Studies on electrode kinetics of schiff bases in aqueous and DMF media

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Electrochemical reduction of schiff bases, viz., salicylidene-2-hydroxyaniline (**1**), acetophenonidene-2-hydroxyaniline (**2**), 4-hydroxyacetophenonidene-2-hydroxy aniline (**3**) and 4-hydroxyacetophenonidene-2-hydroxy-5-chloroaniline (**4**) using techniques of cyclic voltammetry, chronoamperometry and chronopotentiometry in buffer solutions of different pH and in 100% DMF at HMDE have been carried out. The kinetic parameters have been determined and the mechanism for electrochemical reduction of these schiff bases has also been proposed.

Although the preparation, structural and spectral characterisation and the coordination chemistry of schiff bases have been studied extensively[1,2], yet little is reported on the polarographic studies and their metal complexes[3]. Recently, studies on schiff bases derived from salicylaldehyde, acetophenone and 4-hydroxy acetophenone with o-aminophenol and its chloro derivative using voltammetric, potentiometric and spectrophotometric techniques have been reported[4]. In continuation of our earlier work, an attempt is made to study the kinetic parameters for the reduction of these schiff bases **1-4** at HMDE in aqueous and DMF media by cyclic voltammetry, chronoamperometry and chronopotentiometry.

Materials and Methods

The cyclic voltammograms of schiff bases (solutions) were recorded with PARC model 384 B Polarographic analyser equipped with a Houstan DMP-40 digital plotter and PAR 303 A cell assembly as described earlier[4]. The chronoamperometric and chronopotentiometric results were recorded with PAR 175 universal programmer connected to PAR 306 and PAR 176 current voltage converter. A cup shaped cell provided with model PAR 303 SMDE/HMDE, containing platinum wire (auxillary) and SCE (reference) electrodes was used throughout the study. The effective area of the working electrode employed was 0.017 cm^2.

The schiff bases **1-4** were prepared according to the procedure described earlier[4]. Stock solutions (0.1 M) of the schiff bases were prepared in DMF and the ionic strength and varying pH

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values of solutions were maintained as mentioned previously[4]. The schiff bases **1-4** were also studied in 100% DMF with tetrabutyl ammonium perchlorate (TBAP) (0.1 M) in final volume of 5 ml. The ligand solutions were deaerated with nitrogen. The characteristic $i \rightarrow E$, $i \rightarrow t$ and $E \rightarrow t$ plots were recorded under specific conditions as mentioned in the respective Tables.

Results and Discussion

Cyclic voltammetry

All the schiff bases **1-4** at pH 8, show one cathodic peak and its anodic counterpart in the potential range -0.5 V to -0.4 V versus Ag/AgCl. A representative diagram for schiff base **1** at pH 8 has been given (Fig. 1A). The reduction and oxidation steps of all the schiff bases have been earlier explained on the basis of reversible 2 electron exchange[4]. The electrode process in all the cases is found to be coupled with protons of the medium. The peak currents are almost constant in the pH range 5.0-7.5 and found decreasing on either side of it. The ratio of anodic to cathodic currents is always less than unity at lower scan speeds and the difference between the cathodic and anodic peak potentials, ΔE_p, is greater than 0.3 V. Further, the peak potentials are also dependent on scan speeds. Similar results are obtained at all pH values in the range 1-10. These observations clearly indicate that the two electron reduction of schiff bases **1-4** at HMDE is not totally reversible. The plots of i_{p_c} versus $v^{1/2}$ are linear and pass through origin at all the pH values. This shows that the electrode process is controlled by diffusion in all the cases. Table 1 presents the cyclic voltammetric data of schiff bases **1-4** at two selected pH (3.5/5.2 and 8) values where they ex-

Table 1 – Cyclicvoltammetric data for schiff bases 1-4 at different pH and in DMF

[$\mu = 0.1$ MTBAP; conc. = 1 mM; W.E. = HMDE; R.E. = Ag/AgCl]

Schiff base	pH/DMF	Scan rate V/sec	i_{p_c} μA	i_{p_a} μA	i_{p_a}/i_{p_c}	$-E_{p_c}$ V	$-E_{p_a}$ V	E_p V
1	3.5	0.05	0.53	0.35	0.65	0.150	0.090	0.060
		0.10	0.75	0.50	0.67	0.160	0.090	0.070
	8.0	0.05	0.58	0.42	0.72	0.400	0.340	0.060
		0.10	1.85	1.30	0.70	0.410	0.340	0.070
	DMF	0.05	1.09	1.00	0.92	0.760	0.630	0.130
		0.10	1.65	1.50	0.91	0.770	0.630	0.140
2	5.2	0.05	1.40	0.65	0.47	0.284	0.200	0.084
		0.10	2.06	0.95	0.46	0.286	0.200	0.086
	8.0	0.05	0.50	0.32	0.63	0.436	0.371	0.065
		0.10	1.60	1.10	0.64	0.440	0.375	0.065
	DMF	0.05	1.16	1.10	0.95	0.908	0.780	0.128
		0.10	1.81	1.76	0.94	0.926	0.780	0.146
3	3.5	0.05	0.50	0.31	0.62	0.162	0.097	0.065
		0.10	0.71	0.45	0.63	0.169	0.099	0.070
	8.0	0.05	0.58	0.39	0.67	0.493	0.425	0.068
		0.10	1.64	1.15	0.70	0.498	0.426	0.072
	DMF	0.05	1.00	0.91	0.91	0.875	0.760	0.115
		0.10	1.40	1.25	0.89	0.880	0.760	0.120
4	3.5	0.05	0.48	0.30	0.62	0.085	0.017	0.068
		0.10	0.75	0.52	0.69	0.090	0.018	0.072
	8.0	0.05	0.55	0.37	0.67	0.452	0.387	0.065
		0.10	1.46	0.95	0.65	0.458	0.383	0.075
	DMF	0.05	1.20	1.07	0.89	0.855	0.720	0.135
		0.10	1.80	1.63	0.90	0.860	0.720	0.140

ist as a single component viz. either protonated or the free form[4].

The cathodic and anodic processes of schiff bases 1-4 in DMF appear in the potential region −0.95 V-0.6 V and the difference in peak potentials, ΔE_p, is always greater than 0.1 V which indicates that the reduction process is not the same as that in the aqueous medium. However, the plots of ^ip_c versus $v^{1/2}$ are linear and pass through the origin (Fig. 1.C). The cyclic voltammograms for the schiff base 1 in DMF is given in Fig. 1B. The peak potentials and peak currents data of all the four schiff bases are given in Table 1.

Chronoamperometry

The diffusion coefficients of the schiff bases in different solvents were studied by chronoamperometry. The chronoamperograms of the schiff bases 1-4 in both aqueous and DMF media are well defined at their respective peak potentials or beyond that. In each case, the plots of it$^{1/2}$ versus t are horizontal showing that the charge transfer

process is diffusion controlled. The linear portion of these plots are extrapolated to zero time to obtain $(it^{1/2})_{t=0}$. This quantity is used to evaluate the coefficients of the corresponding schiff bases with Cottrell equation[5] (1),

$$i = \frac{nFA\,D_{ox}^{1/2}\,C_{ox}^{\bullet}}{\pi^{1/2}\,t^{1/2}} \qquad \cdots (1)$$

where t = time in seconds, i = instantaneous currents in microamperes, $C_{ox}^{\bullet}$ = concentration of schiff base in millimoles per litre.

The data obtained are presented in Table 2 and the plot of it$^{1/2}$ versus t for the schiff base 1 in DMF is given in Fig. 1 D.

Chronopotentiometry

In order to verify the diffusion coefficient data of the schiff bases in different solvent media and to evaluate electrode kinetic parameters, chronopotentiometric study was also undertaken. The typical E→t plots for the schiff bases 1-4 in aque-

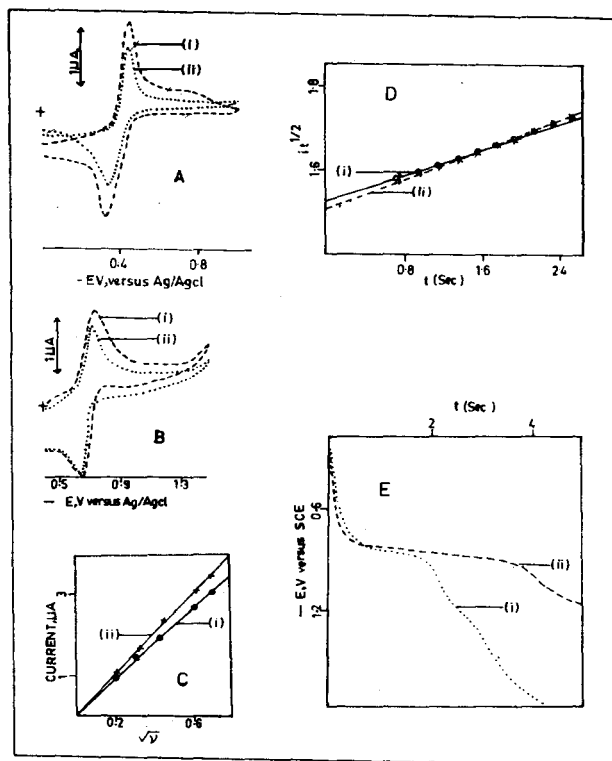Table 2 – Chronopotentiometric data of schiff bases **1-4** in aqueous and DMF media

Conc.: 1 mM

Schiff base	pH/DMF	Current applied μA	Transition time, τ, sec	it$^{1/2}$
1	3.5	1.5	1.31	1.72
	8.0	2.0	1.20	2.19
	DMF	1.5	3.14	2.66
		2.0	1.57	2.51
2	5.2	1.5	0.66	1.22
	8.0	2.0	1.10	2.10
	DMF	1.5	6.70	3.88
		2.0	3.35	3.66
3	3.5	1.5	1.17	1.62
	8.0	2.0	0.97	1.97
	DMF	1.5	3.00	2.59
		2.0	1.60	2.52
4	3.5	1.5	1.10	1.57
	8.0	2.0	0.90	0.90
	DMF	1.5	3.10	2.64
		2.0	1.59	2.52

Fig. 1(A)– Cyclic voltammogram of schiff base **1** at pH 8.0 scan speed, ν, (i) 0.2 V/sec and (ii) 0.1 V/sec. conc.=1 mM; W.E.=HMDE. (B) Cyclic voltammogram of schiff base **1** in 100% DMF scan speed, ν, (i) 0.2 V/sec (ii) 0.1 V/sec; conc.=1 mM; W.E.=HMDE; supporting electrolyte TBAP. (C) Plots of i_p versus $\nu^{1/2}$ for schiff base **1** (i) and schiff base **2** (ii) in 100% DMF. (D) Plots of it$^{1/2}$ versus t for the reduction of schiff base **1** in 100% DMF at applied voltage (i) −0.85 V (ii) −0.90 V vs SCE, Conc.=1 mM, (E) Chronopotentiograms of schiff base **1** (i) and schiff base **2** (ii) in DMF at applied current 2 μA; supporting electrolyte TBAP; conc.=1 mM

ous and DMF media were obtained by applying the current densities in the range 1-3 μA. They were well defined and the transition times, τ, obtained were in the range 0.5 to 3 seconds for aqueous solutions and 0.5 to 6.7 seconds for DMF solutions. The i$\tau^{1/2}$ values (Table 2) for each schiff base were found fairly constant but they were different from each other. The consistancy in the result indicates that the reduction process involved in each schiff base is diffusion controlled. The chronopotentiograms of the schiff bases **1** & **2** in DMF are given in Fig. 1E. With the help of chronopotentiometric data, the diffusion coefficients of schiff bases **1-4** have been calculated using equation[6] (2),

$$\tau^{1/2} = \frac{\pi^{1/2}\, n\, \text{FAD}_{ox}^{1/2}\, C_{ox}}{2\, i} \qquad \dots (2)$$

and the values are reported in Table 3. The values so obtained in two different media are in good agreement with those obtained from chronoamperometric data.

Kinetic studies

The peak separation values, ΔE_p, were used to calculate the standard reaction rate constant k_s^0 for the reduction of each schiff base in aqueous and DMF media using Eq. (3) of Nicholson[7]

$$\psi = \frac{\gamma^a\, k_s^0}{(\pi(\text{nF}/\text{RT})\text{D}_{ox})^{1/2}} \qquad \dots (3)$$

Here ψ is the function of ΔE_p, γ is the ratio of the diffusion coefficients of the reduced and oxidised forms of the electroactive species $(D_{red}/D_{ox} \simeq 1)$, α is the transfer coefficient and all other symbols have their usual meanings.

The potential, E_t at a definite time, t, expressed by Eq. (4),

$$E_t = \frac{\text{RT}}{\alpha n_a \text{F}} \ln\left(\frac{n\text{FAC}_{ox}\, K_{fh}^0}{i}\right) + \frac{\text{RT}}{\alpha n_a \text{F}} \ln[1 - (t/\tau)^{1/2}] \qquad \dots (4)$$

is utilised by plotting E_t versus $\log[1 - (t/\tau)^{1/2}]$, as it satisfies the condition of linear diffusion[8] at this

Table 3 — Kinetic parameters for the reduction of schiff bases 1-4 at different pH

[Conc. = 1.0 mM (aqueous and DMF media); $\mu = 0.1$ M (TBAP); scan speed $(v) = 0.1$ V/sec; W.E. = HMDE; R.E. = Ag/AgCl/SCE]

Schiff	pH/DMF	$D \times 10^6$		$*an_a$	$*k^0_{fh} \times 10^{14}$ cm/sec	ψ	$**k^0_s \times 10^2$ cm/sec
		*CP	**CA				
1	3.5	0.32	0.49	0.85	0.410	2.63	0.910
	8.0	0.62	0.78	0.90	0.450	2.63	1.150
	DMF	0.75	0.67	0.69	0.782	0.16	0.064
2	5.2	0.29	0.29	0.87	0.220	0.95	0.250
	8.0	0.31	0.30	0.93	0.240	25.12	1.410
	DMF	1.53	1.12	0.71	0.245	0.23	0.120
3	3.5	0.26	0.43	0.82	0.380	2.63	0.850
	8.0	0.55	0.70	0.91	0.420	2.20	0.910
	DMF	0.75	0.63	0.73	0.537	0.36	0.143
4	3.5	0.24	0.41	0.80	0.250	2.20	0.690
	8.0	0.52	0.67	0.83	0.290	1.66	0.670
	DMF	0.75	0.61	0.73	0.614	0.16	0.193

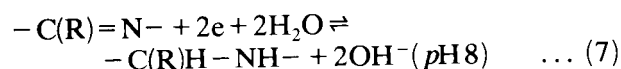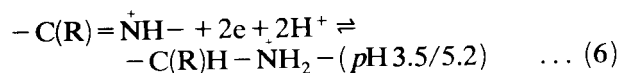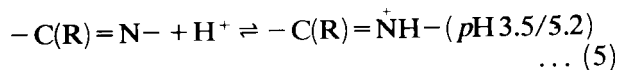*Calculated from chronopotentiometric (CP) data
**Calculated by cv using the diffusion coefficients from chronoamperometric (CA) data

potential. By using intercept and slope values of various plots, the forward rate constant k^0_{fh} and an_a of the schiff bases in aqueous and DMF media have been calculated. The values of k^0_s, k^0_{fh} and an_a so obtained are presented in Table 3. The values of k^0_s suggest that the electrode process in both aqueous and DMF media are not reversible[9]. The k^0_s values in DMF are almost ten times less than those in aqueous media which indicates that electrode processes in DMF are relatively more irreversible. The k^0_s values in aqueous medium are found higher in the basic range of pH than in the acidic range. Among all the four schiff bases studied it is marked that the schiff base 2 is quickly reduced and is less irreversible in acidic medium and schiff base 4 in basic medium.

Mechanism of the electrode processes

Our earlier findings[4] showed that the formal potentials of the single redox couple in 1-4 are pH dependent. The anodic shifts of peak potentials (Table 1) with decreasing pH suggest the resultant effect of protons in the electron transfer rate steps. Earlier potentiometric data[4] had shown the protonation of the schiff bases 1-4 in acidic

pH. It can thus be concluded that the schiff bases 1, 3 and 4 at pH 3.5 and schiff base 2 at pH 5.2 fully exist in protonated form through a chemical reaction at the nitrogen of $-C(R)=N-$ (where $R = N$ or CH_3). However, all the schiff bases 1-4 exist as such at pH 8. Hence, the electrode reactions at pH 3.5/5.2 and 8.0 are considered as follows:

$$-C(R)=N- +H^+ \rightleftharpoons -C(R)=\overset{+}{N}H- \ (pH\ 3.5/5.2) \quad \ldots (5)$$

$$-C(R)=\overset{+}{N}H- +2e+2H^+ \rightleftharpoons \\ -C(R)H-NH_2- (pH\ 3.5/5.2) \quad \ldots (6)$$

$$-C(R)=N- +2e+2H_2O \rightleftharpoons \\ -C(R)H-NH- +2OH^- (pH\ 8) \quad \ldots (7)$$

The electrode reaction (6) is comparatively less irreversible than the reaction (7). In DMF, the following electrochemical reaction (8) can be proposed as the rate of electrolytic reaction in DMF is less than those of the reactions (6) and (7),

$$SB + 2e \rightleftharpoons (SB)^{2-} \quad \ldots (8)$$

Based on the experimental data in Table 3, the electron transfer rates in aqueous and DMF media were found in the order, reaction (8) < reaction (6) < reaction (7).

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