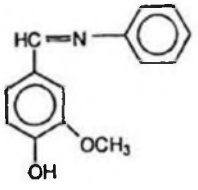
Electrochemical Reduction of Vanillideneaniline - A Polarographic Study

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The electroreduction behaviour of vanillideneaniline has been studied using Normal Pulse Polarography in 50% aqueous ethanol using BR buffers of different pH in the range 4 - 10. A one step, irreversible, diffusion controlled reduction is observed in all the cases. Kinetic parameters such as diffusion coefficient, heterogeneous rate constant and thermodynamic parameters are evaluated and the reduction mechanism is proposed.

Interest in the study of Schiff bases continues due to their anticancer [1,2], antifungal [3], antibacterial [4,5], antitumour [6] and antipyretic [7] properties. Literature survey revealed that no studies have been reported on the reduction mechanism of vanillideneaniline schiff base (A) in aqueous ethanol medium.



A

EXPERIMENTAL

The schiff base was prepared by mixing 12 ml of vanillin with 9 ml of aniline in a small evaporating dish and heating on a boiling water bath for 20 minutes. Then the mixture was cooled. During cooling, the mixture was stirred thoroughly for the effective formation of the crystals. The product was recrystallised from rectified spirit (m.pt. 152°C).

Britton - Robinson buffers of pH 4 - 10 were prepared by using 0.04 M acetic acid, boric acid, phosphoric acid and 0.2 M sodium hydroxide solution. All chemicals used were of AnalaR grade. Stock solution of depolariser was prepared in ethanol. Test solutions were prepared from the stock solution of the depolariser, buffer and supporting electrolyte, thermostated at 25±1°C and purged with purified nitrogen gas for 10 minutes before polarograms are taken.

Elico pulse polarographic analyser model CL-90 with Polaroc ord Model: LR-108 x - y recorder was used for polarographic measurements. A three electrode system (dme, SCE and Pt wire) was used. The pH was measured with Elico LI-120 pH meter.

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RESULTS AND DISCUSSION

Reduction of Vanillideneaniline

Vanillideneaniline exhibits a well defined, single wave in the pH range 4 - 10. Polarograms are recorded with mercury column heights of 55, 60, 65, 70 and 75 cms. The current at the plateau of the wave is found to vary as $h^{1/2}$ (Fig 1A) indicating the current to be diffusion controlled. The transient dependence of current on the mercury head has been studied in terms of log i *vs* log h_{eff} plots corresponding to different potentials (Fig 1B). The slope of these log - log plots is zero at the potential corresponding to the foot of the wave and it gradually increases as the potential corresponding to the limiting current is reached. This shows that the current is totally kinetically controlled at the foot of the wave, but it becomes diffusion controlled at the plateau. In between, the magnitude of the current is controlled by both [8]. So the polarographic reduction of vanillineaniline is irreversible in nature.

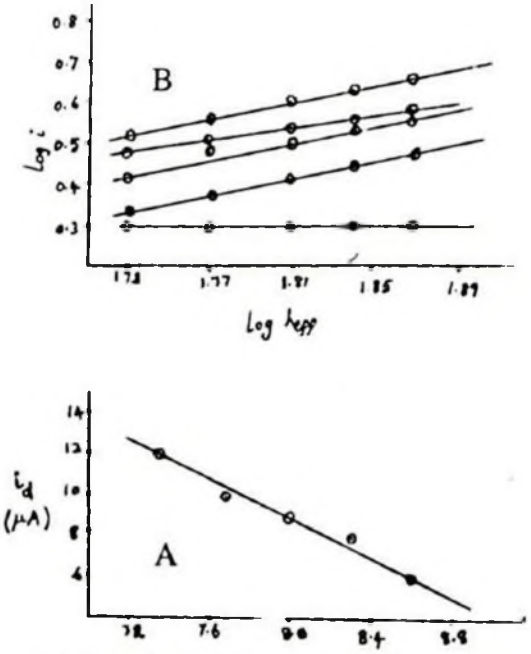


Fig1. Dependence of Current on Hg Column Height

A Diffusion Current *vs* $h^{1/2}$
B Log i *vs* log h plots at different potentials

The plot of E *vs* log $[i/(i_d - i)]$ is linear. The half wave potential is determined from this plot. As expected, the slope of this plot indicates the wave to be irreversible. The value of the diffusion current indicates the number of electrons involved in the electrode process to be 4.

The effect of temperature on the polarograms has been studied. The data is presented in the Table 1.

Table 1

Polarographic Data of Vanillideneaniline

[Vanillideneaniline] =1×10^{-3} M;[KCl] = 0.1 M
Solvent = 50% (v/v) EtOH; pH = 5.8;
Mercury height (h) = 65 cm

Temp °K	$-E_{1/2}$ V	i_d μA	$D \times 10^6$ $cm^2.s^{-1}$	$k^o_{f,h} \times 10^7$ $cm.s^{-1}$	ΔG^* $kJ.mol^{-1}$
294	1.94	10	4.74	0.39	30.55
299	1.78	9	3.84	3.23	28.80
304	1.73	8	3.03	11.81	27.88
309	1.43	7	2.32	1.96	30.36
314	1.40	6	1.71	0.35	32.83

Temperature coefficient of diffusion current = 0.2
Temperature coefficient of half wave potential = 0.04

The half wave potential values shift towards positive value with increase in

temperature indicating favoured reaction at elevated temperature. The small value of the temperature coefficient of diffusion current also confirms the diffusion controlled nature of the waves [9]. The heterogeneous rate constant ($k^{\circ}_{f,h}$) is calculated using Meites and Isreal's extended method [10].

The activation energy for diffusion Q_D is calculated using the following equation [11]:

$$\log \frac{i_d}{m^{2/3}t^{1/6}} = \log 0.627nFD^{1/2} - \frac{1/2\ Q_D}{2.303\ RT}$$

The free energy of activation $\Delta G^{\neq}$ is obtained from the relation:

$$k^{\circ}_{f,h} = \frac{kT}{h}\ \theta \exp(-\Delta G^{\neq}/RT)$$

where θ is the thickness of the electrical double layer which is assumed to be 2×10^{-8} cm. The enthalpy of activation $\Delta H^{\neq}$ for the electrode reaction is calculated by equating the slope of log $k^{\circ}_{f,h}$ *vs* 1/T plot to $-\Delta H^{\neq}/2.303\ R$ (Fig 2). The entropy of activation is also calculated.

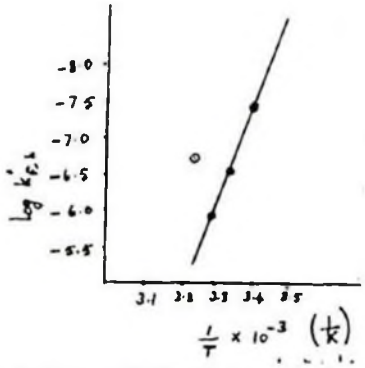


Fig2. Arrheneus plot for electro reduction of vanillideneaniline

The values are found to be Q_D = 23.11 kJ/mol, $\Delta H^{\neq}$ = 68.93 kJ/mol and $\Delta S^{\neq}$ = 0.13 kJ/mol/°K at 299°K.

Effect of Medium

Effect of medium on the polarograms are studied using different media. The results are presented in Table 2.

Table 2

Half wave Potential Values of Vanillideneaniline in Different Media

[Schiff Base] = 1 x 10^{-3} mol.dm^{-3}
[Inert salt] = 0.1 mol.dm^{-3}
Solvent = 50 % v/v EtOH; Temp = 26°C

Inert Salt = KCl		pH = 5.8	
pH	$-E_{1/2}$ (V)	Inert Salt	$-E_{1/2}$(V)
4.0	1.34	LiCl	1.52
5.2	1.35	NaCl	1.75
5.8	1.78	KCl	1.78
6.4	1.83	NH_4Cl	1.76
8.2	1.85		
9.9	1.90		

The half wave potential is found to shift to negative value with increase in pH indicating easier reduction at acidic pH. Ease of reduction is also affected by inert electrolyte in the medium. The order of $-E_{1/2}$ is found to be $Li^+ < Na^+ < NH_4^+ \sim K^+$. This is in accordance to the ionic size [12].

Effect of Solvent

Polarographic behaviour is studied in different solvents - aqueous ethanol,

Table 3

Parameters of Vanillideneaniline in Different solvents

[Schiff Base] = 1 x 10^{-3} mol.dm^{-3}; Supporting Electrolyte] = 0.1 mol.dm^{-3} KCl
Temp = 26°C; pH = 5.8

Solvent Content v/v	$-E_{1/2}$ V	i_d µA	rx10^8 cm	Dx10^6 $cm^2.s^{-1}$	$-E_{1/2}$ V	i_d µA	rx10^8 cm	Dx10^6 $cm^2.s^{-1}$	$-E_{1/2}$ V	i_d µA	rx10^8 cm	Dx10^6 $cm^2.s^{-1}$
	Aqueous Ethanol				Aqueous Acetonitrile				Aqueous DMF			
50%	1.78	9	4.8	3.84	1.84	14	4.97	9.29	1.71	13	2.33	8.01
40%	1.72	8	6.8	3.03	1.80	12	6.32	6.83	1.69	12	3.05	6.83
30%	1.89	7	9.1	2.32	1.74	11	7.20	5.74	1.92	10	4.97	4.74
20%	1.64	6	12.6	1.71	1.82	10	7.86	4.74	1.77	9	7.69	3.84
10%	1.69	5	30.2	1.19	1.61	9	10.67	3.84	1.82	8	11.29	3.03

aqueous dimethylformamide and aqueous acetonitrile (10 - 50 % in each case). In each solvent studied i_d (and hence D values) decrease with increase in polarity / viscosity of the medium as indicated by the increase in the radius of the solvated species.

Combining Ilkovic and Stock-Einstein equations results in the following relationship:

$$i_d = 607\ ncm^{2/3}.t^{1/6}\left[\frac{3.32x10^{-5}}{(4/3\pi Nr^3)^{1/3}\ \eta}\right]^{1/2}$$

Using this equation, the radius of the diffusing species (r) is calculated and included in the Table. One can note that the value of r also increases with increase in organic solvent component as expected from the variations of D.

Effect of Substituent

The relative effects produced on the half wave potential of organic compounds by various substituents are dependent not only upon their mesomeric and inductive effects but also upon their position in the molecule and the buffer system used [13]. In the present study, an effort has been made to compare the shift in half wave potential values by changing the position of the substituents. The relevent data are presented in Table 4.

Table 4

Half wave potential Values of Different Schiff Bases

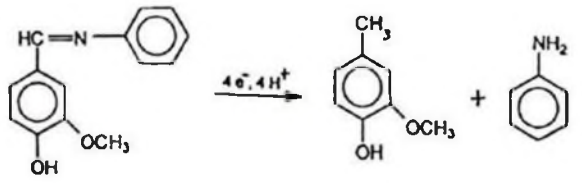
[Schiff Base] = 1 x 10^{-3} mol.dm^{-3}
[Supporting Electrolyte] = 0.1 mol.dm^{-3} KCl
Solvent = 50 % v/v EtOH; Temp = 26°C;
Mercury Height = 65 cm

Schiff base	$-E_{1/2}$ V
o-methoxy benzylidene	1.71
Vanillideneaniline	1.79
Salicylideneaniline	1.93

The half wave potential values of different substituted Schiff bases are in the following order: o methoxy (1.71V) < m-methoxy-p-hydroxy (1.79 V in vanillideneaniline) < o-hydroxy (1.93 V in salicylidene aniline).

If +M effect alone were operating, o-methoxy and o-hydroxy derivatives should have comparable $E_{1/2}$ values, but the value is lower for o-methoxy compound. This suggests that o-methoxy group exhibits electron withdrawing inductive effect rather than electron releasing mesomeric effect (the bulky o-methoxy group twists the benzene ring out of plane); m-methoxy-p-hydroxy compound has $E_{1/2}$ value in between the two extremes as m-methoxy group shows only -I effect whereas p-hydroxy group exhibits +M effect.

Electrochemical reduction of vanillideneaniline using mercury pool cathode and platinum wire anode in a divided cell leads to the formation of aniline as the product. On the basis of the above results, the following mechanism may be proposed for the electrochemical reduction of vanillideneaniline in the entire pH range 4 - 10.



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