme 5).

The apparent standard redox potential, E° and the pK'_a values of different forms of HAL are listed

in Tables 1 and 2.

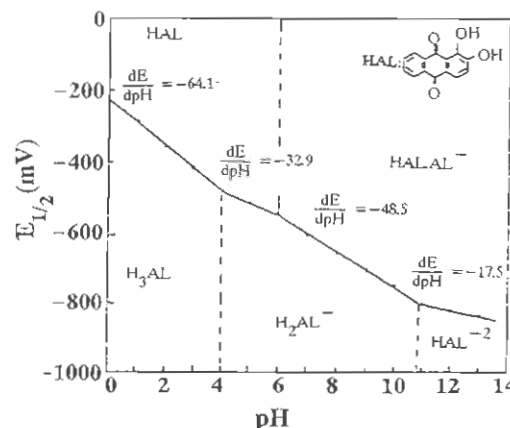


Fig. 4 : The pH- Potential diagram for HAL (alizarin)

CONCLUSION

This work demonstrates the aqueous electrochemistry of some anthraquinone derivatives at the surface of CPE and the formation of different forms. This allows the detection of the existence of various redox equilibria as a function of the solution pH. The values of the formal potential and pK'_a of the involving some different redox and acid - base couples are estimated using their $E_{1/2}$ - pH diagrams.

In view of the fact that, the $E_{1/2}$ values of SAQ and ALQ are similar to $E_{1/2}$ values of CAQ, the ability of these compounds in electrocatalysis of reduction are under further investigation in our laboratory.

Received: 11th October 2000; Accepted: 18th June 2001

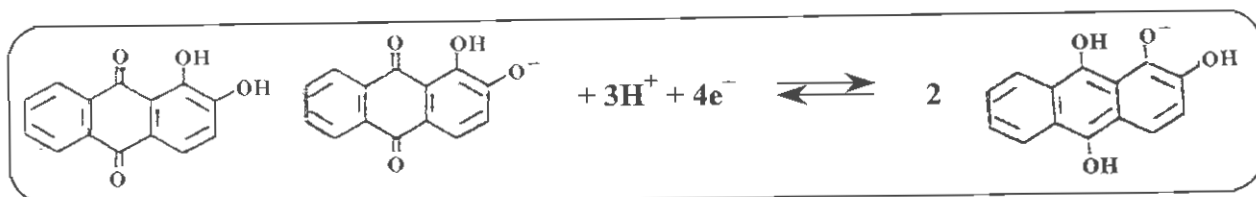
Table 3 : Cyclic Voltammetric data of 1mM CAQ in aqueous buffered solution (pH=2)

v (Vs^{-1})	$E_{1/2}$ (V/SCE) ^a	ΔE_p (mV)	I_{pc} (μA)	I_{pa} (μA)	I_{pa}/I_{pc} ^(b)	$I_{pc}v^{1/2}$ ($\text{mAV}^{-1/2}\text{s}$)	$I_{pa}v^{1/2}$ ($\text{mAV}^{-1/2}\text{s}$)	q_c (μC)	q_a (μC)	q_a/q_c ^(b)
0.02	-0.212	70	0.38	0.27	0.71	0.00269	0.00191	1.19	-1.81	1.52
0.05	-0.212	88	0.66	0.50	0.75	0.00295	0.00224	1.04	-1.37	1.32
0.10	-0.215	96	0.96	0.73	0.76	0.00303	0.00231	0.84	-1.23	1.46
0.20	-0.217	108	1.35	1.17	0.87	0.00302	0.00262	0.77	-0.94	1.22
0.40	-0.218	119	1.97	1.84	0.93	0.00311	0.00291	0.65	-0.81	1.25

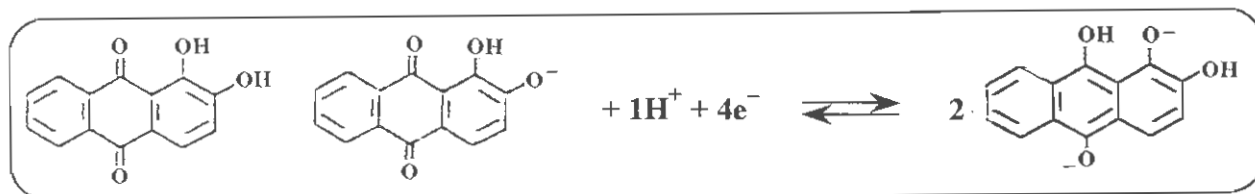
(a) $E_{1/2} = (E_{pa} + E_{pc})/2$ with a mean value of about 0.215 V (SCE).

(b) The mean value of I_{pa}/I_{pc} is 0.80

(c) The mean value of q_a/q_c is 1.35



Scheme 4



Scheme 5

REFERENCES

- [1] Berdy, J., Aszalos, M. and McNitt, K. L., In "Handbook of Antibiotic Compounds", Quinone and Similar Antibiotics, III CRC Press Inc., Boca Raton, Florida (1980).
- [2] Riebergen, R. J. D., Hartigh, J. D., Holthuis, J. J. M., Hulshoff, A., Oort, J. V., Kelder, S. J. P., Verboom, W., Reinhoult, D. N., Bos, M. and Van Der Linden, W.E., Electrochemistry of Potentially Bioreductive Alkylating Quinones, Part 1. Electrochemical Properties of Relatively Simple Quinones as Model Compounds of Mitomycin and Aziridiny Quinone-Type Antitumour Agents, *Anal. Chim. Acta*, **233**, 251(1990).
- [3] Hart, J. P., In "Electroanalysis of Biologically Important Compounds", Ellis Horwood Limited (1990).
- [4] Fieldler, H. P., Kulik, A. and Schuez, T. C., Biosynthetic Capacities of Actinomycetes. 2. Juglomycin Z., A New Naphthoquinone Antibiotic from *Streptomyces Lendae*, *J. Antibiot.*, **47**, 1116(1994).
- [5] Lown, J. W., Discovery and Development of Anthraquinone Antitumour Antibiotics, *Chem. Soc. Rev.*, 165(1993).
- [6] Ksenzhek, O. S. and Petrova, S. A., In "Electrochemical Properties of Reversible Biological Redox Systems", Nauka, Moscow (1986).
- [7] Petrova, S. A., Kolodyazhny, M. V. and Ksenzhek, O. S., Electrochemical Properties of Some Naturally Occuring Quinones, *J. Electroanal. Chem.*, **277**, 189(1990).
- [8] Dyrust, G., Kadish, K. M., Scheller, F. and Renneberg, R., In "Biological Electrochemistry", Academic Press, New York, p. 1 (1982).
- [9] Golabi, S. M. and Pournaghi, M. H., Electrochemical Behaviour of P-Benzo Quinone, 2,3,5,6-Tetrachloro-Quinone and 1,4-Naphthoquinone in Chloroform-I. in the Absence of Proton Donors, *Electrochim. Acta*, **33**, 425(1987).
- [10] Raof, J. B. and Golabi, S. M., Electrochemical Behaviour of Some 1,4-Naphthoquinone Derivatives at the surface of Glassy Carbon Electrode in Acetonitrile, *Iran J. Sci. & Tech.*, **22**, 123 (1998).
- [11] Albert, A. and Serjeant, E. P. In "The Determination of Ionization Constants", 3rd Ed., Chapman and Hall, London (1984).
- [12] Bailey, S. I. and Ritchie, I. M., a Cyclic Voltametric Study of the Aqueous Electrochemistry of Some Quinones, *Electrochim. Acta*, **30**, 3(1985).
- [13] Raof, J. B. and Golabi, S. M., Electrochemical Properties of Carbon-Paste Electrodes Spiked with Some 1,4-Naphthoquinone Derivatives, *Bull. Chem. Soc. Jpn.*, **68**, 2253(1995).
- [14] Golabi, S. M., Davarkhah, R. and Nematollahi, D., Modified Carbon Paste Electrode: An Electroanalytical Tool for Estimation of Thermodynamic Parameters of Water Insoluble Quino-

- nes, *Scientia, Iranica*, **4(3)**, 112(1997).
- [15] Golabi, S. M. and Raouf, J. B. Catalysis of Dioxygen Reduction to Hydrogen Peroxide at the Surface of Carbon Paste Electrodes Modified by 1,4-Naphthoquinone and Some of Its Derivatives, *J. Electroanal. Chem.*, **416**, 75(1996).
- [16] Raouf, J. B. and Golabi, S. M., Electrochemical Behaviour of Plumbagin at Solid Electrodes in Non-Aqueous Media, *Bull. of Electrochemistry*, **13** (7), 311(1997).
- [17] Raouf, J. B. and Rostami, A. A. and Kashavarz, M., Electrochemical Behaviour of Some Amino-9-10-Anthraquinone Derivatives at Solid Electrodes in Non-Aqueous Media, *Bull of Electrochemistry*, **16** (2), 92(2000).
- [18] Katz, E. Y. and Solovev, A. A., Chemically Modification of Platinum and Gold Electrodes by Naphtoquinone using Amines Containing Sulfydryl or disulfide Groups, *J. Electroanal. Chem.*, **291**, 171(1990).
- [19] Miller, J. C. and Miller, J. N., In "Statistics for Analytical Chemistry", 3rd Ed., Ellis Horwood Limited, Chichester, p.110 (1994).