STUDIES ON THE HYDROLYSIS OF METAL IONS

Part II—Nickel

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Abstract

A detailed investigation of the hydrolysis of nickel in the lower concentration range has been made. The results have been analysed on the basis of 'Core + links' theory and on the assumption of the formation of one predominant complex. Evidence is obtained for the formation of $Ni_2(OH)_6{}^{2-}$ and its stability constant is calculated to be $10^{38.78}$

Introduction

Cuta *et al.*[1] have suggested that $NiOH^+$ initially formed polymerize to give species like $Ni_7(OH)_{10}{}^{2+}$ and $Ni_8(OH)_{10}{}^{6+}$. The work of Veprek-Siska[2] also indicates the occurrence of slow reactions with the formation of poly-nuclear complex of the type $Ni_2(OH)_2{}^{2+}$. Achenza[3] has suggested the formation of mononuclear complex $Ni(OH)_2$ and has also reported its stability constant. Gayer and Woonter[4] have measured the pH values of a series of nickel chloride solutions and have explained the results on the basis of the formation of $NiOH^+$. It is, therefore, clear that there is ambiguity, regarding the nature of complexes. In recent years, the hydrolysis of nickel ion has been studied by Sillen and co-workers[5] employing the self-medium method. These experiments are confined to high concentrations of nickel ion (0·1 to 0·8 M). However, data are not available for lower concentration range of nickel. Since there is still great abscurity regarding the nature of complexes particularly in the lower concentration range of nickel, a detailed investigation of the hydrolysis of nickel ion in the concentration range of 10 to 40 mM was undertaken and the results are presented in this paper.

A1

Experimental

The chemicals used were either extra pure or Analar in quality. Nickel perchlorate is prepared by dissolving nickel carbonate in perchloric acid, recrystallized and dissolved in conductivity water. The free acid was exceedingly small and there was no need to apply any correction for the same (pH of 1 M stock solution = 4·3). Since the time of attainment of equilibrium is very large, the titration technique is not followed. In all cases, nickel ion was mixed up with carbonate-free sodium hydroxide and kept for the attainment of equilibrium for different intervals of time. pH measurements were taken, 15 minutes after the addition of sodium hydroxide and also after various intervals of time till a constant pH is reached. In all cases equilibrium was attained in about 70 hours. Some of the solutions gave rise to precipitates during the period of attainment of equilibrium. The pH of these solutions are not used for interpretation purposes.

The values of $\bar{n}$ and pOH are calculated using the following relation[6] :

$$\bar{n} = \frac{B - (C_H - H^+)}{C_M} \; ; \quad pOH = pK_w - pH.$$

The pK_w in solutions of 0·5 M ionic strength was taken to be 13·62.[6]

The pH of these solutions is measured with radiometer pH meter reading correct to 0·001 pH, the overall accuracy of pH in these measurements is $\pm$ 0·005 pH. The temperature of these experiments is maintained at $30° \pm 0·1°$ C.

Notations

B: Concentration of sodium hydroxide solution added.

C_H : Total free acid of the initial solution (in the present work it is neglected).

$\bar{n}$: Average number of the hydroxyl ion per metal ion.

C_M : Total metal (nickel) concentration.

M: Metal ion (nickel ion).

$[OH^-]$, $[H^+]$, $[M]$: Concentrations of free hydroxyl, hydrogen and metal ions respectively.

β_{11}, β_{12}, β_{mi} : Stability constants of MOH, M $(OH)_2$ and $M_m (OH)_i$

k_{11}, k_{12}, k_{mi}: Equilibrium constants of the hydrolytic reactions forming MOH, M $(OH)_2$ and $M_m (OH)_i$.

K_W: Ionic product of water.

RESULTS

$\bar{n}$–pOH curves at various metal ion concentrations (10, 20, 30 and 40 mM) are given in Fig. 1. The ionic strength has been maintained at 0·5 M employing sodium perchlorate. Examination of Fig. 1 indicates that at various metal ion concentrations the $\bar{n}$–pOH curves are parallel.
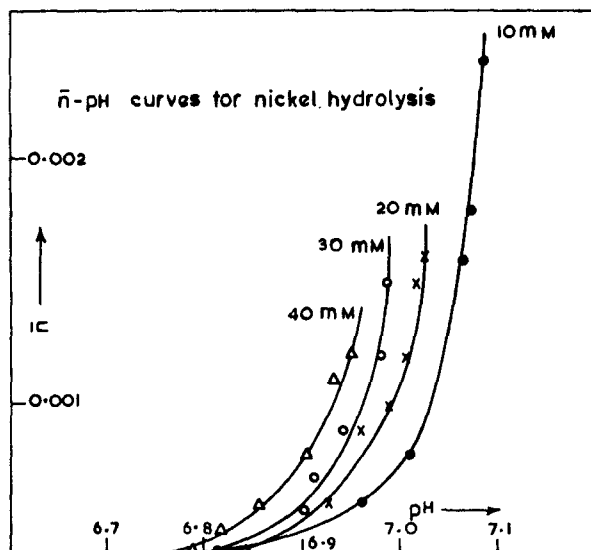

FIG. 1

DISCUSSION

1. *Analysis of $\bar{n}$–pOH curves for polynuclear complex formation by Sillen's 'Core + links' method[7].*—Since the $\bar{n}$–pOH curves are parallel, it can be concluded on the basis of 'Core + links' theory that the general formula of the complex is B $(A_t B)_n$. The value of 't' as obtained from the spacing between the curves is 6. This value is also confirmed by the plot of $\bar{n}/6$ *vs.* log C_{Ni} + 6 pH given in Fig. 2. In this plot curves ['$y(x)$ curves'] obtained at different metal ion concentrations coincide when the correct value of 't' is used. The composition of the first 'Core + links' complex on the basis of the above analysis is $Ni_2 (OH)_6^{2-}$. The equilibrium constant for the hydrolytic reaction k_{mi} (= $\beta_{mi} K_w^i$) can be obtained by the direct

analysis of the plot given in Fig. 2. The following additional relation-ships are used:

$$g(v) = f(u) = \Sigma k_n u^n \tag{1}$$

$$\log(1 + g) = \int_{-\infty}^{x} y \, dx + \log(1 - y) + y \log e \tag{2}$$

$$\log u = x - y \log e - \int_{-\infty}^{x} y \, dx \tag{3}$$

The values of 'u' and the function $g(v)$ can be determined from the area under the curve. The details of analysis are given in Table I.
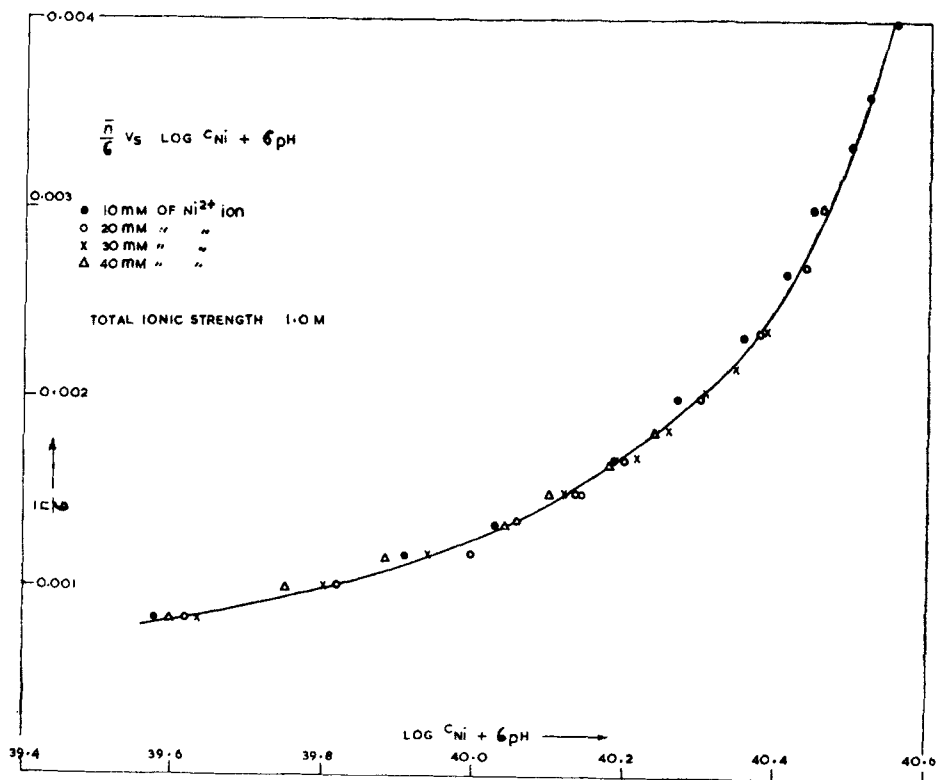

$\dfrac{\bar{n}}{6}$ Vs LOG ^{c}Ni + 6pH

• IO mM OF Ni^{2+} ion
o 20 mM " "
x 30 mM " "
△ 40 mM " "

TOTAL IONIC STRENGTH I·0 M

LOG ^{c}Ni + 6pH ——→

FIG. 2

The residual integral is $4 \cdot 76 \times 10^{-4}$ $x.y.$ unit and forms nearly half of the total area even for the highest value of $\bar{n}/6$. This not only introduces an uncertainty in the calculation but also makes the slope of the plot of $g u^{-1}$ vs. u negative. Hence it has not been possible to obtain the stability constant by the above method.

TABLE I

Direct analysis of y (x) *curve*

x	$y = \bar{n}/6$	$\int\limits_{-\infty}^{x} y.dx$	log $(1 + g)$	log (g)	log (u)
39·60	0·0008	0·000476	0·0004733	−1·9586	39·600
39·70	0·00088	0·000480	0·0004721	−1·9586	39·699
39·80	0·000965	0·000490	0·0004890	−1·9469	39·799
40·00	0·00121	0·000544	0·0005494	−1·9031	39·999
40·20	0·00167	0·000669	0·0006638	−1·8153	40·198
40·40	0·00249	0·000915	0·0009060	−1·6946	40·398
40·50	0·00340	0·001121	0·0011180	−1·5901	40·497

2. *Calculation of the stability constant assuming the presence of one predominant complex*[5].—The results are analysed assuming the presence of one predominant complex. Since the $\bar{n}$ values are low and since the complexes formed are predominantly polynuclear, it is reasonable to assume that only one polynuclear eomplex is present predominantly.

$$\bar{n} = \frac{p \, [\text{Ni}_q \, (\text{OH})_p^{(2q-p)+}]}{C_{Ni}} .$$ (4)

As the values of $\bar{n}$ are low, $\text{Ni}^{2+} \approx C_{Ni}$, the above expression can be written thus:

$$\log (\bar{n} \, C_{Ni}) = \log p + \log \beta_{qp} + q \log C_{Ni} + p \log [\text{OH}^-].$$ (5)

The value of p is obtained from the slope of the log $(\bar{n} \, C_{Ni})$ *vs.* log $[\text{OH}^-]$ plot. The value of 'q' is determined as follows: A line parallel to log $[\text{OH}^-]$ axis is drawn. The value of $\{\log (\bar{n} \, C_{Ni}) - p \log [\text{OH}^-]\}$ which is equal to $\{\log p + \log \beta_{qp} + q \log C_{Ni}\}$ is computed. The value of log β_{qp} is next calculated by giving various values for q. That particular value of q which gives constant values for log β_{qp} at various metal ion concentrations is taken to be the nuclearity. Thus both the formula and the stability constant of the polynuclear complex are calculated. The plots of log $(\bar{n} \, C_{Ni})$ *vs.* log $[\text{OH}^-]$ are given in Fig. 3 and the results of analysis of the plots in Table II. It is obvious that the formula of the complex

TABLE II

β values for various assumed values of q (p *value* = 6)

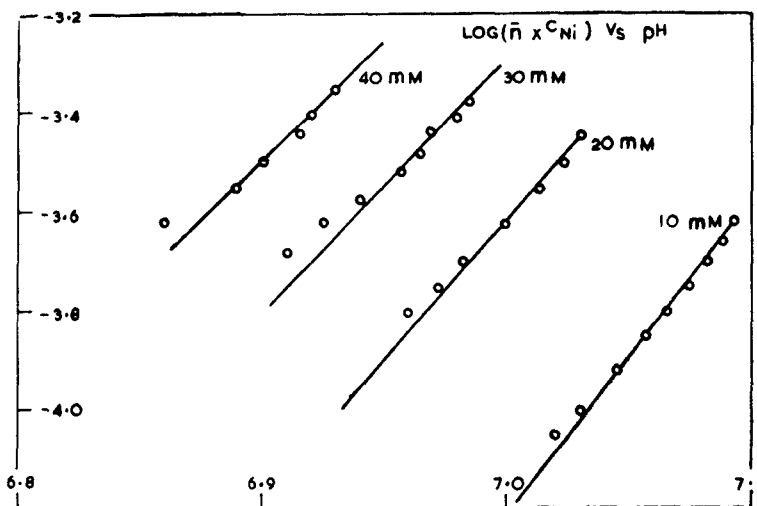| Assumed values of q	log β values at various nickel ion concentrations			
	10 mM	20 mM	30 mM	40 mM
1	37·53	37·25	37·05	36·75
2	38·87	38·77	38·74	38·75 (av. 38·78 ± 0·04)
3	40·32	40·29	40·44	40·74
4	41·72	41·81	42·14	42·75

LOG($\bar{n}$ x c_{Ni}) Vs pH

FIG. 3

is $Ni_2(OH)_6^{2-}$ and the stability constant $10^{38\cdot78\pm0\cdot04}$. Working at higher concentrations of the metal (0·1 to 0·8 M) Sillen has reported the formation of $Ni_4(OH)_4^{4+}$. It is therefore obvious that the nature of the complexes produced depends to a great extent on the concentration of nickel ion.

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