The Polarography of Cobalt(II), Nickel(II), and Zinc(II) in Pyridine, 4-Methylpyridine, and 2-Methylpyridine

By G. H. AYLWARD,† R. W. LEE,* and E. C. WATTON†

(†*School of Chemistry, Macquarie University, North Ryde, New South Wales,* 2113, *Australia; and* **School of Chemistry, University of New South Wales, Kensington, New South Wales,* 2033, *Australia*)

Summary The electrode behaviour demonstrated by octahedral species of bivalent cobalt, nickel, and zinc in pyridine and 4-methylpyridine is significantly different from that of the corresponding tetrahedral species in 2-methylpyridine, and may be a direct consequence of the metal atom and its charge environment.

PYRIDINE and related heterocyclic bases form an interesting series of solvents for the study of non-aqueous polarography of the transition metals. This is principally because the nature of the reducible species in solution can be established with some confidence and thus the effect of this upon the electrode process may be determined.

In the present study bivalent cobalt, nickel, and zinc were reduced in pyridine, 4-methylpyridine, and 2-methylpyridine. The metals were added to pyridine and 4-methylpyridine in the form of the perchlorates and to 2-methylpyridine as the bis-(2-methylpyridine)dichloride; all in the presence of lithium perchlorate as supporting electrolyte. Under these conditions it was established by comparing the solution spectra with published data[1] that nickel and cobalt exist in pyridine and 4-methylpyridine as doubly charged octahedral cations with the metal co-ordinated to six solvent molecules and that in 2-methylpyridine cobalt exists as the neutral, tetrahedral bis(2-methylpyridine)-dichloride. This would also appear to be the situation with nickel in 2-methylpyridine because the visible spectrum of the pure 2-methylpyridine complex in the polarographic solution, both in position and extinction (ϵ 180) is consistent with bivalent nickel in a tetrahedral environment. Although this spectrum has not been previously reported it agrees fairly closely with that reported for the solid material by Quagliano[2] and is in excellent agreement with that of the pure solid material prepared for use in this work.

Conductivity measurements suggest that zinc exists in forms quite analogous with those containing the nickel or cobalt and there is also published data to support this view.[3]

The preliminary data from the direct-current polarography are summarized in Table 1. The data were obtained using a three-electrode system in order to compensate for the large *iR* loss in these solvents of high resistance.

The polarographic behaviour of cobalt(II) in pyridine (py) and 4-methylpyridine (4-mepy) is very similar. The half-wave potentials are within 23 mv, the limiting current is diffusion-controlled and the diffusion coefficients are similar. The log-plot slopes indicate a greater apparent reversibility for the reduction in 4-methylpyridine. This similarity of polarographic behaviour in pyridine and 4-methylpyridine also exists with nickel(II) and zinc(II) in these solvents.

The polarographic behaviour of cobalt (II), nickel(II), and zinc(II) in 2-methylpyridine (2-mepy) differs considerably from their behaviour in the other two solvents. The

TABLE 1

The d.c.-polarographic properties of cobalt(II), *nickel*(II), *and zinc*(II) *in various non-aqueous solvents with* 0·1 M-LiClO$_4$ *at* 25·0°

Metal	Concn. (mM)	Solvent	$E_{\frac{1}{2}}$ (v.*vs.* Ag/Ag$^+$)	$\frac{-\mathrm{d}E}{\mathrm{d}\log i/(i_d - i)}$ (mv)	$\Delta E_{\frac{1}{2}}$[a] (mv)
Co	0·49	py	−1·006	42·1	−23
Co	0·52	4-mepy	−0·983	33·4	0
Co	0·50	2-mepy	−1·111	87·1	−128
Ni	0·51	py	−0·760	38·9	−10
Ni	0·45	4-mepy	−0·750	33·6	0
Ni	0·56	2-mepy	−0·477	46·5	+273
Zn	0·52	py	−0·970	35·6	+7
Zn	0·49	4-mepy	−0·977	34·1	0
Zn	0·50	2-mepy	−1·116	76·9	−139

[a] $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}$ (solv.) − $E_{\frac{1}{2}}$ (4-mepy).

TABLE 2

The d.c.-polarographic properties of cobalticinium perchlorate with 0·1 M-LiClO$_4$ *in various non-aqueous solvents at* 25·0°

Concn. (mM)	Solvent	$E_{\frac{1}{2}}$ (v *vs.* Ag/Ag$^+$)	*id* (μA)	$\frac{-\mathrm{d}E}{\mathrm{d}\log i/(i_d - i)}$ (mv)
1·03	2-mepy	−0·870	2·47	62·8
1·06	4-mepy	−0·839	2·58	56·0
1·02	py	−0·820	2·33	57·9

reduction of cobalt(II) and zinc(II) occur at more negative potentials, and the log-plot slopes indicate a much more irreversible reduction. The reduction of nickel(II) occurs at a far more positive potential and the log-plot indicates a slight decrease in the apparent reversibility.

The small shifts in half-wave potentials for the reduction of the cobalticinium ion in the three solvents (Table 2) were taken to establish that the solvent effects on the potential of the Ag/Ag$^+$ reference electrode were not significant in making comparisons of half-wave potentials.

The large difference in the reduction potential of nickel(II) in 2-methylpyridine compared with 4-methylpyridine may be due to the presence of a chemical reaction coupled with the charge-transfer process; for instance, a coupled chemical reaction may precede the charge-transfer process and produce a more easily reducible electroactive species of nickel(II) in 2-methylpyridine. Drop-time dependence and phase-angle studies of alternating-current polarograms will show the presence and nature of these coupled chemical reactions.

Log-plot slopes indicate the reversibility of the charge-transfer process but give no information as to whether this process is coupled with a chemical reaction.

As a preliminary investigation of the applicability of alternating-current polarographic techniques to these high resistance systems, a study of the cobalticinium ion in pyridine was chosen. An alternating-current polarogram for the reduction of the cobalticinium ion in pyridine is shown in the Figure. The waves in pyridine are very symmetrical and are almost of theoretical height and width for a reversible one-electron reduction. This is in agreement with the log-plot of the direct-current polarogram (57·9 mv) which indicates a reversible one-electron reduction.

The alternating-current polarographic studies are in progress and the results will be reported in a later publication. If the nickel(II), cobalt(II), and zinc(II) reductions in 4-methylpyridine and 2-methylpyridine can be shown to be simple charge-transfer processes not complicated by coupled chemical reactions, then their differences may be directly related to an intrinsic property of each metal atom in a charged octahedral environment compared with an unchanged tetrahedral environment.

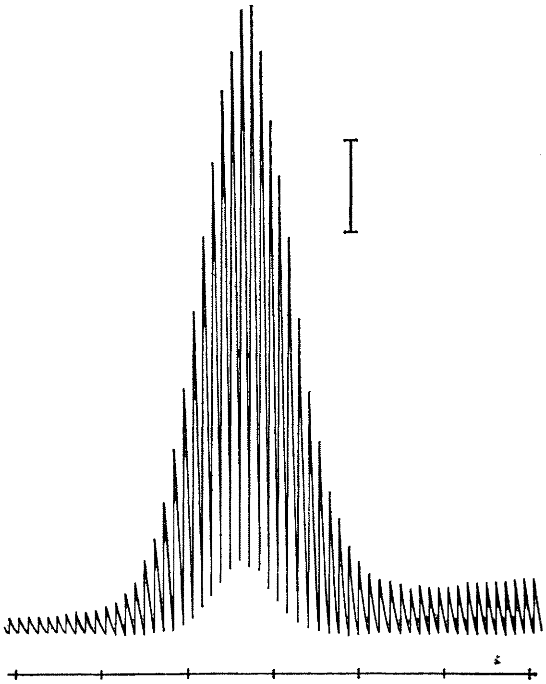

FIGURE. *Alternating-current polarogram of* 8·6 × 10^{-4}M *cobalticinium perchlorate* + 0·1M-LiClO$_4$ *in pyridine at* 25·0°. *Frequency* 55 Hz; *amplitude* 10mv *r.m.s.*

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