------Raf. Jour. Sci., Vol. 19, No.1, pp 18-25, 2008 ------

Square Wave Voltammetric Behaviour of N – Benzylidene Aniline and Some of Its Derivatives in Dimethyl Sulphoxide

Sadallah T. Sulaiman **Omar A. Shareef**
Department of Chemistry
College of Science
Mosul University

(Received 10/12/2006, Accepted 18/6/2007)

ABSTRACT

The square wave voltammetric (SWV) behavior of eight substituted N-benzylidene anilines (I-VIII) C_6H_5-CH=N-C_6H_4R Where R=H,p-CH_3,m-CH_3,p-OCH_3,m-OCH_3,p-Cl,p-Br,and p-I respectively have been studied in Dimethyl sulphoxide (non aqueous medium) in presence of $LiClO_4$(as supporting electrolyte). All these compounds show a well defined one reduction peak with the exception of p-Br and p-I which show two reduction peaks appeared at potential Ep= -1.854,-1.894, -1.826, -1.916, -1.832 and -1.732 vs. Ag/AgCl,KCl for compounds I-VI, respectively .The peaks obtained are recommended for trace determination of these compounds . Regression analysis on the standard curve for all compounds studied indicate a linear relationship between peak current and concentration over the range $3.8 \times 10^{-6} - 1.5 \times 10^{-4}$ M with a correlation coefficient of more than 0.99.

دراسة سلوك فولتماتري الموجة المربعة لمركب N-البنزاليدين انيلين وبعض معوضاته في مذيب ثنائي مثيل السلفوكسايد

الملخص

يتضمن البحث دراسة الخواص الفولتمترية لمركب البنزالدين انيلين وبعض معوضاته (المثيل,الميثوكسي,والهالوجين) (I – VIII) في محيط ثنائي مثيل السلفوكسايد DMSO بوجود بيركلورات الليثيوم كالكتروليت مساعد باستخدام تقنية فولتمتري الموجة المربعة (SWV) . ولوحظ ظهور موجة اختزال جيدة لكافة المركبات(ماعدا معوضات I, Br أعطت موجتين) وعند الجهود -1.732, - 1.832,-1.916,-1.826,-1.894,-1.854 ضد قطب الفضة / كلوريد الفضة للمركبات (I- VI) على التوالي, ويمكن اعتماد هذه الموجات لتقدير كميات ضئيلة من هذه المركبات والتحليل الانحداري للمنحني القياسي لكل المركبات المدروسة اشار الى وجود علاقة خطية بين التيار والتركيز في المدى 3.8×10^{-6} الى 1.5×10^{-4} مولاري وان معامل الارتباط اكثر من 0.99.

INTRODUCTION

Square wave voltammatry (SWV) represents the most rapid electrometric method for analysis of many polarographically active organic compounds (Sulaiman and Ahmad, 2005) ,drugs (Berzas and Rodriguez, 1997) and biological active compounds (Yu et al., 1997) .Recently, the biological activity of substituted benzylidene anilines become very important for example Solamons et al (Solamons et al., 1997) tested the inhibitor factor of a series of hydroxylated benzylidene anilines and benzylamine of epidermal growth factor receptor –associated protein tyrosine kinase (PTK).On the other hand, Young et al (Young Han et al., 2003), found that N- benzylidene aniline and N- benzylamine are potent inhibitor of Lignostilbene – α , β dioxy genase In general the Schiff bases have many pharmaceutical behavior as antiinflammatory (Mitta and Singhal, 1986), antimalaria (Yan et al., 1978) and to formation of some complexes for treatment of some diseases (Prabhu and Dodwad, 1983).

The main purpose of the present paper is to point out the possibility of using square wave voltammetric technique to study the electrochemical behavior of some benzylidene substituted aniline and application of the method for microdetermination of these important schiff bases .

EXPERIMENTAL

Apparatus

All experiments were performed using the EG and G PAR 384B computerized Polarographic analyzer equipped with 303 static mercury drop electrode and RE0093 digital plotter.

A three-electrode system were used. The working electrode was a hanging mercury dropping electrode (HMDE); the reference electrode was Ag/AgCl,KCl (3M) electrode and the counter electrode was a Pt wire electrode Temperature control was made by the use of Haak NK 22 water thermostat (±0.1^{0}C). All voltammetric measurements were made under N^2 atmosphere.

Preparation of Schiff bases

Benzylidene aniline Schiff bases I-VII were prepared according to the procedure described by Dayagis et al (Dayagis and Wiley, 1970), and were recrystallised several time with ethanol (.Shareef O.A. thesis 2000).

Standard solution :

Stock solution (10^{-3}M) of each of the eight Schiff bases (1-VIII) were freshly prepared by dissolving the appropriate weight of the corresponding compounds in DMSO.

Lithium perchlorate :

0.1 M $LiClO_4$ was prepared by dissolving 0.05 g of $LiClO_4$ (from fluka) in 5 ml DMSO.

General Procedure :

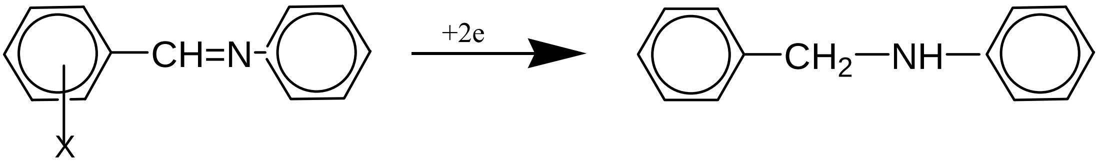
The square wave voltammetric mode was used with pulse height 100 mv , frequency 100Hz and scan rate 200 mv sec^{-1}. The polarographic cell was thermostated at

25 C°, The solution was de-airated by passing through it a slow stream of N_2 for 240 sec The square wave voltammogram was recorded on a degassed 0.1 M $LiClO_4$ in 5 ml DMSO (blank) .The residual current was recorded. A certain amount of standard benzylidene aniline Schiff base was added to this solution and the voltammogram was recorded again with blank subtraction. The concentration of each sample was then determined from calibration plots of peak current (Ip) versus concentration over the range 3.8×10^{-6}- 1.57×10^{-4}M.

Result and Discussion

Voltammetric behaviour of unsubstituted benzylidene aniline (I)

The square wave voltammetry of 9×10^{-5}M compound (I) was recorded in DMSO containing 0.1 M $LiClO_4$ as supporting electrolyte is shown in Fig 1a. as it can be seen from this figure a well-defined peak appeared at -1.84 V by using Ag/AgCl electrode. This peak belong to the reduction of –CH=N- group via 2e process at HDME.



(I)

X= H , p-CH_3, m- CH_3, p-OCH_3, m-OCH_3, p-Cl, p-Br, p-I.

Study of optimum conditions : The effect of various parameters related to the square wave voltammetry like, effect of deposition time, effect of conditioning time, effect of scan increment and scan rate were performed with a set of experimentsl by changing the above parameters individually and gradually. The optimum result obtained are shown below (Table 1)

Table 1 (optimum conditions) for SWV in Benzylidene aniline.

Deposition time	30 sec
Condition time	10 sec
Scan increment	20 mv
Scan rate	200 mv sec^{-1}
Frequency	100 Hz
Blank subtraction	Yes

Voltammatric behavior of (Methyl and Methoxy substituted Benzylidene aniline (compound II-V)

Fig 1b shows the square wave voltammetry of 9×10^{-5}M of p-methyl BA (compound II), using the above optimum condition. All the voltammograms of all compounds (II-V) show the appearance of only one well-defined reduction peak ; their peak potentials are shown in Table 2 .

Table 2 :peak potential Ep for compounds I-V

No	Compounds	Ep(v)
I	Benzylidene aniline (BA)	-1.840
II	p-CH_3 BA	-1.894
III	m- CH_3 BA	-1.826
IV	p-OCH_3 BA	-1.916
V	m- OCH_3 BA	-1.832

From this table it is clear that the peak potential Ep increases as follows:
Ep p-CH_3 BA > Ep BA > Ep m-CH_3 BA and
Ep p-OCH_3 BA > Ep BA > Ep m-OCH_3 BA .

This indicate that the para substitutents (CH_3 and CH_3O) increase the stability and strength of the CH=N which in fact make the reduction process more difficult .

Voltammetric behavior of halogenated substituted Benzylidene aniline (compounds VI-VIII)

The square wave Voltammatric behaviur of 9 x 10^{-5}M of each of compounds VI-VIII run at the optimum condition fixed in Table 1 were recorded in DMSO in the presence of $LiClO_4$. The para chloro substituted BA (compound VI) shows the appearance of only one reduction peak at -1.764 V^0 on the other hand, the p-Br and p-I substitutnts give two well-defined reduction peak appeared at -1.682 and -1.822 v for p-Br substitutnt and at -1.732 and -1.908 V for p-I substitutnt (Fig 1C). The new peak appeared in both p-Br and p-I. (-1.680 V and -1.732 V, respectively) belong to the reduction process of the benzene ring substituted with Br or I (Kolthoff and Lingane, 1952).

In general, the Ep values of halogen benzylidene aniline are higher than that of the methyl and the methoxy derivatives (compounds II-V)., this is as expected since the halogen act as electron attracting group (inductive effect)., and make the reduction process more easier.

Quantitative determination of Schiff bases (I-VIII)

Using the optimum condition obtained in Table 1, the square wave voltammograms of compounds I-VIII were recorded separately at different concentrations. The results indicate that the peak current Ip was proportional to concentration for all compounds studied and a good calibration graph were obtained. Some typical results of the method for a series of standard solutions of compound (I,II,VIII) are shown in Table 3. These solutions were prepared by adding an appropriate aliquots of a stock solution of each of compound I,II or VIII to 5 ml DMSO containing 0.1 M $LiClO_4$ as supporting electrolyte. Regression analysis on the standard compounds I-VIII indicated a linear relationship between peak current and concentrations . The slope change in peak current nA per unit changes in concentration in μ mole are shown in Table 4 together with the correlation coefficient R and Standard deviation . The lowest experimental determination limit was found to be 3.8 x 10^{-6}M.

Table 3 : The effect of concentration on peak current of compounds I , II , VIII

Conc x 10^{-6} M	Corr.Ip(nA) Compoud I	Corr.Ip(nA) Compoud II	Corr.Ip1(nA) Compoud VIII	Corr.Ip2(nA) Compoud VIII
3.8	5.4	26.1	6.4	2.5
7.4	48.1	64.4	31.9	18.1
10.7	110.7	100.2	55.6	39.2
13.7	152.3	119.1	80.6	63.1
16.6	200.8	136.3	94.7	76.4
48.3	558	428	330	267.6
78.1	838.3	680	478	382.4
106.6	11120	925	617	494.1
132.3	1403	1151	767	602.2
157.1	1610	1356	917	709.8

The variation of peak potential Ep with concentration :

It was noted that the peak potential of the reduction peak of some of the Schiff base studied (compounds I,III,IV,V,VIII) slightly changed with concentration (Table 4). Some typical data for compounds I and VIII are shown in Table 5 .The plot of Ep versus log C (C= concentration M) shows straight lines as in [Fig 3 for unsubstituted benzylidene aniline compound 1]. with slope=1.07 x 10^{-2} .Since the slope =0.059/n , then n=5.5 this non-integer number indicate that the reduction process proceed irreversibly (Sulaiman and Hammed 1988)]. The slope and the number of electron obtained for the other compounds are summarized in Table 6. All the results obtained support the irreversible reduction process of the studied Schiff base .

Table 4 : Regression analysis of compounds I-VIII

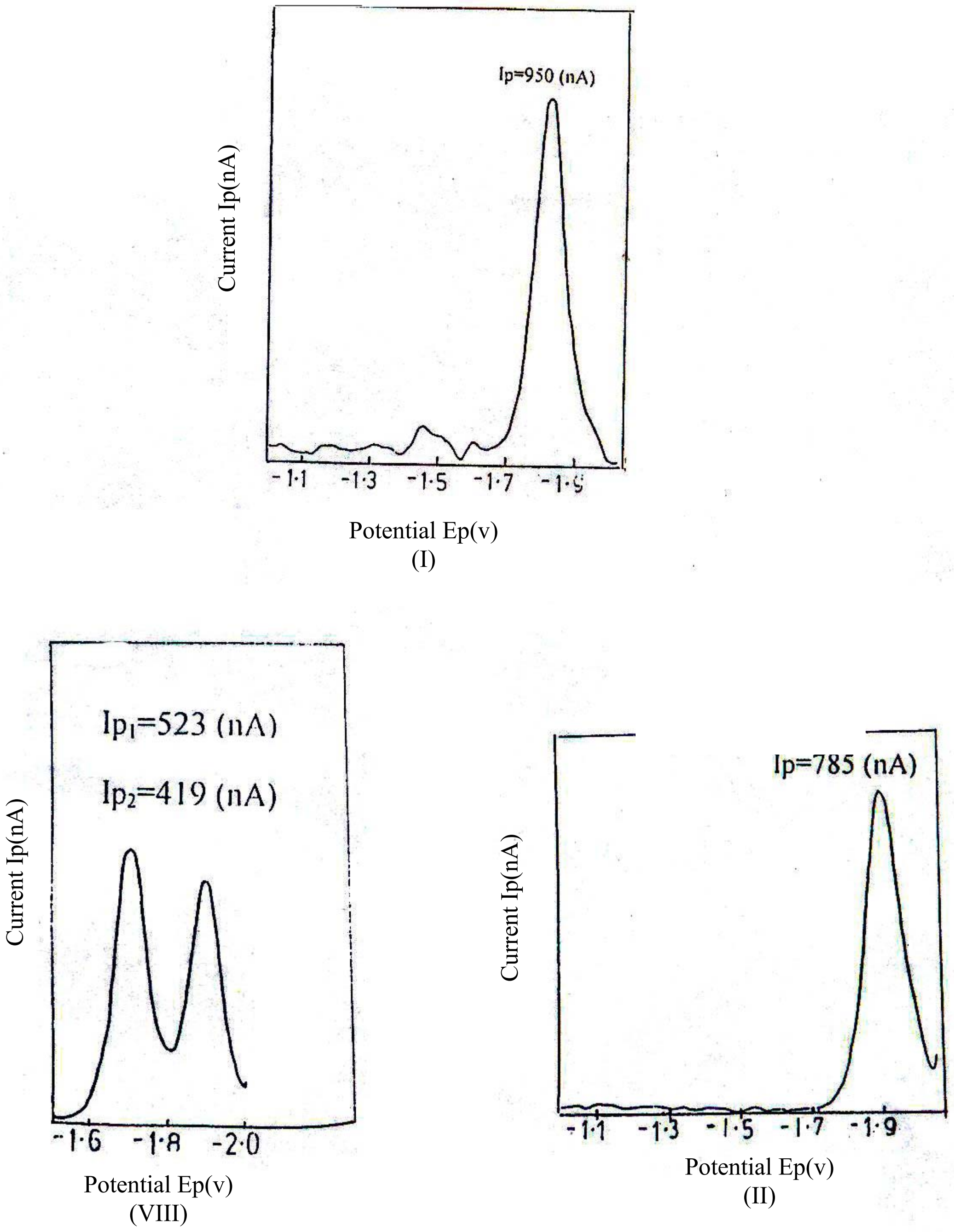
Compounds	Slope	R	S.D.
I (BA)	10.4 x 10^{6}	0.998	0.18
II (p-CH_3 BA)	8.67 x 10^{6}	0.999	0.032
III (m-CH_3 BA)	5.56 x 10^{6}	0.995	0.18
IV (p-OCH_3 BA)	5.8 x 10^{6}	0.994	0.096
V (m-OCH_3 BA)	0.27 x 10^{6}	0.994	0.068
VI (p-Cl BA)	10.64 x 10^{6}	0.999	0.161
VII (Ip1) (p-Br BA)	9.91 x 10^{6}	0.997	0.096
VII (Ip2) (p-Br BA)	3.31 x 10^{6}	0.999	0.045
VIII (Ip1) (p-I BA)	5.87 x 10^{6}	0.998	0.115
VIII (Ip2) (p-I BA)	4.69 x 10^{6}	0.997	0.118

Table 5 : The variation of Ep with concentration

Conc. x 10^{-6} M	**Log C**	**Ep (I) (V)**	**Ep (III) (V)**	**Ep (IV) (V)**	**Ep (V) (V)**	**Ep1 (VIIII) (V)**	**Ep2 (VIII) (V)**
3.8	-5.4	-1.854	-1.836	-1.928	-1.836	-1.742	-1.924
7.4	-5.1	-1.856	-1.834	-1.928	-1.834	1.740	-1.920
10.7	-4.9	-1.858	-1.832	-1.928	-1.834	1.738	-1.916
13.7	-4.8	-1.860	-1.832	-1.926	-1.834	1.734	-1.912
16.6	-4.7	-1.862	-1.832	-1.924	-1.832	1.738	-1.910
48.3	-4.3	-1.862	-1.826	-1.916	-1.832	1.732	-1.908
78.1	-4.1	-1.864	-1.824	-1.916	-1.830	1.732	-1.908
106.6	-3.9	-1.866	-1.822	-1.920	-1.836	1.732	-1.908
132.3	-3.8	-1.870	-1.822	-1.922	-1.828	1.730	-1.906
157.1	-3.7	-1.872	-1.822	-1.922	-1.828	1.730	-1.906

Table 6 : The Slope value and the number of the electron for compounds (I) , (III),(IV),(VIII)

compounds	**Slope**	**No of (e)**
I	1.07×10^{-2}	5.5
III	9.50×10^{-3}	6.2
IV	5.85×10^{-3}	10.0
V	4.58×10^{-3}	12.8
VIII (Ip1)	5.78×10^{-3}	0.115
VIII (Ip2)	4.69×10^{-3}	0.118



(I)

(VIII)

(II)

Fig 1: Square wave voltammetry of $9x10^{-5}$ M of a)compound I , b)compound II , C) compound VIII in DMSO/0.1 M $LiClO_4$.

REFERENCES

Berzas, T.I, Rodriguez, 1997. Voltametric behaviour of Sluphadimeoxol using Square-Wave and adsorptive Stripping Square-Wave techniques J. Anal. Chim. Acta., 349, pp.303-311.

Dayagis S. and Wiley J., The Chemistry of the Carbon Nitrogen Double bond . New York., 1970.

Kolthoff, I.M. and . Lingane, J.J.,1952 Polarography , 2nd Ed, interscience , NewYork 647p.

Mitta, A.K. and Singhal, O.P., 1986, Synthesis of substituted Anilic acid Hydrazides and their Hydrazones as possible antimicrobial agents, J. Indian Chem. Soc. 63, 759P.

Shareef,O.A. Thesis, 2000, Study of the Voltammatric properties of Benzylidene Aniline and its derivatives in aqueous and non aqueous solution Mosul University,Iraq.

Prabhu P.S.and Dodwad, 1983, Study of Uranyl complexes of some Schiff bases, J.Indian Chem, Soc., 60, pp.546-552.

Solamons K., Lieberman, H., Groudwater p.1, Hibbs D., Hursthouse., 1997, Inhibitors of IMPDH enzyme technical of field of the invention. Anti-Cancer Drug Design ,12, pp.635-647.

Sulaiman, S.T., Ahmad, I.S.2005, Square wave voltammetric Determination of Oxadiazole in aqueous solution . Raf.J.of Sci.,16,3,pp.1-6.

Sulaiman, S.T., and Hammed, Y.O., 1988 Differential pulse Polarographic Determination of Isonicotinic acid Hydrazid and Hydrazides in Admixture, Anal.Chim.Acta, 206, pp.379-383.

Young Han -Sun, Hiroki Inoue, Tamami Terada, Shigehiro Kamada, Yoshimasa Saburi, Katsuhiko Sekimata, Tamio Saito, Masatomo Kobayashi, Shigeo Yoshida, Tadao Asami, 2003, Amino acid and Ca^{+2} stimulate different patterns of Ca^{+2} oscillation through the Ca^{+2} sensing receptor. Journal of Inhibition and Medicinal Chemistry, 18, 3, pp.279-283.

Yu, J.J., and Huang, W., 1997, Determination of Ethanol in Wine by Voltammetry with an internal standard . Electroanalysis , 9, pp. 548-554 .

Yan, S.J., Burtan, W.H., Chllon P.L., and Chang C.C., 1978, Potential causal Antimalarial Agents Synthesis of Quin oxaline Benzimidazole and Derivatives containing a Novodiamin moiety. J Hetrocyclic .Chem , 15, 297p.