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Electron Transfer Equilibria Involving Nickel(II, III, IV) and Protons: Cyclic Voltammetric Response

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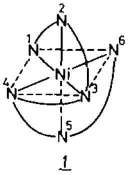
We wish to report the pH-dependent cyclic voltammetric response of octahedral nickel complexes[1] 1, derived from the ligand 2 which will be abbreviated as H_2L. A versatile instrument built in this laboratory was used for the study. A platinum working electrode was used at 25 °C. The pH of the medium was controlled using buffers in 0.1 *M* NaCl which also acted as the supporting electrolyte.



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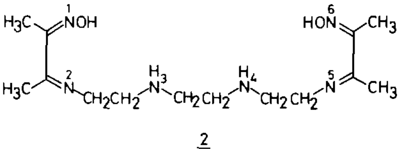

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The results (Fig. 1, Table I) in the pH range 1–5 are considered first. The nickel(II) complex,[1] $Ni(H_2L)(ClO_4)_2$ (starting scan, anodic) and the nickel(IV) species,[1] $NiL(ClO_4)_2$ (starting scan, cathodic) gave *identical* cyclic voltammograms. Let E_{pa} and E_{pc} be respectively the anodic and cathodic peak potentials and let ΔE_p be the separation between them The observed values of ΔE_p lie in the range 30–35 mV. Clearly[2] a *reversible one-step two-electron* electrode process is involved. Controlled-potential reduction of NiL^{2+} at $E < E_{pc}$ and oxidation of $Ni(H_2L)^{2+}$ at $E > E_{pa}$ fully corroborated the two-electron involvement. While ΔE_p remains invariant, E_{pa} and E_{pc} vary considerably with pH. Thus protons are also involved in the electrode reaction. For the electrode process,

$$\text{Oxidant} + ne + mH^+ \rightleftharpoons \text{Reductant} \qquad (1)$$

the formal redox potential $E^{\circ\prime}$ at temperature 298 °K is given by:[3]

$$E^{\circ\prime}_{298} \simeq 0.5(E_{pa} + E_{pc}) + 0.059(m/n)pH \qquad (2)$$

For the system under study the observed results are in complete agreement (Table I) with the electrode reaction:

$$NiL^{2+} + 2e + 2H^+ \rightleftharpoons Ni(H_2L)^{2+} \qquad (3)$$

which has $E^{\circ\prime}_{298} = 0.71 \pm 0.01$ V *vs.* sce. This value is in complete agreement with that (0.70 ± 0.01 V *vs.* sce) determined by using direct potentiometry.[1] pH-Metric titration studies[3] have shown that in the pH range 1–5, the nickel(II) species exists solely as $Ni(H_2L)^{2+}$ while the nickel(IV) species is always NiL^{2+} irrespective of pH. This together with the observation[4] that redox processes involving equal number of protons and electrons are facile, provide the rationalization for reaction (3).

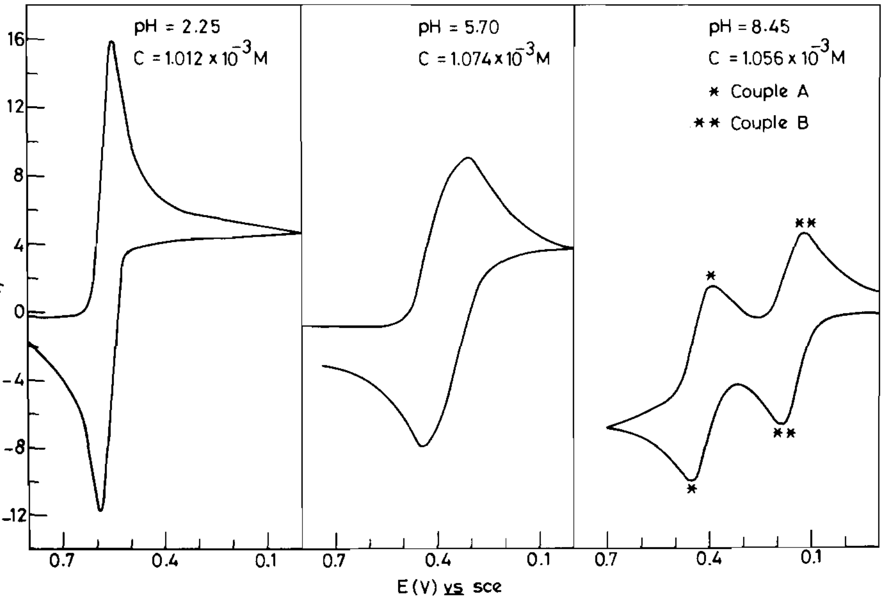

Fig. 1. Cyclic voltammograms at different pH values.

TABLE I. Cyclic Voltammetric Data[a] (298 °K).

pH	ΔE_p(V)	$0.5(E_{pa} + E_{pc})$ (V *vs.* sce)	0.059(m/n)pH (V)	$E^{\circ\prime}_{298}$(V) *vs.* sce
1.15	0.030	0.640	0.07[b]	0.71
2.25	0.035	0.573	0.13[b]	0.70
3.45	0.035	0.508	0.20[b]	0.71
4.10	0.035	0.468	0.24[b]	0.71
8.45	A 0.060	0.420	–[c]	0.42
	B 0.070	0.155	–[c]	0.16
9.00	A 0.070	0.420	–[c]	0.42
	B 0.070	0.145	–[c]	0.15
9.35	A 0.070	0.420	–[c]	0.42
	B 0.075	0.148	–[c]	0.15

[a] Data collected over the scan rate 0.011–0.140 V sec^{-1}; results are insensitive to scan rate. [b] m = 2, n = 2. [c] m = 0, n = 1.

As the pH is raised above 5, the nickel(II) species $NiHL^+$ and finally NiL contribute to the solution composition.[3] Above pH 8.5, the latter species alone exists. Evidently the two-electron two-proton process (3) is no longer feasible as an equilibrium reaction above pH 5. Indeed as the pH is raised above 5, the i–E response begins to undergo a qualitative change. What is initially observed is a broadening of the voltammogram and an increase in ΔE_p (Fig. 1). What is actually happening is that the couple (3) is being replaced by two one-electron couples whose peak potentials recede with increasing pH. The two couples become clearly observable at pH just above 6. At pH $\geqslant$ 7, the couples are well separated (Fig. 1). The couple at more positive potential (couple A) has $\Delta E_p \simeq 60$ mV, with E_{pa} and E_{pc} *independent of pH.* A nickel(III) intermediate is clearly implicated. The reversible electrode reaction corresponding to couple A is:

$$NiL^{2+} + e \rightleftharpoons NiL^{+} \qquad (4)$$

which has $E^{\circ\prime}_{298} = 0.42 \pm 0.01$ V *vs.* sce (Table I). The other couple (couple B) corresponds to the nickel(III)–nickel(II) reaction. It has ΔE_p close to 60 mV. The peak potentials are pH-dependent up to pH 8.5. Beyond this pH the peak potentials become independent of pH since protons are no longer involved in the electrode reaction:

$$NiL^{+} + e \rightleftharpoons NiL \qquad (5)$$

The $E^{\circ\prime}_{298}$ for this reaction is 0.15 ± 0.01 V *vs.* sce (Table I). Further studies on this and related systems are in progress.

Acknowledgements

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References

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