SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES ON IRON(II) COMPLEXES OF 2-(2-PYRIDYLETHYL) IMINO-3-BUTANONE OXIME (HDPE) AND 2-(2-PYRIDYLMETHYL) IMINO-3-BUTANONE OXIME (HDPM)

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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES ON IRON(II) COMPLEXES OF 2-(2-PYRIDYLETHYL) IMINO-3-BUTANONE OXIME (HDPE) AND 2-(2-PYRIDYLMETHYL) IMINO-3-BUTANONE OXIME (HDPM)

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We report the synthesis of iron (II) complexes with Schiff bases derived from a series of ligands (L = 2-(pyridylethyl) imino-3-butanone oxime (HDPE) and 2-(pyridylmethyl) imino-3-butanone oxime (HDPM). The reaction of $[Fe^{II}(OH_2)_4 Cl_2]$ in aqueous suspension with L (stoichiometry 1:2) yields after addition of $NaClO_4$ deep dark red crystals of $[Fe^{II}(LH)_2](ClO_4)_2$. The complexes have electronic spectra dominated by an intense metal-to-ligand charge-transfer (MLCT) transition in the visible region of the spectrum. Their redox potential dependence on pH was extensively studied. The results from the electrochemistry, the potentiometric pKa values and the elemental analysis unequivocally confirm that the iron complex with HDPE has been isolated as $[Fe^{II}(HDPE)(DPE)]$ ClO_4. At pH <4 a single reversible one-electron, two-proton transfer was observed for $[Fe^{III}(L)_2]^+$ – $[Fe^{II}(LH)_2]^{2+}$ ($E^{\circ}{}_{298}$ = 0.883 V for L = HDPM and $E^{\circ}{}_{298}$ = 0.770 V for L = HDPE, *vs*. NHE). In the pH range of 4.5 < pH < 7.0 a single reversible one-electron, one-proton couple was observed for $[FeIII(L)2]^+$ -$[FeII(LH)(L)]^+$ ($E^{\circ}{}_{298}$ = 0.646 V for L = HDPM and $E^{\circ}{}_{298}$ = 0.578 V for L = HDPE, *vs*. NHE). At pH>7 a single reversible one-electron couple $[Fe^{III}(L)_2]^+$-$[Fe^{II}(L)_2]$ was observed ($E^{\circ}{}_{298}$ = 0.246 V for L = HDPM and $E^{\circ}{}_{298}$ = 0.186 V for L = HDPE, *vs*. NHE). The protonation constants have been determined by potentiometric titration and electrochemical analysis of the iron (II) species. The pKa values using both techniques were in close agreement. From the potentiometric titration data, the acid-dissociation constants pK_{a1} and pK_{a2} were found to be 4.37 and 6.38 for $[Fe^{II}(HDPM)_2]^{2+}$ and pK_a to be 6.82 for $[Fe^{II}(HDPE)(DPE)]^+$. Electrochemical analysis gives acid-dissociation constants pKa_1 and pKa_2 of 4.30 and 6.,80 for $[Fe^{II}(HDPM)_2]^{2+}$ and pK_a of 6.77 for $[Fe^{II}(HDPE)(DPE)]^+$.

KEYWORDS: iron(II), oxime, Schiff base, electrochemistry

INTRODUCTION

Studies of metal complexes of tridentate and hexadentate amine-imine-oxime ligands have appeared frequently in the literature.[1-12] Most of these studies have

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focused on stabilization of nickel (IV) complexes. The synthesis and X-ray structural analysis of nickel complexes $[Ni^{II}(HDPE)_2]^{2+}$ were reported recently[13] and electrochemical studies of $[Ni^{II}(HDPE)_2]^{2+}$ and $[Ni^{II}(HDPM)_2]^{2+}$ were the subject of intensive electrochemical studies in our laboratory.[14] In addition, synthesis of Schiff bases containing imino-oxymate groups and their complexes with iron have been reported by Chakravorty *et al.*[6-8] In the present manuscript we report another new Schiff base containing a pyridyl group and its complexes with iron. The ligands HDPE(I) and HDPM(II) hold protons where dissociation properties are dependent on the oxidation state of the metal ion. This paper explores the effect caused by an electron on complex stabilization, pKa and electrochemical properties of complexes III and IV.
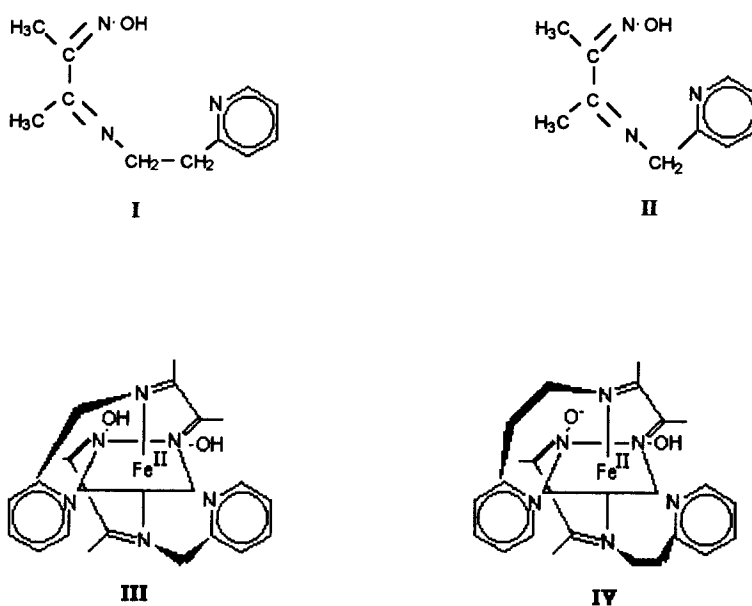
Scheme

EXPERIMENTAL

Materials

All chemicals were analytical grade reagents, and distilled water was used to prepare solutions. Argon, ultra pure grade purchased from White Martins was used for deoxygenating purposes.

Synthesis

The ligands, 2-(2-pyridylethyl)imino-3-butanone oxime and 2-(2-pyridylmethyl)imino-3-butanone oxime, hereafter referred to as HDPE and HDPM, respectively were prepared according to the method described in the literature.[15] The $[Fe^{II}(HDPM)_2]^{2+}$ and $[Fe^{II}(HDPE)(DPE)]^{+}$ complexes were prepared by

adding $[Fe^{II}(OH_2)_4Cl_2]$ (1.3 mmol) to an aqueous suspension of the ligand (2.6 mmoles) under argon with constant stirring.[16] The solution gradually turned to a bright red color. Addition of 0.5 g of $NaClO_4$ induced precipitation of an amorphous dark red solid for HDPM and for HDPE. The solids were collected by filtration and washed with methanol and ether, dried under reduced atmosphere, protected from light and kept in the refrigerator. The results of elemental analysis indicate that the iron complex with HDPE was isolated as $[Fe^{II}(HDPE)(DPE)]ClO_4$. Further results in the present work corroborates this stoichiometry. *Anal.* Calcd. for $[Fe^{II}(HDPM)_2](ClO_4)_2$: C, 37.70; H,4.11; N,13.19; Found; C,37.75; H, 4.13; 12.99. $[Fe^{II}(HDPE)(DPE)](ClO_4)$, *Anal.* Calcd. C, 43.33; H, 5.62; N, 13.78. Found: C, 43.12; H, 4.99; N, 14.12.

Physiochemical Measurements

Electronic spectra were recorded on a Shimadzu UV – 190 spectrophometer (reproducibility wavelength = 0.2 nm) using 1 cm quartz cells. The pH measurements were made with a Micronal Model B375 pH meter standardized with standard buffers of pH 4.0, 7.0, and 9.0, in a double-walled glass vessel thermostated to $25 \pm 0.1\,°C$ under argon atmosphere. The pKa values for deprotonation of the complexes were calculated by using the PKAS program developed by Motekaitis and Martell.[17]

Electrochemistry

Cyclic voltammetric behavior of $[Fe^{II}(HDPE)(DPE)]^+$ and $[Fe^{II}(HDPM)_2]^{2+}$ was examined under prepurified and solvent-saturated argon atmosphere at 25.0°C with the use of a three-electrode cell, using a BioAnalytical System, BAS. The working electrode was a glassy-carbon disk electrode. As reference electrode a Ag/AgCl [sat'd KCl/sat'd AgC1] electrode was used. The potentials are reported *vs.* NHE by using a correction term of 197 mV.

RESULTS AND DISCUSSION

Spectrophotometric Studies on $[Fe^{II}(HDPM)_2]^{2+}$ and $[Fe^{II}(HDPE)(DPE)]^+$

The electronic spectra of the complex $[Fe^{II}(HDPM)_2]^{2+}$ exhibit an absorption band in the visible region (Fig. 1) at 519 nm ($\varepsilon = 7{,}500$ M^{-1} cm^{-1}) and two shoulders at 640nm and 464 nm ($\varepsilon = 4{,}600$ M^{-1} cm^{-1}). A second band was found at 380 nm ($\varepsilon = 6\ 000$ M^{-1} cm^{-1}). Both bands at 640nm and 464nm are assigned to charge transfer (CT) bands.[18] The first transition is a CT from a metal t_{2g} orbital (considering ideal Oh symmetry) to the ligand dimine[19] LUMO π^*. The shoulder for both complexes has been suggested by Chakravorty[20] as originating from the ($^1A_{1g}$-$^1T_{1g}$) (v_1) transition. This explanation is confirmed by an observed red shift of the CT band and the invariance of the position of the shoulder in spectra obtained in alkaline medium. It is known that the ligand field bands of hexadentate Ni(IV) and Co(III) complexes are not affected by deprotonation. Both CT bands could arise from the pyridine ring of the metal and the red shift could be from charge flow from the $= N-O^-$ group to the metal.[21] The presence of CT bands
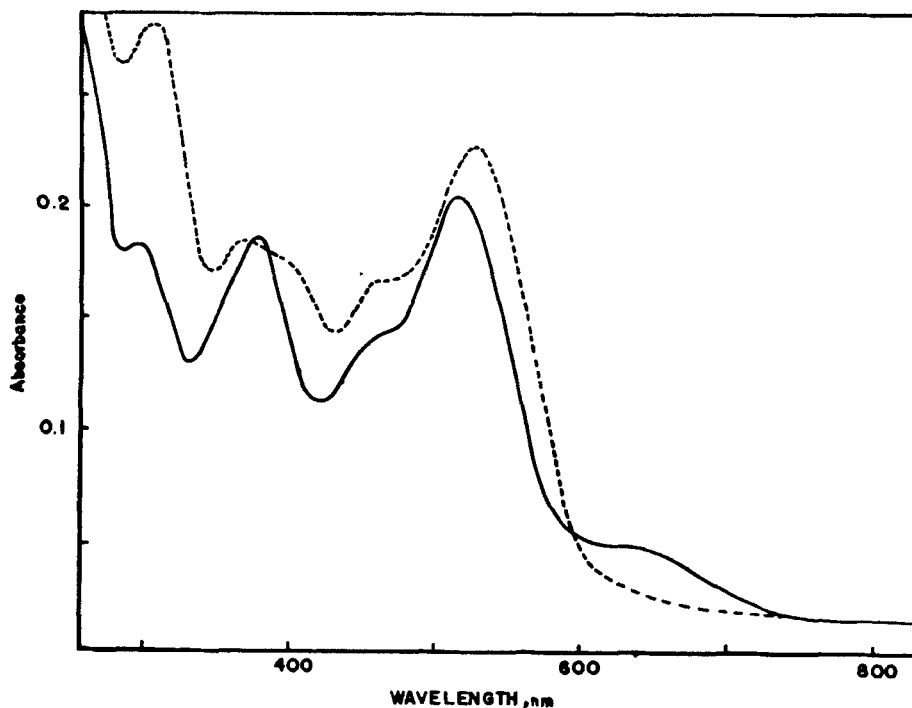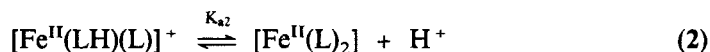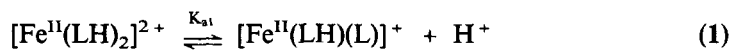
Figure 1   Electronic spectra [Fe^{II}(HDPM)$_2$]$^{2+}$ (———) and [Fe^{II}(HDPE)(DPE)]$^+$ (-----).

strongly suggests an asymmetric *cis* position for the pyridine in the structure of the complex consistent with the X-ray structure[1] and other analogous O_h symmetry complexes.[22] The electronic spectra in the UV region exhibit a band at 194 nm and two bands at 226 nm and 248 nm. The visible electronic spectral shape found in the [Fe^{II}(HDPE)(DPE)]$^+$ complex exhibits the same spectral shape found in [Fe^{II}(HDPM)$_2$]$^{2+}$ with minor shifts of the absorption bands (Fig. 1). A band at 531 nm ($\varepsilon = 6,000$ M^{-1} cm^{-1}) and a shoulder at 464 nm ($\varepsilon = 4,500$ M^{-1} cm^{-1}) were found along with a second band at 373 nm ($\varepsilon = 4,700$ M^{-1} cm^{-1}) and a shoulder at 389 nm. The electronic spectra in the UV region exhibit three bands at 198 nm ($\varepsilon = 20,300$ M^{-1} cm^{-1}), 312nm ($\varepsilon = 20,300$ M^{-1} cm^{-1}), and 256 nm ($\varepsilon = 16,700$ M^{-1} cm^{-1}).

Potentiometric pKa Determination on Iron Complexes with HDPE and HDPM ligands

Potentiometric titration data on [Fe^{II}(HDPM)$_2$]$^{2+}$ have revealed two acid dissociation constants K_{a1} and K_{a2} corresponding to Equations 1 and 2.

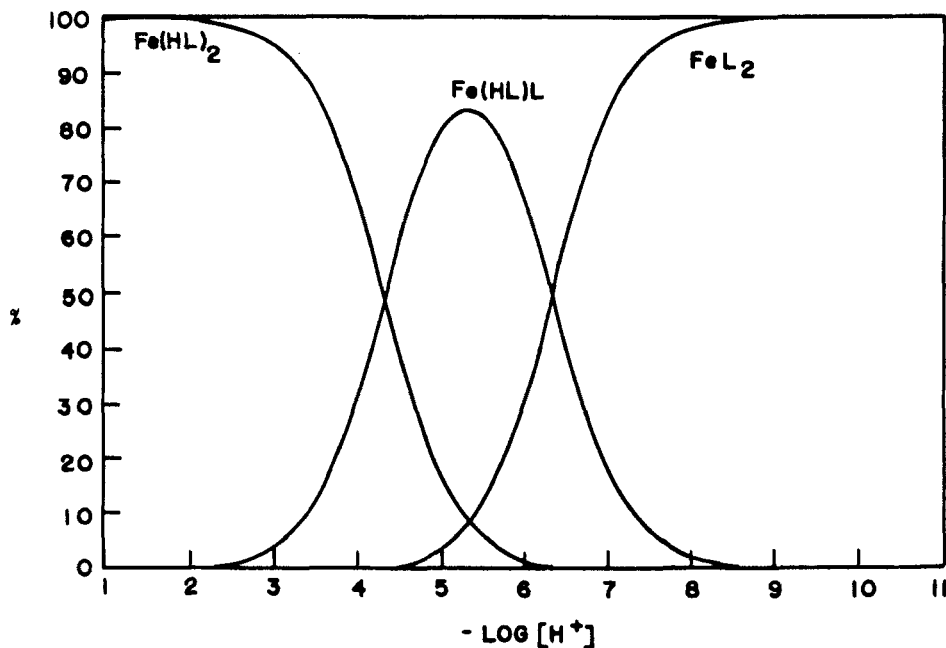$$[\text{Fe}^{II}(\text{LH})_2]^{2+} \xrightleftharpoons{K_{a1}} [\text{Fe}^{II}(\text{LH})(\text{L})]^+ + \text{H}^+ \tag{1}$$

$$[\text{Fe}^{II}(\text{LH})(\text{L})]^+ \xrightleftharpoons{K_{a2}} [\text{Fe}^{II}(\text{L})_2] + \text{H}^+ \tag{2}$$

Figure 2 Species distribution curves of $[Fe^{II}(HDPM)_2]^{2+}$ represented by Fe $(HL)_2$, $[Fe^{II}(HDPM)(DPM)]^+$ as Fe (HL)L, and $[Fe^{II}(DPM)_2$ as FeL_2 as a function of pH.

The corresponding pK_{a1} and pK_{a2} values at 25°C were 4.37 and 6.38 for HDPM. The species distribution curves (Fig. 2) involving the three species in Eqs. **1** and **2** were drawn using the above equilibrium constants. Careful examination of Fig. 2 shows that at pH < 4.37, the species $[Fe^{II}(HDPM)_2]^{2+}$ is the major component and increases at lower pH values, while for pH>6.38, the major species is $[Fe^{II}(DPM)_2]$. The monoprotonated species $[Fe^{II}(LH)(L)]^+$ predominates at pH values between 4.37 and 6.38, reaching a maximum at pH = 5.4. The pKa for $[Fe^{II}(HDPE)(DPE)]^+$ was found to be 6.82. The monoprotonated species dominates at pH values lower than 6.82 and the completely deprotonated one is the major species at pH values higher than 6.82 (Fig. 3). This confirms that the isolated form of the iron complex with HDPE ligand is $[Fe^{II}(HDPE)(DPE)]ClO_4$.

Electrochemical Studies of Fe(II)/Fe(III) Couples. [Fe^{II}(HDPE)(DPE)]$^+$ (III) and [Fe^{II}(HDPM)$_2$]$^{2+}$ (IV)

The Nernst equation provides a rationalization of the pH dependence on the peak potential. The following equation describes the numbers of protons (m) and electrons (n) involved in the electrode processes:

$$Ox + ne^- + mH^+ \rightleftharpoons Red \qquad (3)$$
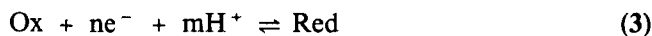
In our discussion, we assume that the concentration of protons in the bulk solution is the same as at the electrode surface. At 25°C, we may write:[5]
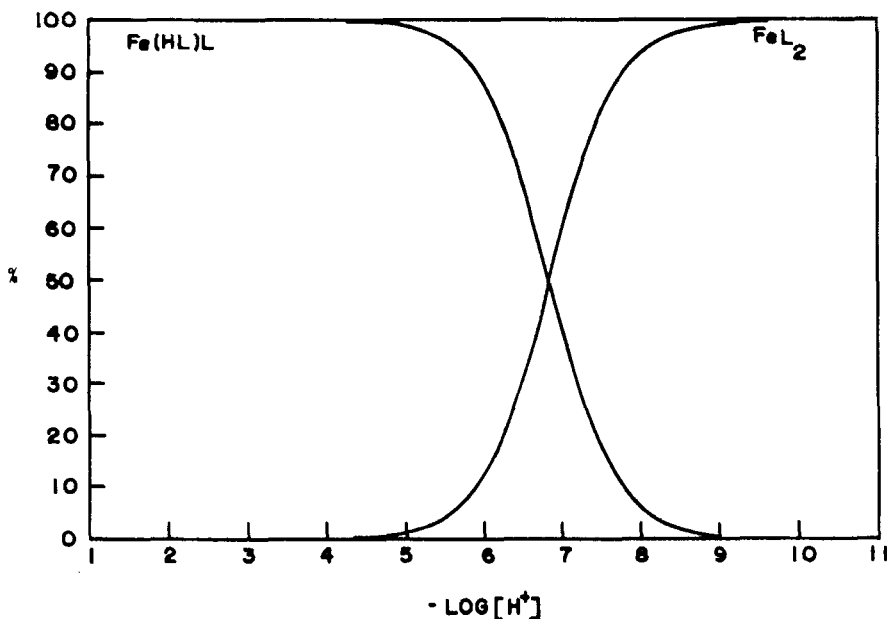
Figure 3 Species distribution curves of $[Fe^{II}(HDPE)(DPE)]^+$ represented by Fe(HL)L, and $(Fe^{II}(DPE)_2]$ by FeL_2 as a function of pH.

$$E_{1/2} = E^{o'}_{298} - (0.059/n) \log (D_{OX}/D_{RED})^{1/2} - 0.059 \ (m/n) \ pH \qquad (4)$$

where $E_{1/2}$ is the half-wave potential, $E^{o'}_{298}$ is the formal electrode potential, and D_{OX} and D_{RED} are the diffusion coefficients for the oxidized and reduced species, respectively. Assuming that $D_{OX} = D_{RED}$, and that the CV cathodic and anodic peak potentials, Epc and Epa, are, respectively 29.5/n mV more cathodic and 29.5/n mV more anodic, than $E_{1/2}$ then Eq. **4** reduces to [23]

$$E^{o'}_{298} = E_{1/2} + 0.059 \ (m/n) \ pH \qquad (5)$$

where

$$E_{1/2} = 0.5 \ (E_{pc} + E_{pa})$$

If protons are not involved (m = 0), Eq. **5** reduces to

$$E^{o'}_{298} = E_{1/2} \qquad (6)$$

In order to obtain the number of protons (m) involved in the electrode reaction, we assume n is known, then Eq. **5** can be written in the form,

$$m = -(n/0.059) \ (\Delta \ E_{1/2}/\Delta pH) \qquad (7)$$

where $\Delta E_{1/2}$ is the difference of redox potentials at two different pH values. Experimental data are summarized in Tables 1 and 2. Fig. 4 shows a typical voltammogram for Complexes **III** and **IV**. The regions of the $E_{1/2}$ *vs.* pH curves which are assigned to couples A, B, and C are shown in Figs. 5 and 6.

TABLE 1 Calculated contribution on $E^{\circ'}_{298}$ for proton and electron transfer.

| Couple | Contribution $E^{\circ'}_{298}{}^a$ | | $E^{\circ'}_{298}/V$ | |
	$(E^{\circ'}_{298})$el	$(E^{\circ'}_{298})$pr	$[(E^{\circ'}_{298})$el/ $+ (E^{\circ'}_{298})$pr]	Experiment[b]
A (III)	0.246	0.636	0.882	0.864(0.883)c
B (III)	0.246	0.378	0.648	0.636(0.646)c
C (III)	0.246	–	–	0.246(0.242)c
A (IV)	0.186	0.400	0.586	0.539(0.576)c
B (IV)	0.186	–	–	0.189(0.186)c

[a] Reference 9; [b] Values obtained from $E^{\circ'}_{298}$ vs. pH diagram (Figures 4 and 5); [c] Calculated from $E^{\circ'}_{298} = E_{1/2} + 0.059$ (m/n) pH. (III) = $[Fe^{II}(HDPM)_2]^{2+}$ (IV) = $[Fe^{II}(HDPE)(DPE)_2]^{+}$

TABLE 2 Cyclic voltammetric data for $[Fe^{II}(HDPE)(DPE)]^{+}$ and $[Fe^{II}(HDPM)_2]^{2+}$ obtained at various pH values at 298K and I = 0.1M $NaNO_3$.

| | | $[Fe^{II}(HDPE)(DPE)]^{2+}$ | | | | | | $[Fe^{II}(HDPM)_2]^{2+}$ | | | |
Couple	pH	$E_{1/2}/V^a$	$\Delta E_p/mV^b$	$i_{pc}/i_{pa}c$	buffer[e]	Couple	pH	$E_{1/2}/V^a$	$\Delta E_p/mV^b$	$i_{pc}/i_{pa}c$	buffer[e]
A	2.73	0.419	50	–	(A)	A	0.95	0.759	70	0.89	(*)
A	3.45	0.365	48	0.98	(B)	A	1.50	0.696	68	0.93	(*)
A	3.57	0.351	47	1.00	(B)	A	1.95	0.643	72	0.87	(*)
A	4.07	0.313	48	0.98	(B)	A	2.71	0.574	110	0.85	(B)
A	4.56	0.286	47	0.98	(B)	A	2.81	0.559	84	0.86	(B)
A	5.04	0.264	46	1.02	(B)	A	2.93	0.544	90	0.97	(B)
A	5.54	0.243	50	1.03	(C)	A	3.49	0.473	81	0.98	(B)
A	6.23	0.218	53	1.00	(C)	A	3.78	0.443	78	0.98	(B)
A	6.76	0.197	53	1.03	(C)	B	4.63	0.369	89	1.08	(B)
A	6.84	0.194	48	1.03	(D)	B	5.55	0.324	90	0.97	(F)
A	7.05	0.189	44	0.98	(D)	B	5.90	0.297	74	0.94	(F)
B	7.64	0.184	46	1.08	(D)	B	6.10	0.282	75	0.87	(F)
B	8.02	0.188	42	1.04	(D)	B	6.58	0.260	78	1.03	(F)
B	8.11	0.185	43	1.05	(E)	C	6.96	0.249	80	0.92	(F)
B	8.92	0.187	42	1.02	(E)	C	7.36	0.244	80	1.00	(F)
B	9.40	0.184	40	1.07	(E)	C	7.73	0.243	73	0.97	(G)
B	9.90	0.188	42	0.98	(E)	C	8.25	0.244	80	0.98	(G)
						C	8.59	0.248	87	1.00	(G)
									77		
						C	9.44	0.246		1.00	(G)

[a] V vs. NHE; [b] Scan rate 20–200 mV.s^{-1}; [c] Current Peak ratio; [d] N° of protons, calc. from Eq. (7); [e] Bufferconc = 2.5 × 10^2 M; (*) Nitric Acid sol., (A) – Trichloroacetic acid, (B) – Acetate, (C) – Ftalate, (D) – Imidazol, (E) – Glicin, (F) – Phosphate, (G) – Borate

Couple A: Complex III

Below pH 1 the Complex III is unstable due to hydrolysis. The voltammograms of Complex III appear to be consistent with an electrochemically *pseudo*-reversible concerted one-electron two-proton reduction process and are described by Eq. **8** for pH ranging from 1 to 4. From Eq. **7** a value of m = 1.9 protons was obtained.

$$[Fe^{III}(DPM)_2]^{+} + e^{-} + 2H^{+} \rightleftharpoons [Fe^{II}(DPMH)_2]^{2+} \qquad (8)$$
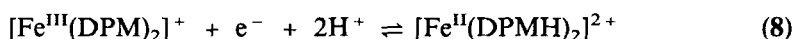
The difference of peak potentials ΔE_p lies within the range 40-80 mV at low scan rates. At high scan rates the system behaves in an irreversible fashion due to the Ohmic iR drop. In addition, the Complex III shows an inverse $E_{1/2}$ dependence on pH. The plot of $E_{1/2}$ vs. pH is linear with slopes of 120 mV/pH unit (Fig. 5) with
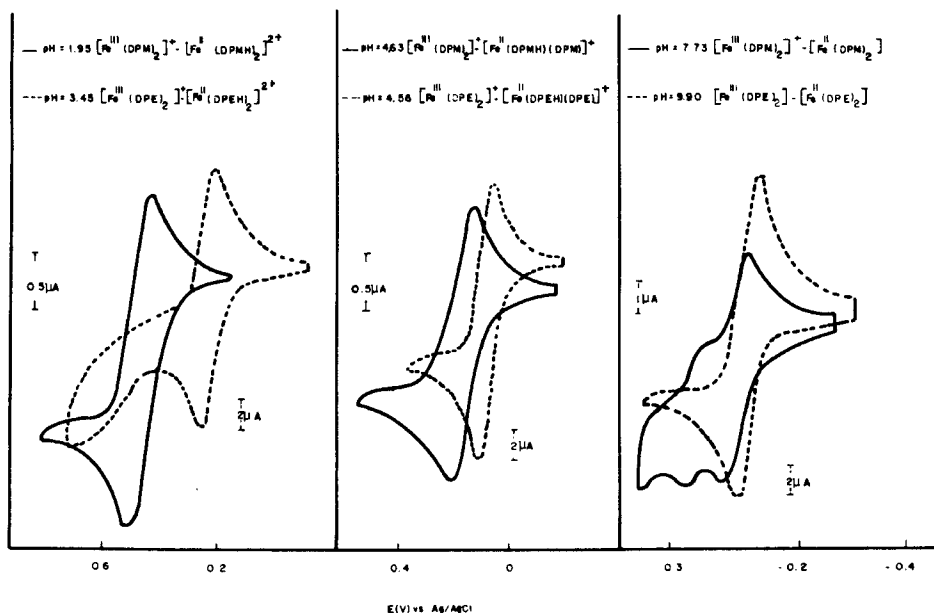
Figure 4 Cyclic Voltammograms for $[Fe^{II}(HDPM)_2]^{2+}$ (———) and $[Fe^{II}(HDPE)(DPE)]^+$ (---) system at different pH values.

the potential decreasing as the pH increases up to pH $= 6.96$. From the plot of $E_{1/2}$ *vs.* pH a value of 0.864V was found for $E^{\circ'}{}_{298}$. Equation 5 provided values of $E^{\circ'}{}_{298}$ for each pH unit. The average resulted in an $E^{\circ'}{}_{298}$ of 0.88 V. The same value was found by Chakravorty[7] with the hexadentate ligand amine-imine-oxyme.

Complex IV

It is clear from the elemental analyses and pKa data that Complex IV was isolated in its monoprotonated form. In this sense, the mechanism proposed for Complex III cannot be considered for Complex IV. From Eq. 7, a value of m $= 0.7$ protons was obtained. Therefore, a one-electron and one-proton transfer mechanism agrees better with the experimental data as described by Eq. 9.

$$[Fe^{III}(DPE)_2]^+ + e^- + H^+ \rightleftharpoons [Fe^{II}(DPEH)(DPE)]^+ \qquad (9)$$
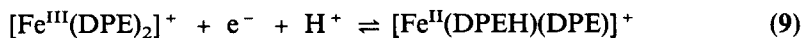
By applying n $= 1$ and m $= 1$, Eq. 5 provides values of $E^{\circ'}{}_{298}$ for each pH unit whose average value resulted in $E^{\circ'}{}_{298}$ of 0.578V. It is seen from the plot of $E_{1/2}$ *vs.* pH (Fig. 6) that potential decreases as pH increases up to pH $= 6.84$. From the same plot, a value of 0.539V was found for $E^{\circ'}{}_{298}$. The hydrolysis reaction rate occurs for low pH values, thus the voltammogram data were obtained for pH > 3. The higher "lability" is due to an extra carbon in the intermediate chain leading to an unstable complex even at high pH values.

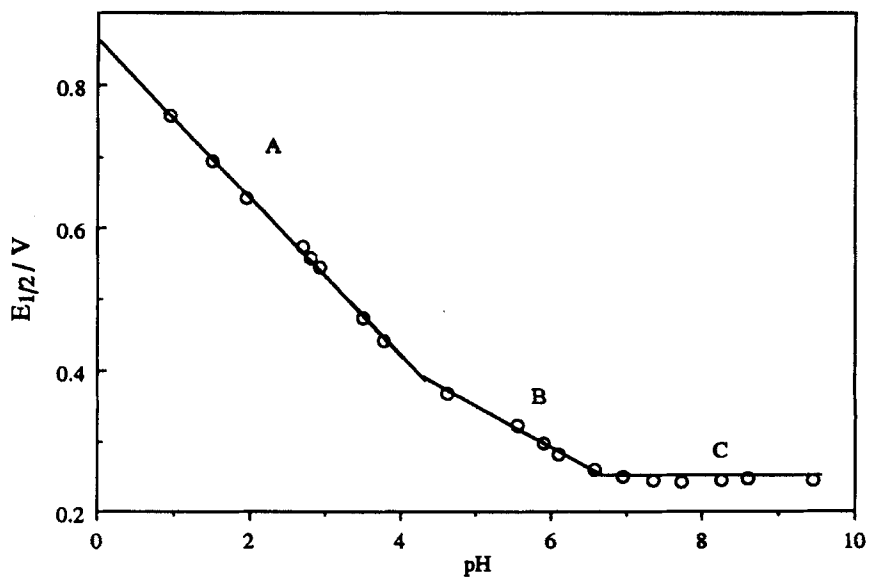**Figure 5**   Dependence of reduction potential of $[Fe^{II}(HDPM)_2]^{2+}$ on pH at 25°C in 0.10 M $NaNO_3$.
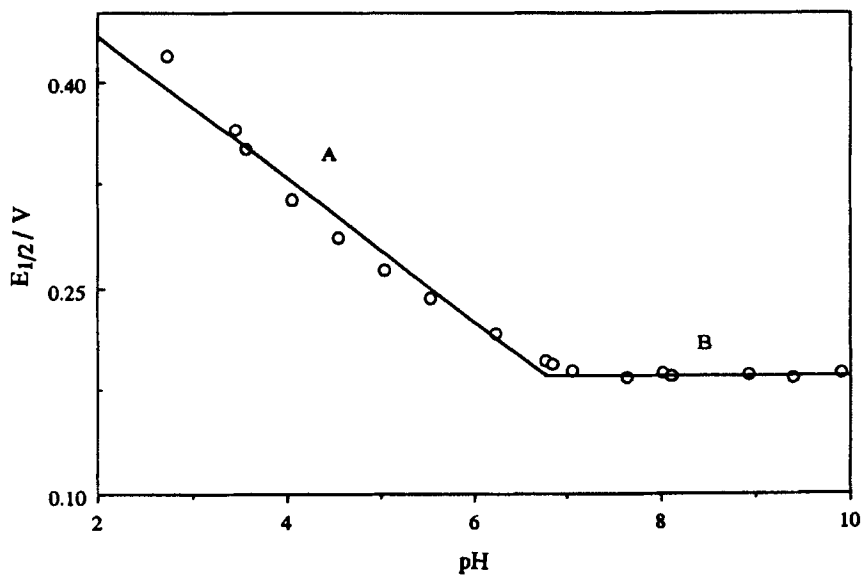

Figure 6   Dependence of reduction potential of $[Fe^{II}(HDPE)(DPE)]^{2+}$ on pH at 25°C in 0.10 M $NaNO_3$.
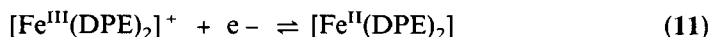
Couple B: Complex III

The ΔEp values of 50–80 mV for Complex **III** were kept constant for pH values in the range 4.5–6.5 and at low scan rates clearly show a *pseudo*-reversible electron transfer process. The cyclic voltammograms corresponding to couple B are consistent with the transfer of one electron and one proton and are described by Eq. **10**.

$$[Fe^{III}(DPM)_2]^+ + H^+ + e^- \rightleftharpoons [Fe^{II}(DPMH)(DPM)]^+ \qquad (10)$$
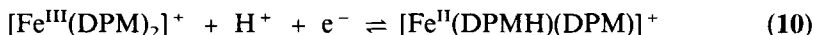
The $E^{o'}_{298}$ values were obtained either from application of Eq. **5** or by plotting $E_{1/2}$ *vs.* pH (Fig. 5) and the average was found to be 0.646 V or 66 mV higher than the value obtained for hexadentate amine-imine-oxime by Chakravorty.[7]
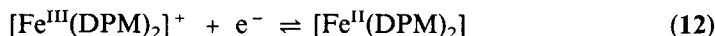
Complex IV

At pH values pH>7, ΔEp was approximately 50 mV. The plot of $E_{1/2}$ *vs.* pH shows a constant value for $E_{1/2}$ as pH increases, clearly suggesting a reversible one-electron process with no participation of protons (m = 0):

$$[Fe^{III}(DPE)_2]^+ + e- \rightleftharpoons [Fe^{II}(DPE)_2] \qquad (11)$$

The plot of $E_{1/2}$ *vs.* pH yields (Eq. **5**) a value of $E^{o'}_{298} = 0.189V$.

Couple C

An additional wave hardly discernible at low pH values (Fig. 4), becomes much more prominent at pH>7. It is not obvious why this happens and its origin is not clear. The ΔEp value for Complex **III** indicates a one electron transfer reaction. As for Complex **IV** in couple B, the $E_{1/2}$ values are constant as pH increases. By using n = 1 in Eq. **5** the value of 0.246 V was found for $E^{o'}_{298}$.

$$[Fe^{III}(DPM)_2]^+ + e^- \rightleftharpoons [Fe^{II}(DPM)_2] \qquad (12)$$

The same potential was found from the plot of $E_{1/2}$ *vs.* pH. Chakravorty and Mohanty[7] found the same trend for hexadentate amine-imine-amine complexes and reported a $E_{1/2}$ value of 0.11V.

Electrochemical pK_a Determination on $[Fe^{II}(HDPM)]^{2+}$ and $[Fe^{II}(HDPE)]^{2+}$

The pKa values of $[Fe^{II}(HDPM)_2]^{2+}$ and $[Fe^{II}(HDPE)(DPE)]^+$ were estimated from the plot of $E_{1/2}$ *vs.* pH (Figs. 5 and 6) for iron species involved in the couples as described above for two, one and no protons transferred. The acid-dissociation constants are $pK_{a2} = 6.77$ for $[Fe^{II}(HDPE)(DPE)]^+$ and, $pK_{a1} = 4.30$ and $pK_{a2} = 6.80$ for $[Fe^{II}(HDPM)_2]^{2+}$. These values are in very close agreement with those obtained form the potentiometric titration. The obtained values for protonation constants of the hexadentate ligand[7] are not significantly different from those of Complexes III and IV. It is important to note that the pKa value for Complex III is in close agreement with the potentiometric titration.

CONCLUSION

Results from CHN elemental analysis, potentiometric titration and electrochemistry indicate formation of [Fe(HDPE)(DPE)]$^+$ as the final product from the reaction of two equivalents of HDPE and [Fe(OH$_2$)$_4$Cl$_2$]. It is known from the literature[4] that protonated species of Ni(H$_2$L^1) (L^1 = 2-(2-aminoethyl imino-3-butanone oxime) have not been isolated and only Ni(L^1)$^{2+}$ was obtained, even in acidic solution.

Attempts to isolate the protonated species failed, due to their strong lability at pH < 5. The spectroscopic observation of the metal → ligand CT band at 518 nm for [Fe(HDPM)$_2$]$^{2+}$ and 531 nm for [Fe(HDPE)(DPE)]$^+$ indicates that the observed shift in band maxima in going from the double protonated species to the monoprotonated species could be due to a smaller effective charge caused by the flow of negative charge from the = N-O$^-$ ion.[4]

The observed redox processes are due to the metal ion rather than coordinating ligands and this can be easily confirmed by comparing values obtained from the literature on [Ni(HDPE)$_2$]$^{2+}$ and [Ni(HDPM)$_2$]$^{2+}$. These values[14] can be easily correlated through the following empirical equation

$$(E^{o'}_{298})_{Ni} \approx 0.36 + (E^{o'}_{298})_{Fe} \qquad (13)$$

The presence of a pyridine ring causes no significant effect on the electrochemical and spectroscopic features of these complexes.

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