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Hydrolysis of Nickel(II) Ion in Aqueous 3 M Sodium Chloride Medium

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The hydrolytic reaction of nickel ion was studied at 25°C in an aqueous 3M sodium chloride medium. In the range of the total nickel concentration of 0.0145—1.000M, the emf data obtained could be explained in terms of the formation of the complex $Ni_4(OH)_4$ (the charge is omitted), the formation constant of the species being found to be $\log {}^*\beta_{4,4} = -28.5_5 \pm 0.1_0$, together with some minor species NiOH ($\log {}^*\beta_{1,1} \leq -10.5$) and Ni_2OH ($\log {}^*\beta_{1,2} \leq -10.5$).

The hydrolytic reaction of nickel ion has been studied by a number of workers and the results are summarized.[1] A brief survey of these studies has been made by Burkov, Lilič, and Sillén[2] in their paper on the hydrolytic reaction of nickel ion in the 3 M sodium perchlorate medium. In addition to these studies some recent works should be mentioned.[3,4]

Most of these workers, except Burkov *et al.*,[2] reported formation of the mononuclear complex $NiOH^+$ as the main product of hydrolytic reaction. Burkov *et al.* showed that the main hydrolyzed species of nickel ion is the tetramer $Ni_4(OH)_4{}^{4+}$, and only negligible amounts of mononuclear complexes are formed in solutions of relatively high concentrations of nickel and perchlorate ions.

The present study deals with the hydrolytic reaction of nickel ion in the 3 M sodium chloride medium.

The hydrolytic reaction of nickel ions may, in general, be written as

$$q\mathrm{Ni}^{2+} + p\mathrm{H_2O} + r\mathrm{Cl}^- = \mathrm{Ni}_q(\mathrm{OH})_p\mathrm{Cl}_r{}^{(2q-p-r)+} + p\mathrm{H}^+ \quad (1)$$

and the equilibrium constant of the reaction (1) is defined by

$${}^*\beta^\circ_{p,q,r} = [\mathrm{Ni}_q(\mathrm{OH})_p\mathrm{Cl}_r{}^{(2q-p-r)+}][\mathrm{H}^+]^p/[\mathrm{Ni}^{2+}]^q[\mathrm{Cl}^-]^r \quad (2)$$

Taking into account the formation of chloro complexes, the concentration of nickel ions which are not hydrolyzed $[\mathrm{Ni}^{2+}]_f$, can be written as follows.

$$\begin{aligned}[\mathrm{Ni}^{2+}]_f &= [\mathrm{Ni}^{2+}] + \sum_m\sum_n m[\mathrm{Ni}_m\mathrm{Cl}_n{}^{(2m-n)+}] \\ &= [\mathrm{Ni}^{2+}](1+\sum_m\sum_n m\beta_{m,n}[\mathrm{Ni}^{2+}]^{m-1}[\mathrm{Cl}^-]^n) \\ &= [\mathrm{Ni}^{2+}]\alpha_{\mathrm{Ni(Cl)}} \qquad (3)\end{aligned}$$

where $\beta_{m,n}$ denotes the overall formation constant of

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," 2nd. Ed., Chem. Soc., London (1964).

[2] K. A. Burkov, L. S. Lilič, and L. G. Sillén, *Acta Chem. Scand.*, **19**, 14 (1965).

[3] J. Shanker and B. C. De Souza, *Aust. J. Chem.*, **16**, 1119 (1963).

[4] D. D. Perrin, *J. Chem. Soc.*, **1964**, 3644.

the complex $Ni_mCl_n{}^{(2m-n)+}$ and $\alpha_{Ni(Cl)}$ the side reaction coefficient of nickel ion with respect to chloride ions.

If we define $^*\beta^\circ{}_{p,q}$ by

$$^*\beta^\circ_{p,q} = [H^+]^p\sum_r[Ni_q(OH)_pCl_r{}^{(2q-p-r)+}]/[Ni^{2+}]^q \quad (4)$$

$^*\beta^\circ{}_{p,q}$ is related to $^*\beta^\circ{}_{p,q,r}$ through the equation

$$^*\beta^\circ_{p,q} = \sum_r {}^*\beta^\circ_{p,q,r}[Cl^-]^r \quad (5)$$

If we use $[Ni^{2+}]_f$, insted of $[Ni^{2+}]$ in Eq. (4), the conditional equilibrium constant $^*\beta_{p,q}$ is given by

$$\begin{aligned} ^*\beta_{p,q} &= [H^+]^p\sum_r[Ni_q(OH)_pCl_r{}^{(2q-p-r)+}]/[Ni^{2+}]_f{}^q \\ &= \alpha^{-q}_{Ni(Cl)}\sum_r {}^*\beta^\circ_{p,q,r}[Cl^-]^r \end{aligned} \quad (6)$$

$^*\beta_{p,q}$ will be a constant in the whole range of the nickel concentrations provided that the concentration of chloride ions remains practically unchanged and that only the mononuclear chloro complexes ($m=1$) are formed.

Symbols;

h	Hydrogen ion concentration at equilibrium.
H	Analytical excess of hydrogen ions $=[Cl^-]-2B-[Na^+]$.
B	Total concentration of nickel.
b	Concentration of unhydrolyzed nickel ions.
Z	Average number of hydrogen ions set free per nickel atom $=(h-H-K_wh^{-1})/B$.
p	Number of OH groups bound to hydrolyzed species.
q	Number of nickel atoms bound to hydrolyzed species.
r	Number of chlorine atoms bound to hydrolyzed species.
$^*\beta_{p,q}$	Conditional equilibrium constant of the hydrolytic reaction of nickel ion, defined by Eq. (6).
[ ]	Concentration.
E	Emf.

Method of Measurement

Titration procedures are similar to those adopted in other systems in which cations are very weak acids and solubilities of metal hydroxides are very low.[5,6] Thus, a test solution containing nickel hydroxide precipitates was filtered, and the clear solution was titrated with an acid solution at constant B. The studied range of B values was from 0.0145 M to 1.000 M. Sodium chloride was used as an ionic medium and the total concentration of chloride ions was kept constant (3M).

Titration was performed under an atmosphere of nitrogen, which was free from carbon dioxide and was pre-equilibrated with the solvent.

The hydrogen ion concentration h was measured by means of the cell

Ref | Solution | GE (A)

where GE denotes a glass electrode and Ref the reference half-cell (B):

Ag-AgCl | 3M NaCl saturated with AgCl | 3M NaCl | (B)

The emf of cell (A) can be written at 25°C as

$$E = E^{\circ\prime} + 59.15\log h + E_j \quad (7)$$

constant activity coefficient of hydrogen ions being assumed. Since pH range studied is 6—7.7, the liquid junction potential E_j is practically independent of the hydrogen ion concentration at constant concentration of total nickel and chloride ions. Thus, Eq. (7) can be rewritten in a simpler form as

$$E = E^\circ + 59.15\log h \quad (8)$$

and E°, a constant, is determined by means of the Gran plot[7] at each titration procedure.

The average number of OH groups bound to hydrolyzed species, Z, is obtained as

$$\begin{aligned} Z &= \frac{\sum_p\sum_q\sum_r p^*\beta^\circ_{p,q,r}[Ni^{2+}]^q[H^+]^{-p}[Cl^-]^r}{[Ni^{2+}] + \sum_m\sum_n m\beta_{m,n}[Ni^{2+}]^m[Cl^-]^n + \sum_p\sum_q\sum_r q^*\beta^\circ_{p,q,r}[Ni^{2+}]^q[H^+]^{-p}[Cl^-]^r} \\ &= \frac{\sum_p\sum_q p^*\beta_{p,q}[Ni^{2+}]_f{}^q[H^+]^{-p}}{[Ni^{2+}]_f + \sum_p\sum_q q^*\beta_{p,q}[Ni^{2+}]_f{}^q[H^+]^{-p}} = \frac{h-H-K_wh^{-1}}{B} \end{aligned} \quad (9)$$

Experimental

Reagents. *Sodium chloride* (reagent grade, E. Merck Co.) was mixed with a small amount of water and hydrochloric acid and the slurry was dried and finally ignited at about 500°C in an electric oven.

Nickel chloride (reagent grade, E. Merck Co.) was recrystallized from water by addition of dried HCl gas and crystals were washed with hydrochloric acid solution. The crystals were then dried in a desiccator over potassium hydroxide pellets *in vacuo*. The crystals were dissolved in distilled water in order to prepare a stock solution of nickel chloride. pH of the stock solution was about 3.

Other chemicals were prepared by methods described elsewhere.[2,5,6]

Apparatus. *Glass electrodes*: Beckman (No. 40498) glass electrodes were used in combination with *a Radiometer PHM* 4 *(Copenhagen)*.

Silver-silver chloride electrodes set in *the "Wilhelm" type of half-cell*[8] were prepared according to Brown.[9]

Preparation of Test Solution. Test solutions containing hydrolyzed nickel species were prepared by means of two different methods.

(1) Thallium(I) perchlorate solution, prepared from thallium carbonate and perchloric acids, was electrolyzed in a cell in which the cathode of platinum gauze was separated from the anodic platinum foil with a sintered glass membrane. Metallic thallium was deposited on the cathode by electrolysis in an atmosphere of nitrogen. After washing thoroughly the cathode and the electrolytic cell with distilled water in a nitrogen atmosphere, the electrode and the cell vessel were dried with the stream of dried nitrogen. Slightly acid nickel

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5) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961); **16**, 2221 (1962).

6) H. Ohtaki, *Inorg. Chem.*, **7**, 1205 (1968).

7) G. Gran, *Analyst*, **77**, 661 (1952).

8) W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

9) A. S. Brown, *J. Amer. Chem. Soc.*, **56**, 646 (1934).

chloride in 3M sodium chloride medium was then introduced, and oxygen gas was bubbled at the platinum gause electrode. With dissolution of metallic thallium by oxidation, pH of the solution increased to form nickel hydroxide precipitates. Thallium(I) ions thus formed were also precipitated as chloride. The amount of thallium ions remaining in the solution was so small and the thallium ions are such weak acid that the effect of thallium ions remaining in the medium on emf measurements is negligible. Nickel hydroxide and thallium chloride precipitates were filtered off through G4 glass filters with layers of finely divided platinum powder. Thus, a clear solution was obtained and used for titration.

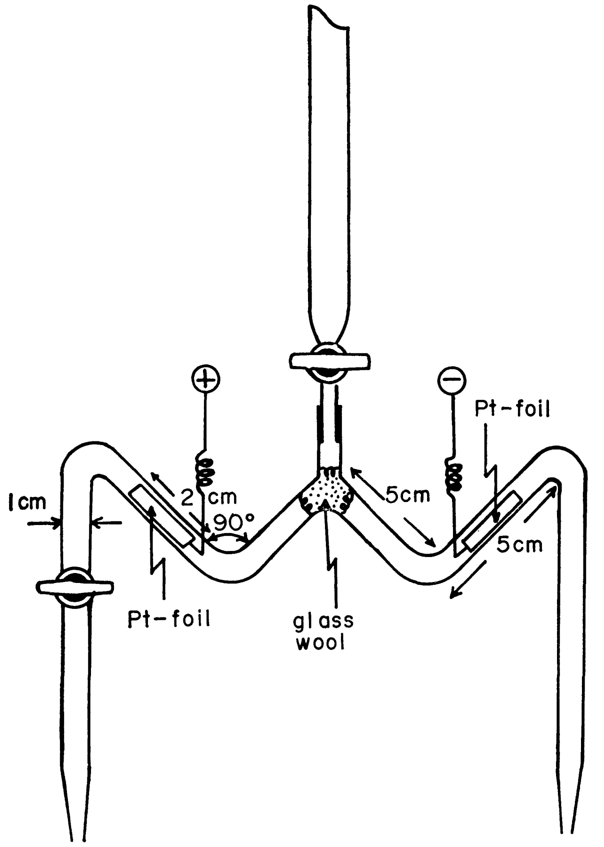

Fig. 1. Apparatus for preparation of sodium hydroxide from sodium chloride solution by electrolysis.

(2) Into the nickel chlodide solution was added a sodium hydroxide solution, prepared by electrolysis of 3M sodium chloride solution with an apparatus depicted in Fig. 1. From a buret 3M sodium chloride solution was flowed and a part of the solution was decomposed at the platinum foil cathode to sodium hydroxide and hydrogen by electrolysis. The solution was introduced to a nickel chloride solution to prepare nickel hydroxide precipitates. The flow rate of the solution was controlled by means of stop cocks. Contact of sodium hydroxide solution with glass wall of the apparatus was short (2–3 seconds), and the dissolution of any significant impurity from the apparatus could be avoided. Filtration and introduction of the solution to a titration vessel were performed in the same way as described.[5,6]

The total concentration of nickel in the test solution was determined gravimetrically by means of electrolysis and weighing as metallic nickel when the concentration of nickel was high, or as nickel dimethylglyoximate when the concentration was low.

A clear solution was titrated with an acid solution at the constant total concentration of nickel at 25.00±0.01°C in a paraffin oil thermostat, placed in a room thermostated at 25±0.2°C. Emf measurements were performed with an accuracy of ±0.1 mV at each point of measurements.

In supplementary titrations, made for testing the reversibility of the hydrolytic reaction of nickel ions, pH of a test solution was varied in the opposite direction of that in the titration described above. In these titrations a clear solution in which nickel hydroxo complexes had been present was diluted by addition of 3M sodium chloride. Thus, the total concentration of nickel *decreased*, whereas pH of the solution *increased.*

Results and Discussion

Values of Z and $-\log h$ for each value of B are represented in Fig. 2 together with those obtained by supplementary titration.

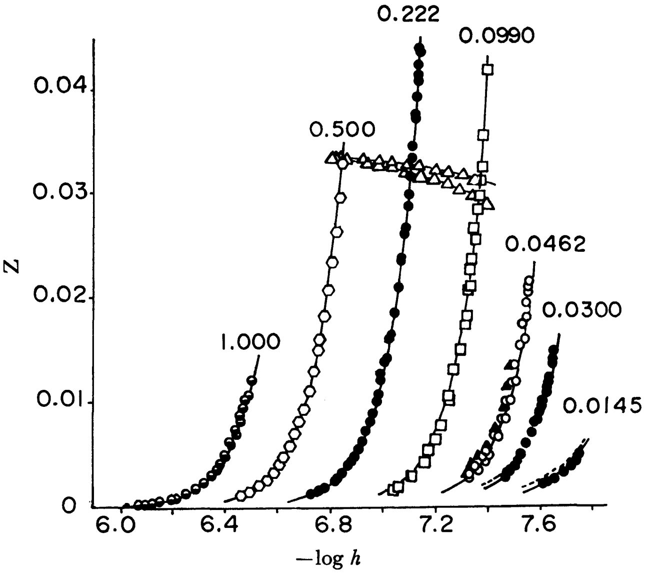

Fig. 2. Z *vs.* $-\log h$. Solid lines are those calculated with values of $\log {}^*\beta_{4,4}=-28.55$, $\log {}^*\beta_{1,1}=-10.5$, and $\log {}^*\beta_{1,2}=-10.5$. Broken lines show curves calculated with values of $\log {}^*\beta_{4,4}=-28.55$ and $\log {}^*\beta_{1,1}=-10.3$.

The concentration of hydrogen ion set free by hydrolysis, BZ, is given by the general formula as

$$\begin{aligned} BZ &= \sum_p\sum_q\sum_r p^*\beta^{\circ}_{p,q,r}[\mathrm{Ni}^{2+}]^q[\mathrm{H}^+]^{-p}[\mathrm{Cl}^-]^r \\ &= \sum_p\sum_q p^*\beta_{p,q}[\mathrm{Ni}^{2+}]_f{}^q[\mathrm{H}^+]^{-p} = \sum_p\sum_q p^*\beta_{p,q}b^qh^{-p} \end{aligned} \tag{10}$$

In cases where the maximum value of Z is very low, we may, without introduction of any appreciable error, simplify the preliminary calculations by employing the approximation

$$[\mathrm{Ni}^{2+}]_f = b \simeq B \tag{11}$$

Substituting this relation into Eq. (10) and rearranging, we obtain

$$Z = \sum_p pK_ph^{-p} \tag{12}$$

where

$$K_p = \sum_q {}^*\beta_{p,q}B^{q-1} \tag{13}$$

Under an assumption of the constant chloride ion concentration, ${}^*\beta_{p,q}$ may become constant and thus K_p may also be given as a constant for a constant B.

Curves of Z plotted against $-\log h$ fitted very well

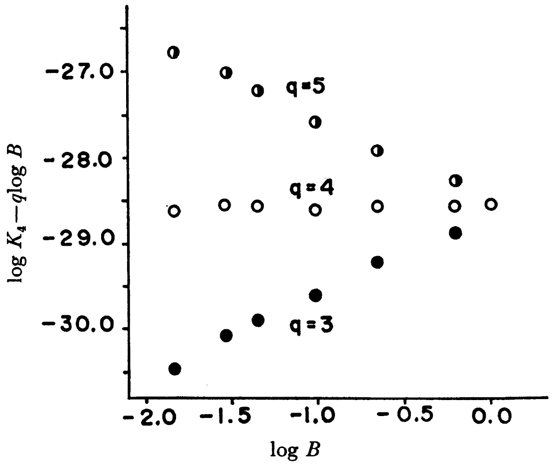

Fig. 3. Variations of log K_4 $-q$log B with log B at various q.

with a normalized curve, $y=px^p=f(\log x)$ with $p=4$. Values of K_4 thus found at each B were plotted against log B with various values of q. Results are shown in Fig. 3. It is seen that values of log K_4 $-q$ log B are independent of B at $q=4$. Thus, the composition of the main species formed by hydrolysis of nickel ion and the equilibrium constant, $*\beta_{4,4}$, is evaluated. The composition of the main species may be written as $\mathrm{Ni_4(OH)_4Cl}_r{}^{(4-r)+}$, although the value of r is not known.

Existence of other minor complexes was examined from data of low Z values, where small discrepancies of experimental results from the normalized curves were observed.

If the composition of minor species is written as $\mathrm{Ni}_{q'}\mathrm{(OH)}_{p'}\mathrm{Cl}_{r'}{}^{(2q'-p'-r')+}$, Eq. (12) may be written as

$$Z = 4K_4h^{-4} + \sum_{p'} p'K_{p'}h^{-p'} \qquad (14)$$

or

$$Zh^4 - 4K_4 = \sum_{p'} p'K_{p'}h^{(4-p')} \qquad (15)$$

If we plot log (Zh^4-4K_4) against log h, all points would fall on a straight line with a slope of $4-p'$, provided that only homoligandic complexes are formed. The plot gave a straight line with a slope of 3, *viz.*, $p'=1$. Values of homoligandic constant K_1 at various B were plotted against log B, and are shown in Fig. 4. At $q'=1$ values of log K_1-log B are almost independent of B, but a slight systematic deviation is observed, which can be interpreted in terms of formation of another homoligandic complex with $q'=2$, *i.e.*, $\mathrm{Ni_2(OH)Cl}_{r''}{}^{(3-r'')+}$.

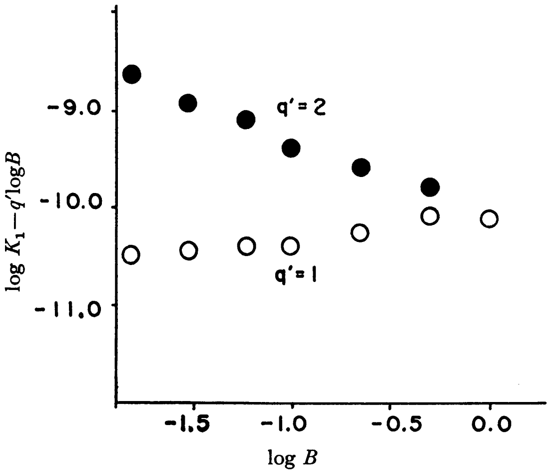

Fig. 4. Variations of log K_1-q' log B with log B at various q'.

This shows that the composition of the predominant species formed by the hydrolytic reaction of nickel ion is $\mathrm{Ni_4(OH)_4Cl}_r$, and complexes $\mathrm{Ni(OH)Cl}_{r'}$, and $\mathrm{Ni_2(OH)Cl}_{r''}$ may also be formed as minor components, although no information was available for values of r.

In order to obtain more reliable information of compositions of complexes and values of $*\beta_{p,q}$, the totality of the experimental data was compared with the normalized projection maps.10)

The computation procedure was as follows. Values of log B and ¾log $B-$log h were calculated by graphical interpolation of Z *vs.* $-$log h curves at constant Z. Plots of the log B values against ¾ log $B-$log h, covering the Z range from 0.002 to 0.035, have been compared with a graph of normalized functions, log $B^*(X)_{Z,\gamma}$, where

$$\log B^* = \log B + \frac{1}{3}\log {*\beta_{4,4}} - \frac{4}{3}\log {*\beta_{1,1}} \qquad (16)$$

$$X = \frac{3}{4}\log B - \log h + \frac{1}{4}\log {*\beta_{4,4}} \qquad (17)$$

and

$$\log \gamma = \log {*\beta_{1,2}} + \frac{1}{3}(\log {*\beta_{1,1}} - \log {*\beta_{4,4}}) \qquad (18)$$

The $\log B^*(X)_{Z,\gamma}$ functions are based on the fundamental equations

$$B = b(1 + {*\beta_{1,1}}h^{-1} + 2{*\beta_{1,2}}bh^{-1} + 4{*\beta_{4,4}}b^3h^{-4}) \qquad (19)$$

and

$$Z = \frac{{*\beta_{1,1}}h^{-1} + {*\beta_{1,2}}bh^{-1} + 4{*\beta_{4,4}}b^3h^{-4}}{1 + {*\beta_{1,1}}h^{-1} + 2{*\beta_{1,2}}bh^{-1} + 4{*\beta_{4,4}}b^3h^{-4}} \qquad (20)$$

with the assumption that complexes $\mathrm{Ni(OH)Cl}_{r'}{}^{(1-r')+}$, $\mathrm{Ni_2(OH)Cl}_{r''}{}^{(3-r'')+}$, and $\mathrm{Ni_4(OH)_4Cl}_r{}^{(4-r)+}$ are formed.

Introducing new variables

$$\eta = {*\beta_{1,1}}h^{-1} \text{ and } \xi = {*\beta_{4,4}}^{1/3}\cdot{*\beta_{1,1}}^{-1/3}\cdot h^{-1}b \qquad (21)$$

two of the three constants can be eliminated from Eqs. (19) and (20) which then will take the form

$$B^* = \xi\eta^{-1}(1+\eta+2\gamma\xi+4\xi^3\eta) \qquad (22)$$

$$Z = \frac{\eta + \gamma\xi + 4\xi^3\eta}{1 + \eta + 2\gamma\xi + 4\xi^3\eta} \qquad (23)$$

Eqs. (22) and (23) show that when Z and γ are kept constant, η becomes a function of only ξ, consequently log $B^*(X)_{Z,\gamma}=$log B^*(¾log B^*+log $\eta)_{Z,\gamma}$ can be evaluated by assigning a series of values of ξ. If no $\mathrm{Ni_2(OH)Cl}_{r''}{}^{(3-r'')+}$ complex forms, experimental data would better fit normalized curves with $\gamma=0$ than those calculated with any finite value of γ.

Solid lines in Fig. 5 show calculated curves with values of log $*\beta_{4,4}=-28.55$, log $*\beta_{1,1}=-10.5$, and log $*\beta_{1,2}=-10.5$. Broken lines show "best fitted" curves with the assumption $*\beta_{1,2}=0$. The former set of curves clearly gave better results than the latter.

Finally the data have been treated by the generalized least squares method with a computer program, "LETAGROP," in which the set of $*\beta_{1,1}$, $*\beta_{1,2}$, and

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10) L. G. Sillén, *Acta Chem. Scand.*, **10**, 803 (1956).

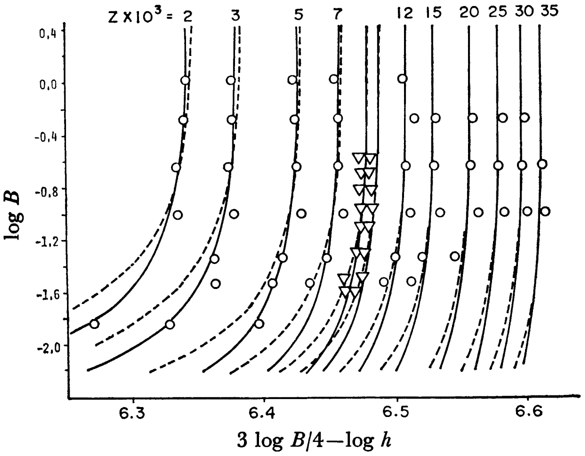

Fig. 5. Comparison of data at constant Z with normalized projection maps. Solid lines are calculated normalized projection maps with values given in (D) and broken lines are calculated "best fitted" curves with assumption of formation of only the $Ni_4(OH)_4$ and NiOH complexes.

$^*\beta_{4,4}$ values were chosen to make the error square sum, $(U=\sum(Z-Z_{calc})^2)$ a minimum. Z_{calc} denotes the value of the function (20) for a particular set of the constants. The values of $\log {}^*\beta_{1,1}$, $\log {}^*\beta_{1,2}$, and $\log {}^*\beta_{4,4}$ thus calculated are

$$\left.\begin{aligned}\log {}^*\beta_{4,4} &= -28.55 \pm 0.02 \\ \log {}^*\beta_{1,1} &= -10.5 \pm 0.1 \\ \log {}^*\beta_{1,2} &= -10.5 \pm 0.5\end{aligned}\right\} \qquad \text{(C)}$$

Values of $^*\beta_{p,q}$ obtained by Burkov *et al.*[2] in 3 M sodium perchlorate medium were $\log {}^*\beta_{4,4}=-27.37\pm 0.02$ and $\log {}^*\beta_{1,2}\approx -10$. Recent studies of hydrolytic reactions of nickel ion showed that $\log {}^*\beta_{1,1}=-10.12$[4] (at $\mu=0.04$, 25°C) and -10.01[3] (at $\mu=1.0$, 28°C). Funahashi and Tanaka[11] evaluated the formation constant of the $NiOH^+$ complex to be $\log {}^*\beta_{1,1}=-9.7$ (at $\mu=0.1$, 25°C) by means of a kinetic method. Agreements of our data with these results may support the formation of the $NiOH^+$ complex in 3 M sodium chloride medium, although the number of chloride atoms which may be contained in the complex is not evaluated.

Formation of chloro complexes must be taken into consideration in a chloride medium. Many workers have reported that nickel ions form the $NiCl^+$ complex[12-18] and even $NiCl_2$ in aqueous solutions. The formation constant of the latter complex is so small and even erroneous that only the former complex is taken into account in the following discussion.

If we take the value of $\log \beta_{1,1}$ for the $NiCl^+$ complex as -0.55 (a simple average of spread values of $\log \beta_{1,1}$ from -0.24[15] to -0.85[17]), $\log \alpha_{Ni(Cl)}$ changes by 0.03 when the concentration of nickel ion varies from 0.0145 to 1.0 M, *viz.*, the value of $\log {}^*\beta_{4,4}$ possibly changes by about 0.1_2. Since about 13% of the decrease of the concentration of free chloride ions may be estimated in the solution of $B=1.0$, the conditional equilibrium constant for the formation of $Ni_4(OH)_4Cl_r^{(4-r)+}$ may decrease by 0.06 in the logarithmic unit for contribution of each chloride ion in the complex.

Calculations of conditional equilibrium constants at each B were performed by means of the "LETAGROP" computation, but no systematic trend of values of $^*\beta_{p,q}$ was found. Thus, we finally propose the values of the equilibrium constants of the complex formation as follows.

$$\left.\begin{aligned}\log {}^*\beta_{4,4} &= -28.5_5 \pm 0.1_0 \\ \log {}^*\beta_{1,1} &\leq -10.5 \\ \log {}^*\beta_{1,2} &\leq -10.5\end{aligned}\right\} \qquad \text{(D)}$$

The maximum Z value at each B increases with decreasing h and then decreases after passing through the maximum at about $B=0.2$. The decrease of Z_{max} with decreasing h may be interpreted in terms of the formation of $Ni(OH)_2$ as the precipitate. If we denote the hydrogen ion concentration at Z_{max} as h_{max}, the following equation can be derived at a given B;

$$Z_{max} \simeq 4{}^*\beta_{4,4}B^3h_{max}^{-4} \tag{24}$$

The solubility product $^*K^{S}_{Ni(OH)_2}$ is defined as

$$^*K^{S}_{Ni(OH)_2} = [Ni^{2+}][H^+]^{-2} \tag{25}$$

Insertion of Eq. (25) into Eq. (24) and rearrangement lead to

$$Z_{max} \simeq 4{}^*\beta_{4,4}({}^*K^{s}_{Ni(OH)_2}\cdot\alpha_{Ni(Cl)})^3h_{max}^2 \tag{26}$$

Thus, Z_{max} may decrease with decreasing h_{max}, provided that $\alpha_{Ni(Cl)}$ remains practically unchanged.

On the other hand, the decrease of Z_{max} with increasing h_{max} in the region of higher B may be interpreted in terms of the formation of Ni(OH)Cl as the precipitate. With a similar method of calculation as that described above, the solubility product of the Ni(OH)Cl precipitate being defined as

$$^*K^{s}_{Ni(OH)Cl} = [Ni^{2+}][H^+]^{-1}[Cl^-] \tag{27}$$

and the constant $[Cl^-]$ being assumed, the following equation can be derived;

$$Z_{max} \simeq 4{}^*\beta_{4,4}({}^*K^{s}_{Ni(OH)Cl}\cdot\alpha_{Ni(Cl)})^3[Cl^-]^{-3}h_{max}^{-1} \tag{28}$$

and thus, Z_{max} may decrease with increasing h_{max}.

The authors wish to thank the late Professor Lars Gunnar Sillén for his valuable advice.

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[11] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

[12] R. H. Herber and J. W. Irving, Jr., *J. Amer. Chem. Soc.*, **78**, 905 (1956).

[13] P. Kivalo and R. Louto, *Suomen Kem.*, **30B**, 163 (1957).

[14] B. Trémillon, *Bull. Soc. Chem. Fr.*, **1958**, 1483.

[15] K. B. Yatsimirskii and V. D. Korableva, *Izvest. VUZ. Khim.*, No. 4, 19 (1958).

[16] K. H. Lieser, *Z. anorg. Chem.*, **304**, 296 (1960).

[17] S. Tribalat and J. M. Caldero, *Compt. rend.*, **255**, 925 (1962).

[18] D. A. Netzel and H. D. Droll, *Inorg. Chem.*, **2**, 412 (1963).