[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Polarography of the Nickel Cyanide Complexes and the Solubility and Constitution of Nickel Cyanide[1]

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The purpose of this work was to clarify the conflicting results on the polarography of nickel in cyanide medium reported by previous workers, to measure the dissociation constant of the $Ni(CN)_4^=$ ion, the solubility of nickel cyanide, and to study the polarographic behavior of monovalent nickel in cyanide medium.

The reduction of aquo nickel ion to the metal at the dropping mercury electrode is known to be highly irreversible, the observed half-wave potential of about −1.1 volts against the S.C.E. is about 0.6 volt more negative than the reversible potential. In excess cyanide, as is well known, the tetracyanide complex is formed. This ion is also reduced to the metal at the dropping electrode, the observed half-wave potential being about −1.4 volts in molar alkali cyanide. Emelianova[3] in an early investigation concluded the reduction of the nickel cyanide complex to be from the divalent to monovalent state. Kolthoff and Lingane[4] were the first to show the reduction to be a two-electron step. Sartori[5] and Hochstein[6] have also studied this reduction. The latter reported a number of peculiar irregularities including variation in half-wave potential with drop time, galvanometer sensitivity, and cyanide concentration. He described a marked shift of half-wave potential to more positive values with increasing cyanide concentration, and a simultaneous increase in wave height. It is difficult to evaluate his results as he does not always make clear whether he is discussing half-wave or tangent potentials, nor whether he is using applied or true cathode potentials. He gives values for the potential of the mercury pool which are evidently tangent potentials of the nickel wave. His failure to use a maximum suppressor and apparently also to remove oxygen makes many of his results uninterpretable. His conclusion that the nickel was reduced only in the form of un-ionized $H_2Ni(CN)_4$, no reduction taking place in basic medium, is flatly contradicted by the results of all other workers.

Experimental

The experimental setup and technique are the same as in previous work and have been described in an earlier communication.[7]

Results and Discussion

Tetracyanonickel(II)ate.—Pure sodium tetracyanonickel(II)ate dihydrate was prepared in the usual way by solution of freshly precipitated nickel cyanide in sodium cyanide and concentration of the filtered solution. After two recrystallizations from water, a nicely-crystalline orange product was obtained. A solution 0.001 *M* in the complex and 0.1 *M* in potassium chloride or sodium hydroxide as supporting electrolyte and with 0.01% gelatin as a maximum suppressor gave a somewhat misshapen wave with a half-wave potential of about −1.4 v. (Fig. 1). The shape of the rising part of the curve is suggestive of a double wave but no conditions could be devised to show unambiguously whether two steps actually occur in the reduction or whether, as seems more likely, the deviation is due to the irreversibility of the electrode reaction. The addition of increasing amounts of cyanide to the medium results in a steepening of the wave and a

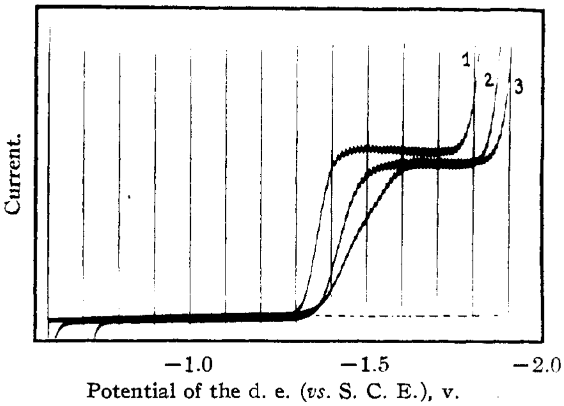

Fig. 1.—Polarograms of 0.001 *M* $Ni(CN)_4^=$: (1) in 1.0 *M* · KCN, (2) in 0.1 *M* KCN, (3) in 0.1 *M* KCl or NaOH.

TABLE I

EFFECT OF CYANIDE ON THE HALF-WAVE POTENTIAL AND WAVE HEIGHT OF $Ni(CN)^=_4$

Drop time 3 sec., 0.006% gelatin present.

Medium, *M*		$Ni(CN)_4^=$ (*M*)	$E_{1/2}$	i_d (−1.7 v.) (μa)	i_d/*C*(relative)
0.1 KCl		0.00100	−1.48	7.65	(1.000)
.1 KCl	0.01 KCN	.00099	−1.47	7.70	1.016
.1 KCl	.10 KCN	.00097	−1.42	7.75	1.043
.1 KCl	1.00 KCN	.00096	−1.36	8.22	1.119

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(1) Taken from a portion of the Doctorate Thesis of David N. Hume, 1943. Presented in part at the San Francisco meeting of the American Chemical Society, April, 1949.

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(3) N. V. Emelianova, *Rec. trav. chim.*, **44**, 529 (1925).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(5) G. Sartori, *Gazz. chim. ital.*, **66**, 688 (1936).

(6) J. P. Hochstein, *J. Gen. Chem. U. S. S. R.*, **7**, 2488 (1937).

(7) D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **65**, 1897 (1943).

shift of the half-wave potential to more positive values (Table I and Fig. 1). The same effects were noted when the drop-time was increased, indicating that the increasing current in more concentrated cyanide medium is probably not due to a catalytic wave.

In order to determine whether or not the increased current in concentrated cyanide medium was due to the presence of an unsuppressed maximum, increasing amounts of gelatin were added. It was found, both in 1 *M* and 0.1 *M* potassium cyanide, that increasing amounts of gelatin caused the wave to diminish and become greatly drawn out. As little as 0.1% of gelatin, an amount sufficient with most substances to reduce the diffusion current only by 1 or 2%, suppressed the nickel cyanide complex wave almost completely.

Experiments with varying concentrations (from 2×10^{-4} to 5.6×10^{-3} *M*) of complex in 0.1 *M* potassium cyanide did not indicate any change of half-wave potential with concentration, galvanometer sensitivity, or drop-time. It was noted that at high concentrations of complex (5×10^{-3} *M*), even in 0.1 *M* potassium cyanide, the wave again began to take shape characteristic of media without excess cyanide.

The same results were obtained when the complex was formed directly by addition of an excess of cyanide to a nickel chloride or nickel nitrate solution. The diffusion current of the complex in 0.1 *M* potassium cyanide is greater than that of the aquo nickel ion of the same concentration by a factor of 1.14.

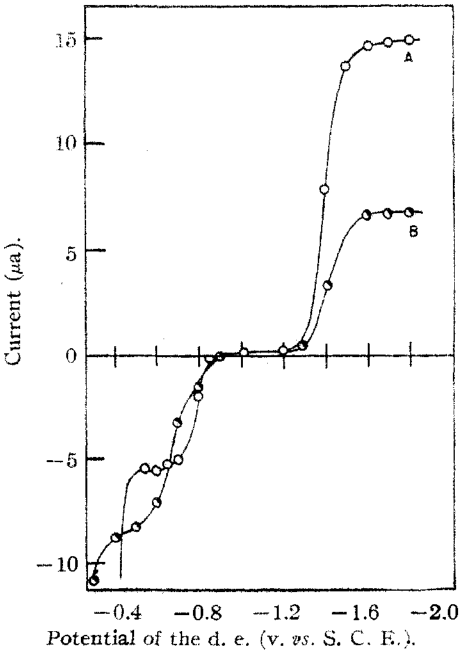

Fig. 2.—Current-voltage curves of mixtures of mono- and divalent nickel cyanide complexes: A, in 0.1 *M* NaCN; B, in 0.1 *M* KCl.

Monovalent Nickel Cyanide Complexes.—The polarograms of the reduction of the divalent nickel cyanide complex gave no definite indication of the formation of the monovalent complex at the dropping electrode. Solutions known to contain the monovalent complex were next examined polarographically. Treatment of 0.1 *M* solutions of the sodium tetracyanonickel(II)-ate with 2% sodium amalgam resulted in the immediate formation of a deep red color characteristic of monovalent nickel complex. The complex thus formed was found to be fairly stable; it retained its color for two or three days in the absence of air. Addition of cyanide to the mixture greatly accelerated reoxidation to the nickel(II) complex. This is in agreement with the findings of previous workers.[8]

Samples of 1 or 2 ml. of the reduced solutions were added to 99 or 98 ml. samples of 0.1 *M* air-free supporting electrolyte, and polarograms were taken. A cathodic wave due to unreduced or reformed nickel(II) cyanide was always obtained at about −1.4 v., and had the usual characteristics of the wave of that substance.

An anodic wave was also obtained, beginning about −0.85 to −0.9 v. (Fig. 2). Gelatin was necessary to suppress the maximum. It was found that good polarograms could not be obtained when a mercury pool was used as the unpolarizable electrode. The pool potential measured against a separate reference electrode was found to be virtually undefined between −0.9 and −1.3 v. This resulted in polarograms having meaningless potential values, unless a separate reference electrode was used.

It was found that in supporting electrolytes containing no added cyanide, the anodic wave was drawn out and poorly defined. Actually the wave is a composite of two waves: the first, oxidation of nickel(I) cyanide to nickel(II) cyanide and the second, the anodic dissolution of mercury. The addition of cyanide greatly improved the form of the first anodic wave and, of course, caused the second anodic wave to become unmeasurably large. The electrode reaction corresponding to the first wave is evidently

$$\mathrm{Ni(CN)_3^{=} + CN^{-} = Ni(CN)_4^{=} + e^{-}}$$

requiring diffusion of both nickel complex and cyanide ions to the electrode.

A reversible oxidation of nickel(I) and reduction of nickel(II) at the dropping electrode would result in a composite anodic–cathodic wave, as was found in the chromium(II)–chromium(III) cyanide system.[7] It is evident that at the dropping electrode, the corresponding nickel reactions are not reversible. Nickel(I) cyanide is oxidized to nickel(II) cyanide but the latter is reduced to the metal. Nickel(I) cyanide is evidently not reduced at the dropping electrode. No separate reduction wave is present, and oxidation of part

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(8) J. W. Eastes and W. M. Burgess, This Journal, **64**, 1187 (1942).

of the nickel(I) cyanide causing a decrease in the anodic current results in an increase in the cathodic current by about twice the same amount. Were the nickel(I) cyanide also reduced, the increase would have been equal to rather than double the decrease.

Since the completion of the experimental work on this problem in 1943, a paper by Caglioti, Sartori and Silvestroni[9] has appeared in which the old interpretation of the reduction of the nickel cyanide complex as a one-electron step is again suggested. Caglioti and his collaborators reported that the sum of the anodic and cathodic diffusion currents of nickel in cyanide medium remained constant as the divalent complex was reduced to the monovalent and then allowed to reoxidize spontaneously. Because this is in conflict with the results of the previous investigation, a careful recheck of the experiments involving the monovalent nickel complex was made by one of us in collaboration with Mr. Norman F. LeBlanc at the Massachusetts Institute of Technology. In a typical experiment a solution 0.00824 *M* in $Ni(CN)_4^=$ ion and 0.1 *M* in added potassium cyanide was partially reduced with sodium amalgam and titrated amperometrically with potassium ferricyanide. It was observed that the disappearance of an anodic diffusion current of 2.60 μa. at -0.65 v. resulted in a simultaneous increase of 5.25 μa. in the cathodic diffusion current at -1.70 v. The repetition of such experiments as these has not revealed any evidence which fails to support the conclusions drawn from the original work.

Polarographically, it is not possible to determine the potential of the nickel(I)–nickel(II) couple. The anodic half-wave potential in 1.0 *M* sodium cyanide was found to be -0.80 v. so that the reversible potential must clearly be more negative than that value. We may then set the minimum (negative) potential for the hypothetically reversible nickel(I) cyanide–nickel(II) cyanide couple on the hydrogen scale as -0.55 v. Grube[10] measured the potential without additional cyanide and found it to be -0.82 v. and noted also that it was shifted to more negative values by the addition of cyanide. The measurements of Tedeschi[11] are uninterpretable, inasmuch as he apparently tried to measure the potential of a pure nickel(I) cyanide solution with no nickel(II) cyanide present.

The Dissociation Constant for the Nickel(II) Tetracyanide Complex.—The three values reported in the literature for the dissociation constant of the $Ni(CN)_4^=$ ion are widely at variance. The irreversibility of the reduction process at the dropping electrode does not permit a direct determination of the constant, but the polarographic results are such as to show clearly that two of the published values are untenable.

Masaki,[12] from measurement of the potential of a nickel wire electrode in solutions of the complex in excess sodium cyanide, calculated a value of 3.6×10^{-13}. Sartori[5] estimated 3.5×10^{-16} from polarographic measurements and Latimer[13] calculated a value of 10^{-22} indirectly from thermal data. The value reported by Masaki would be suspect anyway as the nickel electrode is not reversible and he chose an outdated value for the standard potential of the nickel-nickel ion couple. The order of magnitude obtained is clearly wrong as a dissociation constant of 10^{-13} would lead to a 0.1 *M* solution of pure $Na_2Ni(CN)_4$ having a free cyanide ion concentration of the order of 10^{-3} *M*. The polarograms of the pure compounds in sodium hydroxide or potassium chloride show no detectable trace of cyanide to be present, either immediately, or after some hours of standing. This means that the free cyanide concentration must not be over 10^{-5} *M*, corresponding to a maximum dissociation constant of about 10^{-24}. This agrees fairly well with the indirect estimate made by Latimer. The calculations of Sartori are invalid as he used an equation applicable only to truly reversible systems.

Nickel Cyanide.—In order to detect the existence of intermediate complex ions between the aquonickel and the tetracyanide, a 0.002 *M* nickel chloride solution was titrated with small portions of 0.0560 *M* sodium cyanide and polarograms taken after each increment. A gradual decrease of the aquonickel ion wave was observed and, coincidentally, the development of the characteristic nickel tetracyanide wave. No new waves were observed other than a small and essentially constant pre-wave about 0.2 v. ahead of the aquonickel wave. This is very similar to the small wave obtained by Brdicka[14] on addition of alkali to a cobaltous chloride solution, and attributed by him to a small amount of hydroxy complex. Apparently due to supersaturation, no precipitate of nickel cyanide formed but it was observed that when the ratio of nickel to cyanide in the solution was 1 to 2, approximately equal amounts of aquonickel and cyanide complex were present with no indication of free cyanide. This suggestion that nickel cyanide might be analogous in structure to silver cyanide: the aquonickel salt of $H_2Ni(CN)_4$. To test this hypothesis, nickel cyanide was prepared according to directions found in the literature.

One series of preparations was made by mixing nickel nitrate with approximately equivalent amounts of sodium cyanide, aging overnight in the mother liquor, and washing repeatedly with conductivity water. A visually identical product was obtained by mixing equivalent amounts of nickel nitrate and potassium nickel(II) tetra-

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[9] V. Caglioti, G. Sartori and P. Silvestroni, *Atti. accad. natl. Lincei, Classe sci. fis., mat. e nat.*, **3**, 448 (1947).

[10] G. Grube and M. Lieder, *Z. Elektrochem.*, **32**, 561 (1926).

[11] G. Tedeschi, *Atti Accad. Lincei*, [6] **23**, 894 (1936).

[12] K. Masaki, *Bull. Soc. Chim. Japan*, **6**, 233 (1931).

[13] W. M. Latimer, "Oxidation Potentials," Prentice–Hall, New York, N. Y., 1938.

[14] H. Brdicka, *Collection Czech. Chem. Comm.*, **3**, 396 (1931).

cyanide. A third product was obtained from mercuric cyanide and nickel chloride, reported by Gupta[15] to be the trihydrate. A portion of each of these products was shaken in 0.1 *M* sodium chloride for one week at room temperature to saturation. Preliminary experiments indicated that saturation was reached in considerably less time than this. At the end of the shaking period the solutions were analyzed polarographically. The proportionality between diffusion current and concentration for nickel had been shown by Kolthoff and Lingane and the ratio of the diffusion current of the complex to that of the simple ion had already been shown to be 1.14. The details of the measurements are included in Table II.

TABLE II

SOLUBILITY OF NICKEL CYANIDE IN 0.1 *M* SODIUM CHLORIDE AT 25°

Sample	i_1(μa)	i_2(μa)	$C_{Ni^{++}}$ (*M*)	$C_{complex}$ (*M*)	K_{sp}
1	0.30	0.26	4.7×10^{-5}	3.6×10^{-5}	1.7×10^{-9}
2	.27	.31	4.2×10^{-5}	4.3×10^{-5}	1.6×10^{-9}
3	.13	.54	2.0×10^{-5}	7.5×10^{-6}	1.5×10^{-9}
				Av.	1.7×10^{-9}

Sample 1 From $NiCl_2$ and KCN
2 Gupta's product
3 From $NiCl_2$ and $Na_2Ni(CN)_4$

The sources of error in the measurement include the difficulty of accurately measuring the small currents involved (the correction for residual current being of the same order of magnitude as the current due to the nickel) and the assumption of proportionality between current and concentration at very low concentrations. In view of the uncertainties in the measurements and the diversity of the methods of preparation of the samples, the agreement must be considered very good. It is to be observed that the solubility product obtained is not an activity product but a concentration product applying in a solution of ionic strength 0.1. The corresponding molar solubility is 4.1×10^{-5}, or 8.2×10^{-5} based on the simple formula $Ni(CN)_2$.

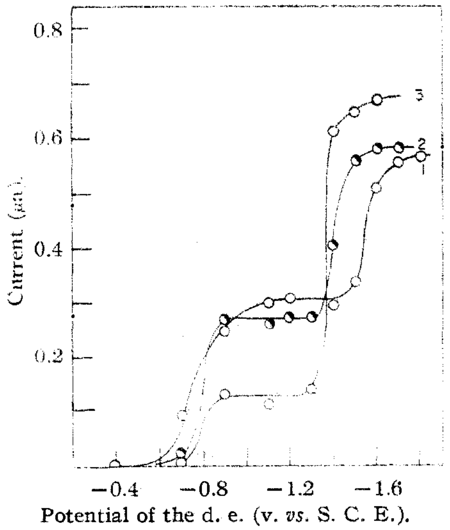

Fig. 3.—Polarographic determination of the solubility of nickel cyanide in 0.1 *M* NaCl: curve 1, $NiCl_2$ and KCN; curve 2, Gupta's product; curve 3, $NiCl_2$ and $Na_2Ni(CN)_4$.

The results shown in Fig. 3 are interesting in several ways. For one thing, the hypothesis that solid nickel cyanide is actually $Ni[Ni(CN)_4]$ is confirmed. No trace of cyanide (which would give an anodic wave −0.5 v.) is detected in the solution, but instead the waves of the aquo nickel and nickel cyanide complex ions were found in approximately equal prominence. For another thing, the solubility product principle is seen to apply, concordant values being obtained. The third preparation evidently was not pure but contained an excess of the complex ion; nevertheless, the solubility product obtained was the same. This proof of the constitution of hydrated nickel cyanide explains the hitherto anomalous value of the magnetic susceptibility obtained by Cambi.[16] Anhydrous nickel cyanide is diamagnetic, as is the tetracyanide complex. The aquonickel ion has two unpaired electrons and is therefore paramagnetic. Hydrated nickel cyanide with two to four molecules of water per nickel atom shows a molal paramagnetic susceptibility about half that of the nickel ion, as would be expected from the polarographic results, since half the nickel atoms are ionically bonded to water molecules and half are bonded covalently to cyanide ions.

Summary

Polarographic studies on the reduction of the $Ni(CN)_4^=$ ion confirm the previously reported irreversibility and mechanism of the reduction, and indicate the dissociation constant of the complex to be of the order of 10^{-22}. Polarograms of saturated solutions of nickel cyanide show waves due to the aquonickel ion and the nickel tetracyanide complex ion but no free cyanide ions can be detected in the solution. This indicates that the solid is actually $Ni[Ni(CN)_4]$ analogous to $Ag[Ag(CN)_2]$. The solubility product in tenth molar sodium chloride is 1.7×10^{-9}, corresponding to a solubility of 4.1×10^{-5} mole per liter. Polarograms of solutions of monovalent nickel cyanide show waves corresponding to irreversible anodic oxidation to the $Ni(CN)_4^=$ ion.

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[15] L. Gupta, *J. Chem. Soc.*, **117**, 67 (1920).

[16] L. Cambi, A. Cagnasso and E. Tremolada, *Gazz. chim. ital.*, **64**, 758 (1934).