The Complex Formation in the Nickel(II)—Cyanide System

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The formation of complexes in aqueous solution between nickel(II) ions and cyanide ions has been studied by potentiometric measurements with a glass electrode at 25.0 °C and ionic strength 3.0 M using sodium perchlorate as ionic medium. These measurements are best described if two mononuclear complexes, $NiCN^+$ and $Ni(CN)_4^{2-}$, are supposed to exist with the stability constants $\beta_1 = (1.08 \pm 0.4)10^7$ M^{-1} and $\beta_4 = (1.16 \pm 0.08)10^{31}$ M^{-4}, respectively (the errors given are three times the standard deviations). The presumptive complexes $Ni(CN)_2$ and $Ni(CN)_3^-$ were found to be so weak that the corresponding stability constants could not be determined. From the calculations approximate maximum values of β_2 and β_3 were estimated to 9×10^{13} M^{-2} and 1×10^{22} M^{-3}, respectively. There was no sign of any fifth or sixth mononuclear complex in the ligand range that was investigated. The conclusion that $Ni(CN)_6^{4-}$ is a very strong complex can definitely be discarded.

Protonated nickel cyanide complexes have been reported to dominate the complex formation at pH <5. In the present investigation no such complexes could be discovered although a careful analysis of potentiometric data in this pH-region was performed. Protonated nickel cyanide complexes, if they exist at all, must therefore be far weaker than suggested previously.[1]

The fourth mononuclear complex strongly dominates the complex formation, and the potentiometric measurements indicate a maximum amount of $NiCN^+$ of only (10 ± 4) %. Therefore spectrophotometric investigations were performed to verify the existence of the first complex. No positive evidence of $NiCN^+$ was obtained, however, indicating that the first complex is considerably weaker than suggested by the results from the potentiometric measurements. The value of β_1 given above may be regarded as a maximum value.

The complex formation in the nickel cyanide system has been subject to several investigations.[1-12,18,21,24,25] The publications on this topic reflect considerably varying opinions about which complex species are formed and about their strength. A common opinion is that a strong fourth mononuclear complex exists, but the reported magnitude of β_4 varies from 3.6×10^{13} M^{-4} (obtained by Masaki[3] from potentiometric measurements with a nickel electrode) to $\beta_4 = 1 \times 10^{30}$ M^{-4} (reported by Christensen et al.[4] from potentiometric measurements with a glass electrode).

No report of a complex $NiCN^+$ seems to have been made, and most authors have not discovered $Ni(CN)_2$ or $Ni(CN)_3^-$ in their investigations. Shibata et al.[5] however, claim from paper electrophoresis measurements that $Ni(CN)_2$ and possibly $Ni(CN)_3H_2O^-$ exist.

Several authors have reported a continued complex formation beyond $Ni(CN)_4^{2-}$.[6-12] This hypothesis is supported by the colour change from yellow to red when increasing amounts of sodium cyanide are added to a solution containing sodium tetracyanonickelate(II). The existence of a fifth mononuclear nickel cyanide complex with $\beta_5/\beta_4 \approx 0.2$ seems to have been established with reasonable certainty. Penneman et al.[10] for instance, conclude from IR measurements that when increasing amounts of sodium cyanide are added to a sodium tetracyanonickelate(II) solution the absorbance peak at 2124 cm^{-1} successively diminishes and a new peak at 2103 cm^{-1} is developed. This latter peak is ascribed to the formation of $Ni(CN)_5^{3-}$. A weak complex $Ni(CN)_6^{4-}$ is also reported. The structure of $Ni(CN)_4^{2-}$ is reported to be square planar[13] and that of $Ni(CN)_5^{3-}$ square pyramidal.[12]

From spectrophotometric measurements Coleman et al.[12] conclude that $Ni(CN)_5^{3-}$ exists but that the small effects observed in previous

measurements [10] and interpreted as $Ni(CN)_6^{4-}$ can in fact be ascribed to changes in the ionic medium. Blackie and Gould,[6] however, claim with the support of NMR investigations that while the fifth nickel cyanide complex is very weak, the sixth complex is so strong that $Ni(CN)_6^{4-}$ is formed quantitatively when sodium cyanide is added beyond a ratio of total cyanide to total nickel concentration of 4:1. The aim of the present investigation has not been to investigate nickel cyanide complexes beyond the fourth one. However, the statement of Blackie and Gould as to an extreme strength of $Ni(CN)_6^{4-}$ can be discarded. The present potentiometric measurements show that $\bar{n} = 4.0 \pm 0.1$ up to about a tenfold excess of cyanide. The results from the NMR investigations performed by Van Geet and Hume [11] are also contradictory to those obtained by Blackie and Gould.

Reasonable evidence for the formation of $Ni(CN)_5^{3-}$ has thus been presented. As pointed out by Coleman et al.,[12] however, efforts to isolate the corresponding salt from nickel(II) solution saturated with potassium cyanide result in $K_2Ni(CN)_4 \cdot nH_2O$ only.

Furthermore, an extensive formation of protonated complex species $HNi(CN)_4^-$, $H_2Ni(CN)_4$ and $H_3Ni(CN)_4^+$ is reported by Kolski and Margerum [1] from kinetic and equilibrium measurements. The magnitudes of the corresponding stability constants imply in fact that protonated nickel cyanide complexes should be the dominating species at pH < 5.

The conclusion from the reports hitherto produced on nickel cyanide complexes is that a very strong complex $Ni(CN)_4^{2-}$ definitely exists (with $\beta_4 \approx 10^{30}$ M^{-4}) and that reasonable evidence for the existence of a complex $Ni(CN)_5^{3-}$ (with $\beta_5 \approx 2 \times 10^{29}$ M^{-5}) has been produced. Since most authors have failed to discover the first three mononuclear complexes, these could be expected to be rather weak compared to the fourth complex. Christensen et al.,[4] for instance, observed no indication of other nickel cyanide complexes than $Ni(CN)_4^{2-}$. Their measurements comprise a rather small material, however, and only the region $1.1 \le \bar{n} \le 3.2$ has been studied. An investigation aiming to study the formation of the low complexes ought to be extended to the region $\bar{n} < 1$. Besides, the precision in their determina-

tion of β_4 is rather low. This fact together with the narrow $\bar{n}$-range examined could explain why contributions from the first three mononuclear complexes might be hidden in their results.

The present investigation was performed with two main aims, namely to study the formation of intermediate nickel cyanide complexes and the possible formation of acid nickel cyanide species. The potentiometric technique elaborated for the studies of the cyanide systems of zinc(II) and cadmium(II) [14] was used.

Further, supplementary spectrophotometric studies in the UV range were performed.

I. POTENTIOMETRIC MEASUREMENTS

Calculations of stability constants

A. Graphical calculations. The stability constants for the mononuclear nickel cyanide complexes were determined graphically from $\bar{n}/[A]$ values as described previously[14].

B. Numerical calculations. Numerical calculations were performed employing the data program "LETAGROP ETITER" [15] to check possible formation of protonated nickel cyanide complexes.

C. To get a so realistic conception of the errors in the stability constants as possible, the $\bar{n}$,[A] data from the measurements were also treated numerically using a data program elaborated by Sandell.[16] In this program a weight for every experimental ($\bar{n}$,[A])-value is calculated from the errors estimated in emf and concentration. In all calculations the values of $pK_{a(HCN)} = 9.484 \pm 0.01$ and $pK_W = 14.184 \pm 0.002$ determined previously [14] were used. The computer UNIVAC 1108 in Lund was used for the numerical calculations.
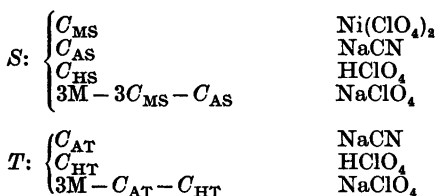
Experimental

Chemicals. Perchloric acid, sodium perchlorate, and sodium cyanide were prepared as described in previous papers.[14,17] Nickel(II) perchlorate was prepared from nickel(II) carbonate (Bakers *p.a.*) and perchloric acid in slight excess. The concentration of nickel(II) was determined by adding excess EDTA and then titrating with a standardized lead(II) nitrate solution. The analysis was performed at pH ≈ 5.5 using xylenolorange as indicator. The

concentration of the excess perchloric acid was measured by means of a potentiometric titration with standardized sodium hydroxide solution.

*Measurements.** Investigations of the nickel cyanide system are rendered difficult by several factors. (*i*) While $Ni(CN)_4^{2-}$ is formed rather quickly from nickel(II) ions and cyanide ions the dissociation of $Ni(CN)_4^{2-}$ in acid solution is a slow process[1] and equilibrium is not established until after about $1-3$ weeks. (*ii*) $Ni(CN)_2$ is only slightly soluble[18] and to avoid precipitation the measurements must be carried out at very low concentrations of nickel perchlorate. (*iii*) To minimize volatilization of HCN carefully closed vessels must be used. (*iv*) The cyanide is slowly decomposed by water according to Christensen *et al.*[4] (*v*) The complex formation occurs in a very narrow ligand range and a high precision in the addition of titrant is required.

The measurements were designed in the following way. The hydrogen ion concentration was determined in solutions obtained by adding a volume v of a solution T to a volume V_0 of a solution S.

$$S: \begin{cases} C_{MS} & \text{Ni(ClO}_4)_2 \\ C_{AS} & \text{NaCN} \\ C_{HS} & \text{HClO}_4 \\ 3M - 3C_{MS} - C_{AS} & \text{NaClO}_4 \end{cases}$$

$$T: \begin{cases} C_{AT} & \text{NaCN} \\ C_{HT} & \text{HClO}_4 \\ 3M - C_{AT} - C_{HT} & \text{NaClO}_4 \end{cases}$$

Two kinds of measurement series were performed, with $C_{AS}=0$ and $C_{AT}\neq 0$ or $C_{AS}\neq 0$ and $C_{AT}=0$. After addition of titrant the solutions were shaken at 25.0 °C for about a week and then the pH was measured for a portion of every solution. After another week in the thermostat the pH was measured again. If equilibrium had not been attained, the procedure was repeated once more. The pH was determined by measuring the emf of the following galvanic cell

Glass electrode | S + T | 3.00 M NaClO$_4$ |

$$\begin{array}{c} \text{10.0 mM NaCl} \\ \text{2.99 M NaClO}_4 \end{array} \bigg| \text{Ag, AgCl}$$

The emf was measured with an Orion digital voltmeter together with a Jena glass electrode U9201/21. This electrode was checked against a hydrogen electrode, and a consistency within 0.2 mV was found in the range $3 < -\log [H^+] < 9$. The glass electrode was calibrated in acetate buffers as described previously.[14] Every titration series was repeated at least once. The reproducibility of the measured emf in the titration series was in general within 1 mV.

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* For further information about experimental details see Ref. 14.

Results

In Table 1 corresponding mean values of added volume of titrant and measured emf are collected.

The results from the graphical and numerical determinations of the stability constants are collected in Table 2. To check the possible existence of protonated nickel cyanide species, numerical calculations were made employing the data program "LETAGROP ETITER".[15] In all the least squares refinements C_H/C_A was used as error carrying variable. First an effort was made to fit the experimental data assuming $Ni(CN)_4^{2-}$ and $HNi(CN)_4^{-}$ to be the predominant complex species.[1] As starting values were chosen $\beta_4 = 1.2 \times 10^{31}$ M^{-4} (obtained graphically) and $\beta_{4H} = 3.3 \times 10^{36}$ M^{-5} (proposed by Kolski *et al.*[1]). The calculations gave $\beta_4 = (1.34 \pm 0.23)10^{31}$ M^{-1} and $\beta_{4H} = (1.2 \pm 2.2)10^{35}$ M^{-5}. (The errors are given as three times the standard deviations). The error in β_{4H} is thus larger than β_{4H} itself. A second calculation was performed postulating the existence of $NiCN^+$ in addition to $Ni(CN)_4^{2-}$ and $HNi(CN)_4^{-}$ and with a starting value of $\beta_1 = 1.0 \times 10^7$ M^{-1} according to the graphical determinations. The values of β_1, β_4, and β_{4H} were varied and the best fit was obtained with the following set of stability constants: $\beta_1 = (1.14 \pm 0.20)10^7$ M^{-1}, $\beta_4 = (1.18 \pm 0.08)10^{31}$ M^{-4} and $\beta_{4H} = 0$.

The description of the measurements in the second calculation was found to be much better than in the first one. Thus there is no indication of formation of acid nickel cyanide species.

A calculation was also performed using "LETAGROP ETITER" postulating only $Ni(CN)_4^{2-}$ to exist. From this calculation $\beta_4 = (1.32 \pm 0.22)10^{31}$ M^{-4} was obtained. The standard deviation (sig$y$) in the error carrying variable (C_H/C_A) was 28.5 compared to 10.5 when postulating both $NiCN^+$ and $Ni(CN)_4^{2-}$. The description of the potentiometric measurements is thus considerably improved if also a first complex is assumed to exist.

An estimation of the hydrolysis of the nickel aquo ion in the actual pH-range based upon reported hydrolysis constants[2] shows that this effect can be completely neglected in the present measurements.

The complex formation curve, $\bar{n}$, (log [A]), calculated from the stability constants β_1 and

Table 1. Corresponding values of added volume, v, of titrant and measured emf, E_H. $V_0 = 50.00$ ml.

	Series 1	Series 2	Series 3	Series 4
E^0_H (mV)	519.5	519.5	520.3	−488.5
C_{MS} (mM)	0.397	0.496	0.397	0.488
C_{MT} (mM)	0	0	0	0
C_{AS} (mM)	0	5.27	0	0
C_{AT} (mM)	21.93	0	25.08	10.00
C_{HS} (mM)	0.073	0.054	0.073	0.095
C_{HT} (mM)	9.92	10.06	9.88	4.99

v ml	E_H mV	v ml	E_H mV	v ml	E_H mV	v ml	E_H mV
		1.000	220.5	16.16	209.6	0.500	215.9	0.800	−759.6
		2.000	226.5	16.36	231.2	0.700	215.8	1.000	−771.0
		3.000	231.0	16.56	239.8	1.300	220.5	1.200	−777.3
		3.300	231.0	16.95	247.5	1.600	223.0	1.400	−778.0
		3.600	232.1	17.45	249.8	2.300	225.3	1.600	−782.6
		4.000	232.1	17.94	253.2	2.600	226.8	1.800	−782.4
		4.600	232.0	18.44	255.8	3.000	227.5	2.600	−781.8
		5.000	229.4	18.97	259.6	3.300	228.7	2.900	−778.2
		5.300	232.6	20.00	263.7	3.600	228.1	3.200	−778.8
		5.600	231.9	20.50	265.4	4.300	227.5	3.500	−779.3
		6.000	230.7	21.00	267.1	4.600	226.5	4.100	−777.7
				21.50	269.2	5.000	222.2	5.000	−776.6
				22.01	270.0	5.300	215.2		
				22.51	271.0				
				22.98	273.9				
				23.48	274.9				
				23.97	276.3				
				26.50	290.6				

Table 2. Results from the calculations of stability constants for the nickel cyanide system (β_i in M^{-i}). The errors given in the numerical calculations are three times the standard deviations.

Calculation method	β_1	β_2	β_3	β_4
Graphical	$(1.0 \pm 0.2)10^7$	$< 9 \times 10^{13}$	$< 1 \times 10^{22}$	$(1.18 \pm 0.05)10^{31}$
Numerical; Letagrop [15]	$(1.14 \pm 0.2)10^7$	0	0	$(1.18 \pm 0.08)10^{31}$
Numerical; Sandell [16]	$(1.08 \pm 0.40)10^7$	0	0	$(1.16 \pm 0.08)10^{31}$

β_4 is drawn in Fig. 1, and in the same diagram some experimental values are plotted.

II. SPECTROPHOTOMETRIC MEASUREMENTS

According to the potentiometric measurements NiCN+ exists to a rather small extent. With regard to the considerable difficulties encountered in these investigations it seemed important to check the existence of NiCN+ with an independent method.

It is probable that NiCN+ has an absorption spectrum different from that of $Ni(CN)_4^{2-}$.[19] So absorption spectra for nickel cyanide solutions were recorded in the wavelength region $210 - 360$ nm with the aid of a Hitachi EPS-3T spectrophotometer and 1 cm quartz cells. In these solutions $\bar{n}$ was varied from 3.9 to 0.02 by altering the concentration of nickel perchlorate and sodium cyanide. The ionic strength was maintained constant $= 3.00$ M with the aid of $NaClO_4$. The absorptivities of nickel(II) ions, cyanide ions, and hydrogen
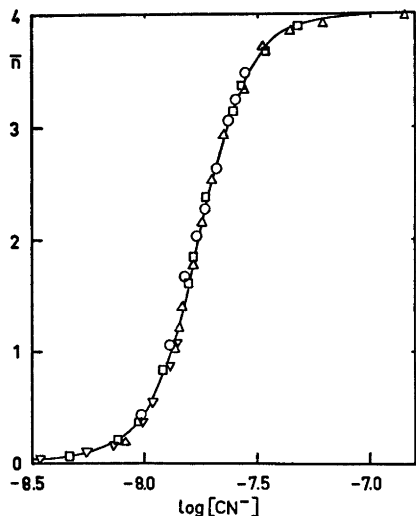
Fig. 1. The complex formation curve for the nickel cyanide system. The full-drawn curve represents $\bar{n}$ calculated from the stability constants. The experimental values of $\bar{n}$ are denoted by O (Series 1), △ (Series 2), □ (Series 3) and ▽ (Series 4) ([CN⁻] in M).

cyanide, respectively, are negligible in the range 210 – 360 nm. $Ni(CN)_4^{2-}$ has three absorbance peaks in the wavelength region investigated, namely at 267, 285, and 310 nm in descending magnitude of height. The absorptivity at 267 nm for $Ni(CN)_4^{2-}$ was found to be about 1.1×10^4 M^{-1} cm^{-1}.

No wavelength displacements of the absorption peaks were observed when $\bar{n}$ was varied nor could any change in absorptivity be discovered. These facts can be interpreted in two ways: (i) $NiCN^+$ exists in much smaller concentrations than implied by the potentiometric measurements. (ii) $NiCN^+$ and $Ni(CN)_4^{2-}$ have very similar absorptivities per Ni – CN bond. In this case $NiCN^+$ may exist in high concentrations. As mentioned above, however, the spectrum of $NiCN^+$ can be expected to show much closer resemblances to the spectrum of the nickel aquo ion than to that of $Ni(CN)_4^{2-}$.[19] Thus interpretation (i) is by far the most probable.

(In some solutions the concentration of nickel was so large that a precipitate was formed. In the spectra, recorded on these solutions after filtering, a displacement of the peaks towards smaller wavelengths was observed. As the

precipitation in the solution proceeded, however, the peaks and the displacements diminished and vanished after about a week. These displacements may possibly be explained by a slight colloidal precipitate).

In addition to the spectrophotometric investigations on nickel cyanide solutions at equilibrium a kinetic study of the acid hydrolysis of $Ni(CN)_4^{2-}$ in 0.10 M $HClO_4$ was made. Measurements on two different solutions were performed. In one solution the concentration ratio of total cyanide to total nickel was about 3.9 and in the other about 0.15. According to the results from the potentiometric measurements the complexed nickel should exist at the start almost entirely as $Ni(CN)_4^{2-}$ in the first solution but largely as $NiCN^+$ in the latter one. Perchloric acid was added to 0.10 M concentration and spectra were recorded with time intervals of about 5 min. The peaks diminished continuously but no wavelength displacements were observed. From measurements of the height of the peak at 267 nm as a function of time the first order dissociation constant, k_d, of $Ni(CN)_4^{2-}$ at $[H^+] = 0.10$ M was determined. For both solutions the same value of k_d was obtained within the limits of accuracy: $k_d = (6.0 \pm 1.0)10^{-4}$ s^{-1}. This coincidence further strengthens the assumption that β_1 is considerably less than the value obtained from potentiometric measurements. Another, not very probable, explanation might be that the dissociation of $NiCN^+$ is the rate-determining step in the acid hydrolysis.

DISCUSSION

Formation of mononuclear nickel cyanide complexes. The nickel(II) – cyanide system shows an unusual course of complex formation in that a very strong complex, $Ni(CN)_4^{2-}$, is completely dominating.

The present potentiometric investigation indicates further the formation of small quantities of a complex $NiCN^+$ while the second and third complexes are so weak compared to $Ni(CN)_4^{2-}$ that they have not been detected (Estimated maximum values of $\beta_1 - \beta_3$ are given above).

The mathematical description of measurement data is thus significantly improved by assuming a first complex to be formed in

addition to $Ni(CN)_4^{2-}$. The maximum amount of $NiCN^+$ is so small, however, that the corresponding effect might easily be caused by a moderate systematic error. Therefore the supplementary spectrophotometric investigation was performed to decide, if possible, whether the presumptive formation of $NiCN^+$ could be confirmed. These measurements indicate that the first complex is even weaker than inferred from the results from the potentiometric measurements.

Different opinions concerning the fundamental reasons for the low stabilities of intermediate nickel cyanide complexes have been reported. Freund and Schneider [7] propose that these low stabilities depend on strains in the structures of possible intermediate species between a tetrahedral tetraaquonickel(II) ion and the square planar tetracyanonickelate(II) ion. This explanation seems rather improbable, however, since nickel(II) probably exists as a hexacoordinated octahedral water complex.[20] Thus the successive exchange of water molecules for cyanide ions should proceed without serious ruptures in the structure. Kolski and Margerum [1] suggest that the predominance of the fourth complex compared to the lower complexes is attributed to the transformation from weak octahedral complexes to a strong square planar complex.

From determinations of ΔC_p° for the cyanide systems of Zn(II), Cd(II), Hg(II), and Ni(II) Izatt et al.[21] draw the conclusion that the relative stabilities of species in a complex system depend strongly on temperature.

Formation of protonated nickel cyanide complexes. Kolski and Margerum [1] report an extensive formation of acid nickel cyanide species $H_xNi(CN)_4^{x-2}$ analogous to those reported for the iron(II) − cyanide system.[22] The reported value of K_{1H} implies that $[HNi[CN]_4^-]/[Ni(CN)_4^{2-}] = 2.5$ at pH = 5. The present potentiometric investigation has been performed at $4 < pH < 5.5$ and according to Kolski and Margerum protonated complexes should here dominate over the unprotonated. However, our measurements can be described with reasonable accuracy supposing only a fourth mononuclear complex, and with good accuracy if also a first mononuclear complex, is postulated. But our analyses of potentiometric data (*vide ultra*) give no support to presume any existence

of protonated nickel cyanide species at equilibrium and certainly exclude a formation of acid complexes to the extent claimed by Kolski and Margerum.[1]

Nor do the results from the spectrophotometric measurements, where the dissociation of $Ni(CN)_4^{2-}$ in 0.1 M $HClO_4$ was followed, give any evidence for acid nickel cyanide species. A possible formation of species $H_xNi(CN)_4^{x-2}$ from $Ni(CN)_4^{2-}$ and H^+ must be expected to be very rapid. If the values of the equilibrium constants for formation of acid nickel cyanide species reported by Kolski et al.[1] are correct practically all $Ni(CN)_4^{2-}$ immediately would be converted to protonated complexes in acid solution. Now no change of the absorption spectrum in UV can be observed after addition of $HClO_4$. To explain this fact Kolski et al.[1] must suppose that the acid species has the same UV spectrum as $Ni(CN)_4^{2-}$. However, it seems probable that addition of a strongly polarizing ion such as H^+ to the tetracyanonickelate(II) ion would affect the energy levels of this ion and thereby change its spectrum.

Since we have not been able to find those protonated species, which are fundamental parts of the kinetic model proposed by Kolski and Margerum for the acid dissociation of $Ni(CN)_4^{2-}$, we have also investigated the kinetics thoroughly.[26] Also these measurements can be satisfactorily interpreted without supposing an extensive formation of protonated tetracyanonickelate(II) species.

The cyanide systems of nickel(II), cobalt(II), and iron(II) show interesting resemblances in that intermediate species expose low stabilities compared to a higher complex which entirely dominates the complex formation. A regular trend in the coordination number for the most stable complex in these systems can be noticed. In the nickel(II) system the fourth complex is the most stable one, while a fifth complex is reported to be formed only at high concentration of cyanide ion. The fifth complex is reported to dominate in the cobolt(II) − cyanide system [23] and the sixth complex is entirely dominating in the iron(II) cyanide system.[2]

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