

**Synthesis, Characterization and Electrochemical Studies on
Nickel (II) Complexes of 2 - (2 - Pyridylethyl) Imino - 3 -
Butanone Oxime (HDPE) and 2 - (2 - Pyridylmethyl) Imino - 3 -
Butanone Oxime (HDPM)**

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As propriedades redox das espécies níquel(II) e níquel(III) derivadas de uma série de ligantes (L = 2 - (piridiletil) imino - 3 - butanona oxima (HDPE) e 2 - (piridilmetil) imino - 3 - butanona oxima (HDPM) são estudadas em meios tamponados em uma faixa abrangente de valores de pH, usando a voltametria cíclica. No pH < 5, foi encontrado um único acoplamento reversível de dois elétrons e dois prótons para $[\text{Ni}^{\text{IV}}(\text{L})_2]^{2+} - [\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$ ($E^{\circ}_{298} = 1.05$ V para L = HDPM e $E^{\circ}_{298} = 0.94$ V para L = HDPE, vs. NHE). No pH > 6, dois processos reversíveis distintos de um elétron foi observado para $[\text{Ni}^{\text{IV}}(\text{L})_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L})_2]^{2+}$ ($E^{\circ}_{298} = 0.80$ V para L = HDPM e $E^{\circ}_{298} = 0.70$ V para L = HDPE, vs. NHE). Um segundo acoplamento para o níquel foi encontrado, o qual envolve transferência de dois prótons e um elétron, $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$ ($E^{\circ}_{298} = 1.33$ V para L = HDPM e $E^{\circ}_{298} = 1.25$ V para L = HDPE). No pH 7.0, $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{LH})(\text{L})]^{2+}$ ($E^{\circ}_{298} = 0.98$ V para L = HDPM e $E^{\circ}_{298} = 0.92$ V para L = HDPE). Finalmente um único acoplamento de um elétron foi encontrado para o processo $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{L})_2]^{2+}$ ($E^{\circ}_{298} = 0.55$ V para L = HDPM e $E^{\circ}_{298} = 0.47$ V para L = HDPE). Dos dados de titulação potenciométrica, pKa1 e pKa2 foram determinadas como sendo 5.85 and 7.57 para L = HDPM, 6.60 e 7.80 para L = HDPE e a partir das análises eletroquímicas dos acoplamentos do níquel (II), pKa1 e pKa2 foram determinadas como sendo 6.20 e 7.22 para L = HDPM, 6.13 e 8.14 para L = HDPE.

The redox properties of nickel(II) and nickel(III) species derived from a series of ligands (L = 2 - (pyridylethyl) imino - 3 - butanone oxime (HDPE) and 2 - (pyridylmethyl) imino - 3 - butanone oxime (HDPM) are studied in buffered media over a wide range of pH values, using cyclic voltammetry technique. At pH < 5, a single reversible two-electron, two-proton couple $[\text{Ni}^{\text{IV}}(\text{L})_2]^{2+} - [\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$ ($E^{\circ}_{298} = 1.05$ V for L = HDPM and $E^{\circ}_{298} = 0.94$ V for L = HDPE, vs. NHE) was found. At pH > 6, two distinct reversible one-electron processes were observed, for $[\text{Ni}^{\text{IV}}(\text{L})_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L})_2]^{2+}$ ($E^{\circ}_{298} = 0.80$ V for L = HDPM and $E^{\circ}_{298} = 0.70$ V for L = HDPE). A second couple for nickel was found which involves two-proton and one-electron transfer, $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$ ($E^{\circ}_{298} = 1.33$ V for L = HDPM and $E^{\circ}_{298} = 1.25$ V for L = HDPE). At pH 7.0 $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{LH})(\text{L})]^{2+}$ ($E^{\circ}_{298} = 0.98$ V for L = HDPM and $E^{\circ}_{298} = 0.92$ V for L = HDPE). Finally a single one-electron couple was found for $[\text{Ni}^{\text{III}}(\text{L})_2]^+ - [\text{Ni}^{\text{II}}(\text{L})_2]^{2+}$ ($E^{\circ}_{298} = 0.55$ V for L = HDPM and $E^{\circ}_{298} = 0.47$ V for L = HDPE). From the potentiometric titration data, pKa1 and pKa2 were found to be 5.85 and 7.57 for L = HDPM and 6.60 and 7.80 for L = HDPE and from electrochemical analysis pKa1 and pKa2 were found to be 6.20 and 7.22 for L=HDPM and 6.13 and 8.14 for L = HDPE.

Key words: nickel(II) complexes; HDPE; HDPM; synthesis.

Introduction

Studies of nickel complexes of different tridentate and hexadentate amine-imine-oxime ligands have appeared frequently in the literature¹⁻⁹. Most of this studies have focused upon the stabilization of nickel (IV) complexes. The stability of macrocyclic hexadentate ligands **I** complexes has been achieved also for cyclic tridentate ligands **II** complexes^{1,5}. In the present article we report the electrochemical studies involving another Schiff base containing pyridyl-imino-oxime ligands **III-IV** and their nickel complexes¹⁰ $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ **V** and $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ **VI**. The ligands HDPM and HDPE possess dissociable protons which are naturally dependent on the redox transformation of the metal ion. Reports from the literature¹¹⁻¹² show that the dissociable protons on ligands are less tightly held in complexes of higher oxidized states of the metal ion. The replacement of the amino by the pyridyl group in the tridentate ligands, allows the investigation of the effect caused by the presence of electrons on the stabilization of the complex on the pKa and electrochemical properties of complexes **V** and **VI**.

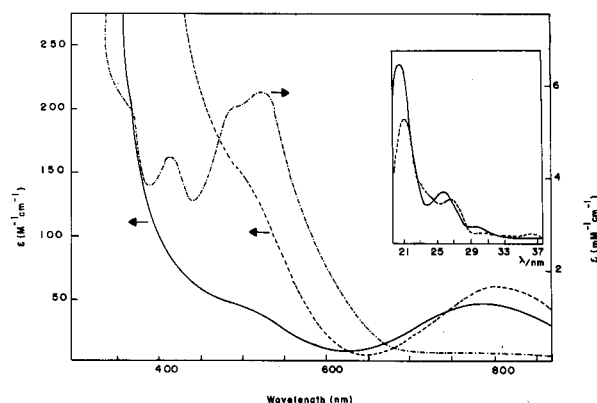
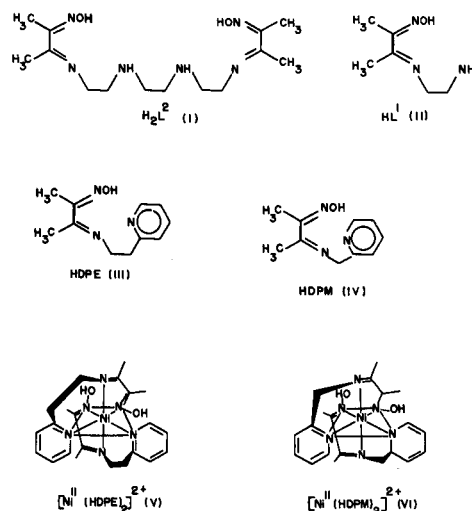


Figure 1. Electronic spectra of $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ (—), $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ (---) and $[\text{Ni}^{\text{IV}}(\text{HDPM})_2]^{2+}$ (-.-.-).

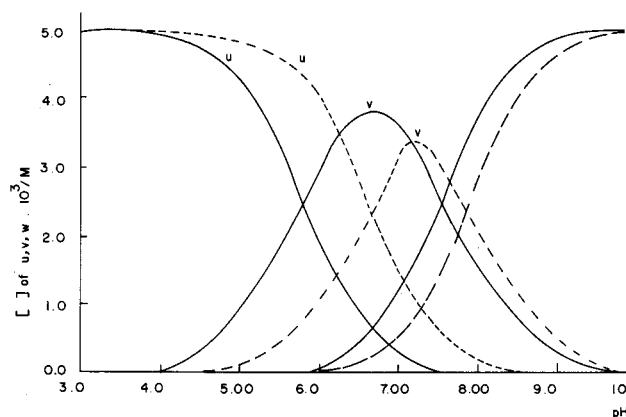


Figure 2. Formation of $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ (—), $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ (---); (u) = $[\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$, (v) = $[\text{Ni}^{\text{II}}((\text{LH})(\text{L}))_2]^+$ and w = $[\text{Ni}^{\text{II}}(\text{L})_2]^{2+}$.

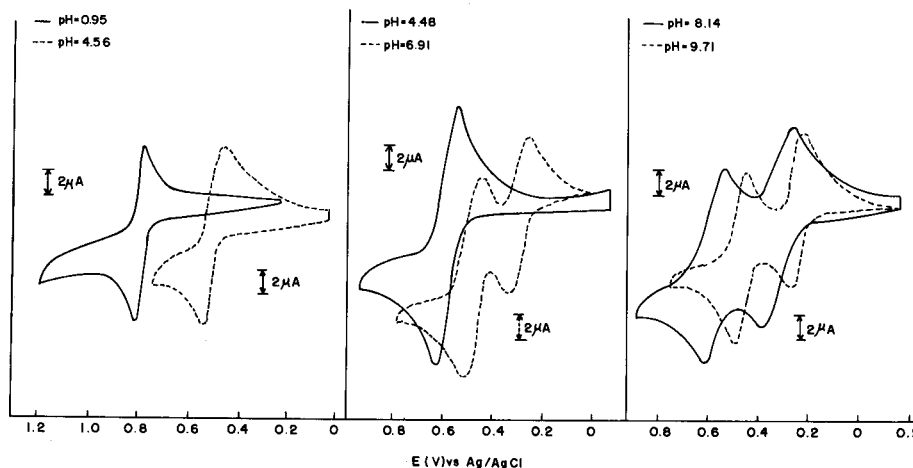


Figure 3. Cyclic Voltammograms for $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ (—) and $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ (---) system at different pH values.

Experimental

Material - All chemicals were analytical grade reagents and the solutions were prepared with distilled water. Argon, ultrapure grade, was purchased from White Martins and used for deoxygenation 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, and their nickel (II) complexes were prepared according to the method described in the literature¹³. The ligands HDPE and HDPM, resulted from the condensation of monoxime-2,3-butanodione (diacetylmonoxime) and 2-(2-aminoethyl) pyridine (HDPE) and 2-(2-aminomethyl) pyridine (HDPM). The $[\text{Ni}^{\text{II}}(\text{L})_2](\text{NO}_3)_2$ complex (1 mmol) was added to an ethanolic solution of ligands (2 mmoles) under constant stirring. The product precipitated as reddish crystals which were filtered off and recrystallized from methanol. Anal. calcd. for $[\text{C}_{22}\text{H}_{30}\text{N}_6\text{Ni}](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and (found): C, 41.99 (42.15); H, 5.45 (5.36); N, 17.81 (17.65). $[\text{C}_{20}\text{H}_{26}\text{N}_6\text{Ni}](\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$, calcd. (Found): C, 40.56 (39.31); H, 4.94 (4.75); N, 18.92 (19.26).

Electronic spectra were recorded on a Shimadzu UV-190 spectrophotometer (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 ± 0.1 °C under argon atmosphere. The pKa values for the deprotonation of the complexes were calculated by using a PKAS program, developed by Motekaitis and Martell¹⁴.

Cyclic voltametric behavior of the $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ complexes were 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.

Results and Discussion

Spectrophotometric Studies on $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$. The electronic spectra of the complex $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ exhibit an absorption band in the visible region

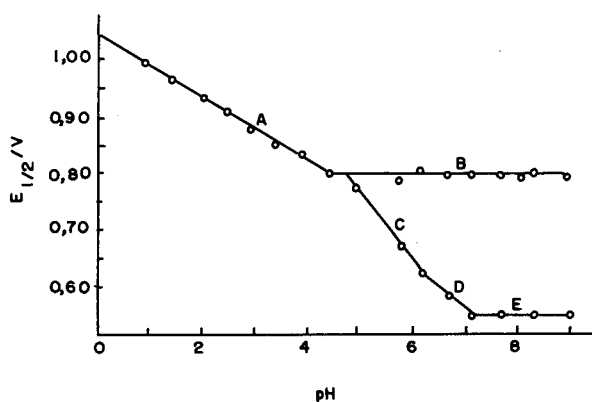


Figure 4. Dependence of reduction potential of $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ on pH at 25°C in 0.10 M NaNO_3 .

(Fig. 1), at 786 nm (ν_1) ($\epsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 500 nm (ν_2) superimposed on a rising ultraviolet tail for $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$. To these bands were assigned a ${}^3\text{A}_{2g} - {}^3\text{T}_{2g}$ transition due to ν_1 and ${}^3\text{A}_{2g} - {}^3\text{T}_{1g}$ due to ν_2 assuming an Oh symmetry. From ν_1 we have Dq of 272 cm^{-1} and B'/B of 0.82 where B and B' are the Racah parameters. The theoretical value of ν_2 was found¹⁵ to be 507 nm. The hidden CT band ν_3 was found to be 322 nm. The allowed electronic transition in the UV region has a shoulder at 293 nm and two bands at 254 nm and 198 nm. The visible electronic spectral shape found in $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ complex exhibit the same spectral shape found in $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$, with minor shifts of the absorption bands (Table 1). A band at 810 nm (Dq = 1235 cm^{-1}), ν_1 , and a shoulder at 500 nm, ν_2 , was found in the visible region, superimposed to a rising ultraviolet tail. The estimated value of ν_2 was found to be 519 nm. The hidden CT band ν_3 was found to be 328 nm. The band in the UV region has shoulder at 289 nm and two bands at 259 nm and 202 nm. The same spectral shape was found for both complexes in ethanolic media. These absorption may be compared with the corresponding values 781 nm (Dq = 1280 cm^{-1}), ν_1 , and a shoulder at 500 nm, ν_2 , for nickel (II) complex of hexadentate ligands⁴ of type I and 790 nm (Dq = 1250 cm^{-1}), ν_1 , and a shoulder at 510 nm, ν_2 , for nickel (II) complex of tridentate ligands⁵ of type II. The visible spectra for $[\text{Ni}^{\text{IV}}(\text{HDPM})_2]^{2+}$ (Table 1) exhibit a CT band at 525 nm ($\epsilon = 6,000 \text{ M}^{-1} \text{ cm}^{-1}$), ν^1 , and a shoulder at 496 nm ($\epsilon = 5,700 \text{ M}^{-1} \text{ cm}^{-1}$), ν^2 , and a second CT band ν^3 at 415 nm ($\epsilon = 4,700 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder ν^4 at 350 nm. These may be compared with the corresponding values 500 nm, ν_1 , and a shoulder at 430 nm, ν_2 , for nickel (IV) complex of hexadentate ligands⁴ of type I and 500 nm, ν_1 , and a shoulder at 415 nm for nickel (IV) complex of tridentate ligands⁵ of type II. The shoulder of I and II is slightly (~ 60 nm) shifted to lower wavelength, if compared with the corresponding absorption of $[\text{Ni}^{\text{IV}}(\text{HDPM})_2]^{2+}$.

Potentiometric pKa determination on $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$. Potentiometric titration data on $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ have revealed two acid dissociation constants K_{a1} and K_{a2} corresponding to

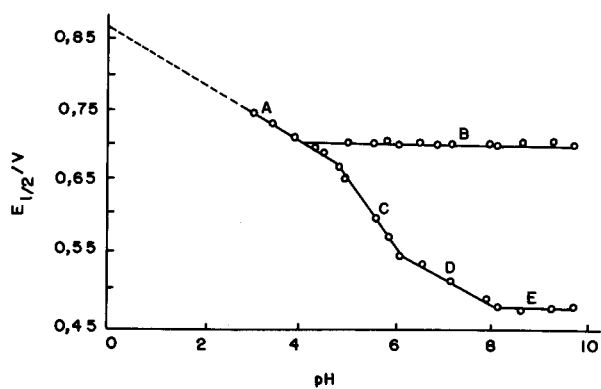


Figure 5. Dependence of reduction potential of $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ on pH at 25°C in 0.10 M NaNO_3 .

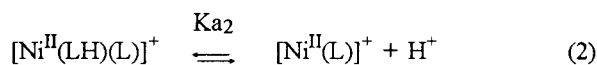
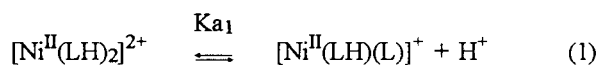
Table 1. Selected Electronic Spectrals Bands (cm^{-1}) of the Nickel Complexes in Aqueous Solution.

Complex	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
I	12,720	20,000 ^a (19,258) ^b	(30,449) ^b	34,130 ^a	37,740	49,505
II	12,350	20,000 ^a (19,700) ^b	(31,100) ^b	34,600 ^a	38,610	49,505
III	19,050	20,160 ^a	24,100 ^b	28,570 ^a		

I = $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$; II = $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$; III = $[\text{Ni}^{\text{IV}}(\text{HDPM})_2]^{2+}$.

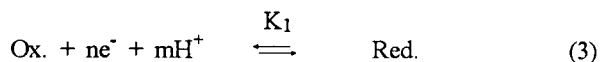
^a - Shoulder.

^b - Calculated. See Ref. 15 for details.



The corresponding $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values at 25°C were found to be 5.85 ± 0.02 and 7.57 ± 0.01 for HDPM and 6.60 ± 0.03 and 7.90 ± 0.02 for HDPE respectively. The formation curves (Fig. 2) involving the three species in equations 1 and 2 were drawn using the above equilibrium constants. Careful examination of Fig. 2 shows that the species $[\text{Ni}^{\text{II}}(\text{LH})_2]^{2+}$ is the major component at $\text{pH} < 4$ for $\text{L} = \text{HDPE}$ and at $\text{pH} < 5$ for $\text{L} = \text{HDPM}$. On the other hand, $[\text{Ni}^{\text{II}}(\text{L})_2]$ is the major species at $\text{pH} > 7.5$ for $\text{L} = \text{HDPE}$ and at $\text{pH} > 8.5$ for $\text{L} = \text{HDPM}$. The intermediate species $[\text{Ni}^{\text{II}}(\text{LH})(\text{L})]^+$ was observed in a narrow pH range around 5.5 for HDPE and 7.0 for HDPM.

pH dependence on peak potential and formal electrode potential. Nernst Equation provides useful information for redox reactions involving simultaneous proton and electron-transfer processes. The number of protons (m) and electrons (n) involved in the electrode processes are described as follows:



In our discussion we are assuming that in protic media the concentration of protons at the electrode surface is equal to the concentration of protons in the bulk solution. At 25 °C we may write:

$$E_{1/2}^{\text{r}} = E_{298}^{\circ} - (0.059/n) \log(\text{DOX}/\text{DRED})^{1/2} - 0.59(m/n)\text{pH} \quad (4)$$

where $E_{1/2}^{\text{r}}$ is the half-wave potential, E_{298}° is the formal electrode potential, and DOX and DRED are the diffusion coefficients for the oxidized and reduced species respectively. Assuming that $\text{DOX} = \text{DRED}$, and that the CV cathodic (E_{pc}) and anodic (E_{pa}) peak potentials are, respectively 29.5/n

mV more cathodic and 29.5/n mV more anodic, Eq. 4 can be reduced to

$$E_{298}^{\circ} = \bar{E}_{\text{p}} + 0.059 (m/n) \text{pH} \quad (5)$$

where

$$\bar{E}_{\text{p}} = 0.5 (E_{\text{pc}} + E_{\text{pa}})$$

Therefore, while ΔE_{p} remains invariant, E_{pa} and E_{pc} vary considerably with pH, as protons are involved in the electrode processes. If protons are not involved ($m=0$), Equation 5 is reduced to

Table 2 - Calculated contribution on E_{298}° for proton and electron transfer.

Couple	Contribution E_{298}° ^a		E_{298}°/V	
	$(E_{298}^{\circ})_{\text{e1}}$	$(E_{298}^{\circ})_{\text{pr}}$	$[(E_{298}^{\circ})_{\text{e1}} + (E_{298}^{\circ})_{\text{pr}}]$	Exp. ^b
A(I)	0.672	0.397	1.069	1.049(1.059) ^c
B(I)	0.794	-	-	0.794(0.794) ^c
C(I)	0.555	0.794	1.349	1.333(1.354) ^c
D(I)	0.555	0.428	0.983	1.077(0.983) ^c
E(I)	0.555	-	-	0.555(0.549) ^c
F(I)	0.672	-	0.672	-
A(II)	0.576	0.422	0.998	0.865(0.939) ^c
B(II)	0.692	-	-	0.692(0.699) ^c
C(II)	0.460	0.844	1.304	1.152(1.254) ^c
D(II)	0.460	0.462	0.922	0.768(0.920) ^c
E(II)	0.460	-	-	0.460(0.468) ^c
F(II)	0.576	-	0.576	-

^a Reference 8; ^b Values obtained from E_{298}° vs pH diagram (Figures 4 and 5); ^c Calculated from $E_{298}^{\circ} = E_{1/2}^{\text{r}} + 0.059 (m/n) \text{pH}$.
(I) = $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ (II) = $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$.

Table 3a. Cyclic voltammetric data for $[Ni^{II}(HDPE)_2]^{2+}$ obtained at various pH values at 298 K and $I = 0.1M NaNO_3$.

pH	$E_{1/2}/V^a$	E_p/mV^b	i_{pc}/i_{pa}^c	m^d	buffer ^e	$E^{o'}_{298}/V^f$
3.01	0.746	30	1.11	-	(A)	0.924
3.51	0.724	46	0.93	1.5	(A)	0.931
3.94	0.708	47	1.00	1.4	(A)	0.940
4.41	0.689	55	1.02	1.4	(B)	0.949
4.56	0.684	58	1.03	1.4	(A)	0.953
5.05	0.697	35	1.00		(A)	0.697
5.62	0.697	40	1.02	0	(C)	0.697
5.91	0.698	47	1.26	0	(B)	0.698
6.14	0.699	44	0.81	0	(C)	0.699
6.58	0.697	40	0.97	0	(C)	0.697
6.91	0.700	45	1.00	0	(C)	0.700
7.20	0.698	47	0.92	0	(E)	0.698
7.94	0.699	50	1.04	0	(D)	0.699
8.17	0.699	56	0.76	0	(E)	0.699
8.64	0.702	55	1.04	0	(E)	0.702
4.88	0.664	88	0.98	-	(B)	1.240
5.05	0.651	115	1.00	1.3	(A)	1.247
5.62	0.592	55	1.35	1.6	(C)	1.255
5.91	0.563	57	1.02	1.7	(B)	1.260
6.14	0.540	97	1.42	1.7	(C)	1.265
6.14	0.540	97	1.42	-	(C)	0.902
6.58	0.524	60	1.42	0.6	(C)	0.912
6.91	0.513	77	1.43	0.6	(C)	0.921
7.20	0.502	75	1.00	0.6	(E)	0.927
7.94	0.474	50	1.20	0.6	(D)	0.942
8.17	0.496	70	0.96	0	(E)	0.469
8.64	0.469	50	1.13	0	(E)	0.464
9.25	0.464	82	1.13	0	(E)	0.468
9.71	0.496	50	1.10	0	(E)	0.469

^aV. vs NHE; ^b Scan rate 20-200 mV.s⁻¹; ^c Current Peak ratio; ^d Number of protons, calc. from Eq. 7; ^e Buffer conc = 2.5x10⁻² M; ^f calc from Eq. 5; (A)-Acetate, (B) - Citrate, (C) - Ftalate, (D) - Imidazol, (E) - Glicin.

$$E^{o'}_{298} = \bar{E}_p \quad (6)$$

In order to obtain the number of protons involved in the electrode reaction (m), for a known n values Eq. 5 can be written in the form

$$m = -(n / 0.059) (\Delta \bar{E}_p / \Delta pH) \quad (7)$$

where $\Delta \bar{E}_p$ is the difference between E_p from $E^{o'}_{298}$ due to the change in pH at the electrode surface.

Electrochemical studies of Ni(II) / Ni(III) and Ni(III) / Ni(IV) couples. $[Ni^{II}(HDPE)_2]^{2+}$ (V) and $[Ni^{II}(HDPM)_2]^{2+}$ (VI). Data are summarized in Table II. Fig 3 shows a typical voltammogram for complex V and VI. A plot of $E_{1/2}$ vs. pH is shown in Fig. 4 and 5.

Table 3a. Cyclic voltammetric data for $[Ni^{II}(HDPM)_2]^{2+}$ obtained at various pH values at 298 K and $I = 0.1M NaNO_3$.

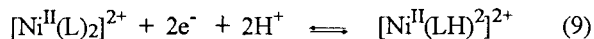
pH	$E_{1/2}/V^a$	E_p/mV^b	i_{pc}/i_{pa}^c	md	buffer ^e	$E^{o'}_{298}/V^f$
0.95	0.996	33	0.97	-	(*)	1.052
1.47	0.966	53	0.89	2.0	(*)	1.053
2.02	0.935	58	0.88	1.9	(*)	1.054
2.48	0.908	53	1.06	1.9	(A)	1.054
2.97	0.881	63	1.00	1.9	(A)	1.056
3.48	0.850	48	0.92	2.0	(B)	1.055
3.97	0.830	48	0.68	1.9	(B)	1.064
4.48	0.797	55	0.66	1.9	(B)	1.061
4.94	0.769	70	0.72	1.9	(B)	1.060
5.83	0.789	80	0.65	0	(C)	0.789
6.23	0.799	70	1.03	0	(D)	0.799
6.77	0.799	80	0.73	0	(D)	0.794
7.23	0.794	80	0.77	0	(C)	0.794
7.75	0.794	80	0.90	0	(D)	0.794
8.14	0.792	85	0.76	0	(E)	0.792
8.39	0.797	105	0.50	0	(F)	0.797
9.04	0.792	115	0.60	0	(E)	0.792
4.94	0.769	70	0.72	-	(B)	1.352
5.83	0.666	75	-	2.0	(C)	1.354
6.23	0.622	115	0.91	1.9	(D)	1.357
6.23	0.622	115	0.91	-	(D)	0.990
6.77	0.584	120	0.53	1.2	(D)	0.983
7.23	0.549	120	0.67	1.2	(C)	0.976
7.23	0.549	120	0.67	-	(C)	0.549
7.75	0.550	82	0.90	0	(D)	0.550
8.14	0.549	85	0.66	0	(E)	0.549
8.39	0.549	120	0.50	0	(F)	0.549
9.04	0.548	133	0.93	0	(E)	0.548

* Estimated value; ^aV. vs NHE; ^b Scan rate 20-200 mV.s⁻¹; ^c Current Peak ratio; ^d Number of protons, calc. from Eq. 7; ^e Buffer conc = 2.5x10⁻² M; ^f calc. from Eq. 5 (A)-Trichlorine acetic Acid, (B) - Acetate, (C) - Fosfate, (D) - Imidazol, (E) - Glicin, (F) Borate.

Couple A. Below pH 5, the voltammograms of both complexes V and VI, appear to be consistent with a chemically ($i_{pc} / i_{pa} = 1$) and electrochemically reversible concerted two-electrons reduction processes without participation of nickel(III) species. The difference of peak potentials ΔE_p lies within the range 40 - 50 mV for scan rates up to 200 mV s⁻¹ for V and ΔE_p within the range 30 - 40 mV for scan rates up to 20 mV s⁻¹ for VI. In addition, progressive irreversibility was observed, most probably due to the iR drop. The complex V shows irreversible chemical behavior at low scan rate due to the lack of stability in this pH range. It was found this complex decomposes by hydrolyses with a rate value of $k_{obs} = 3.23 \times 10^{-3} s^{-1}$. The shape of voltammograms of complex V suggests that no Ni(III) species was present in this pH range. This is suggestive of an initial equilibrium between di- and a mono-protonated species,

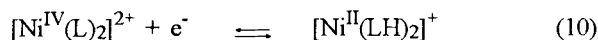


However, the average values calculated from Equation 5, ($m = 1$ and $n = 2$, $E^{\circ}_{298} = 0.825 \pm 0.006$ V) rule out the mechanism proposed for two- electron and one-proton transfer and agrees more closely with a concerted electrode reaction where two electrons and two protons are involved



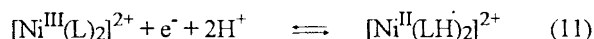
The values calculated by Equation 5 yields an average value of $E^{\circ}_{298} = 0.939$ V and closely agrees with theoretical values⁸ ($E^{\circ}_{298} = 0.998$ V). Eq. 7, yields an m value of 1.9 for complex VI. The calculated E°_{298} is 1.057 (Eq. 5) for $m = 2$ and $n = 2$. From the plot of $E_{1/2}$ vs. pH, a value of 1.049 was found.

Couple B. The ΔE_p (40 - 50 mV) value for complex V was kept constant for pH values in the range 5-9 increasing above pH 5 up to pH 6, ($\Delta E_p > 30$ mV) for complex VI. The peak corresponding to couple B remains invariant to pH change, clearly showing no participation of protons ($m = 0$), whereas the lower peak potential (couple C) undergoes progressive cathodic shift for both complexes. The ΔE_p values of couple B for complexes V and VI (Table III) suggest a reversible one-electron step ($n = 1$):



The E°_{298} for couple B was obtained by applying Equation 5 and by plotting $E_{1/2}$ vs. pH which was found to be 0.699 V and 0.692 V for complex V and 0.794 V for complex VI.

Couple C. Over the range $5 < \text{pH} < 6$, ΔE_p is 90-115 mV. A plot of $E_{1/2}$ vs. pH is linear with slopes of 100 mV / pH units for complex V and 110 mV / pH units for complex VI (ΔE_p is 110 - 120 mV). This is suggestive of a reversible two-proton and one-electron processes as follows:



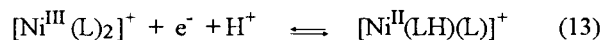
The number of protons involved is calculated through Eq. 7. The value $m = 1.95$ for complex VI corroborates the expected coupling C. However, the value of 1.57 for m in complex V is also suggestive of the coupling described in Eq. 12. Assuming values of $n = 1$ and $m = 1$ for the same pH range, an average value $E^{\circ}_{298} = 0.928$ V is obtained which is far from the value obtained by plotting $E_{1/2}$ vs pH (1.152). This fact brings up more evidence favoring data of elemental analyses which strongly suggests a mixture of di- and mono-protonated species. Applying Equation 5 to couple B and C for complex VI, at the same pH value, e.g. pH = 5, where both couples are at the same E_p value, we may write

$$(E^{\circ}_{298})_C - (E^{\circ}_{298})_B = 0.59 \text{ V} \quad (12)$$

Since $(E^{\circ}_{298})_B = 0.794$ V, the value of 1.384 V for $(E^{\circ}_{298})_C$ was obtained. From Eq. 5, the plot of $E_{1/2}$ vs. pH yield a value of 1.333 V. The average of E°_{298} values was 1.354. The obtained values of protic equilibrium involving the Ni(II) complexes were pK_a 6.60 and 7.80 for complex V

and pK_a 5.85 and 7.57 for complex VI, confirming the pH dependence of the reduction reaction of the couple Ni(III) / Ni(II).

Couple D. The ΔE_p (60-75 mV) values for complex V and (70-80 mV) values for complex VI indicate a pseudo-reversible coupling for these complexes. The ΔE_p value (Fig.3) for complex V is suggestive of one electron transfer reaction. The formation curves (Fig. 2) in the range of pH 6 to 8 show clearly that $[\text{Ni}(\text{HDPE})(\text{DPE})]^+$ is the only species present. The average values of m is 0.6 protons. These values give an indication that one electron and one proton are involved in the equilibrium.



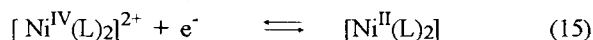
By using $m = 1$ and $n = 1$ in Equation 5, the value of 0.91 V was found for E°_{298} . By applying Equation 13, the theoretical value⁸ E°_{298} was obtained from the same couple (0.992 V). In order to check the validity of Equation 13, a different approach was tested. Assuming $m = 0$ and $n = 1$ for the same pH range, an average value E°_{298} of 0.511 V was obtained. The standard redox potential of 0.768 V was obtained from the plot of $E_{1/2}$ vs. pH (Eq. 5) and 0.464 V from theoretical value⁸. These values rule out the last possibility. The average values of m for complex VI was found to be 1.2 which clearly agrees with the value from Equation 13. The average value of E°_{298} of couple D from Equation 5 is 0.983 V, while from the plot of $E_{1/2}$ vs. pH the obtained value is 1.077 V.

Couple E. The voltammogram peak potential is invariant at pH 8 for V and pH 7.5 for VI, clearly indicating no involvement of protons. The formation curves (Fig. 2) indicates that nickel II species is in the deprotonated form at this pH range.



The average potential E°_{298} of 0.468 was obtained from Equation 5 for complex V and 0.549 for complex VI. From the plot of $E_{1/2}$ vs. pH the obtained value is 0.460 V for complex V and 0.555 V for complex VI.

Couple F. To our knowledge, the following couple has not been reported in the literature and it was not obtainable in our laboratory. The theoretical E°_{298} value (Table 3) was found to be 0.675 for complex V and 0.580 V for complex VI.



The calculated E°_{298} values are given in Table III and the agreement between calculated and experimental formal electrode potentials is excellent in all cases.

Electrochemical pK_a Determination on $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$. The values of pK_a 's for $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$ were estimated from plots $E_{1/2}$ vs. pH (Fig. 4 and 5) for Ni(II) species involved in the couples as described above, for 2, 1 or no protons transferred. The acid dissociation constants pK_{a1} and pK_{a2} were found to be 6.20 and 7.22 for $[\text{Ni}^{\text{II}}(\text{HDPM})_2]^{2+}$ and 6.13 and 8.14 for $[\text{Ni}^{\text{II}}(\text{HDPE})_2]^{2+}$.

Conclusion

The results described in this paper indicate that the proton dissociation on oximate oxygen plays a very important role in the stabilization of higher oxidation states ($> \text{II}$) of nickel complexes. The stabilization of high oxidation states of nickel complexes has been suggested previously and it is due to the negative charge on the oximate oxygen⁶, causing an effective reduction in the positive charge of the metal ion through inductive transmission and σ donation. The results show unequivocally the presence of tetravalent nickel and nickel (III) as intermediates in high pH values. The surprising Nernstian character of electrode reactions is an indication that only minor stereochemistry reorganization energy is required during the redox processes of an octahedral NiN_6 coordination sphere for all oxidation states.

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$180B'Dq)^{1/2}$ were employed to estimate the hidden CT(v_3) band and to adjust the value of a shoulder in the v_2 transition. J. E. Huheey, *Inorganic Chemistry, Principles of Structure and Reactivity*. Harper & Row, Publishers, New York, third edition (1983).