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# Ionic Equilibria in Mixed Solvents. X. Hydrolysis of Nickel(II) Ion in Dioxane-Water Mixtures

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The hydrolytic reactions of nickel(II) ion were studied at 25 °C in water and dioxane–water mixtures containing 3 M (Li)$ClO_4$ as an ionic medium. Emf measurements were carried out in the range of the total nickel(II) ion concentration of 0.02469—0.7891 M in water, 0.02488—0.7996 M in a 0.1 mole fraction (35.21% w/w) dioxane-water mixture and 0.05170—0.9016 M in a 0.2 mole fraction (55.01% w/w) dioxane-water mixture, respectively. Some supplementary measurements were performed in a 0.5 mole fraction (83.02% w/w) dioxane–water mixture. Only the $Ni_4(OH)_4^{4+}$ complex was found in all solvent systems and its formation constant in log $^*\beta_{44}$ was $-27.32\pm0.08$ (in water), $-27.11\pm0.08$ (in a 0.1 mole fraction dioxane–water mixture), and $-27.04\pm0.05$ (in a 0.2 mole fraction dioxane–water mixture). In order to test the relative change of the formation consatnt of the $Ni_4(OH)_4^{4+}$ complex over the whole solvent composition examined, the variation of the formation constant was measured with the continual change of solvent composition at constant $Z$. Approximate values of the solubility products of $Ni(OH)_2$ and $NiOHClO_4$ precipitates were estimated from maximum values of $Z$.

A number of authors studied the hydrolysis of nickel(II) ion in water and the results are summarized in "Stability Constants" and its supplement.[1] Among them, Burkov, Lilič and Sillén,[2] Ohtaki and Biedermann,[3] and Kennedy[4] reported that the $Ni_4(OH)_4^{4+}$ complex is the main product. Although Ohtaki and Biedermann[3] and Kennedy[4] proposed some minor species such an $NiOH^+$, $Ni_2OH^{3+}$ [3] and $Ni_2(OH)_2^{2+}$,[4] information for minor species has not clearly been established yet.

In general, the hydrolytic reaction of nickel(II) ion is written by the following equation.

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

The concentration of hydrogen ion set free on hydrolysis is given as follows,

$$BZ = \sum_p \sum_q p^*\beta_{pq} b^q h^{-p} \qquad (2)$$

$$= h - H + K_w h^{-1} \qquad (3)$$

where $K_w$ is the autoprotolysis constant of the solvent. The formation constant ($^*\beta_{pq}$) of a species is defined by Eq. (4).

$$^*\beta_{pq} = [\mathrm{Ni}_q(\mathrm{OH})_p{}^{(2q-p)+}][\mathrm{H}^+]^p/[\mathrm{Ni}^{2+}]^q \qquad (4)$$

Symbols

| | |
|---|---|
| $h$ | Hydrogen ion concentration at equilibrium |
| $H$ | Analytical excess of hydrogen ions $=[ClO_4^-]-[Li^+]-2B$ |
| $B$ | Total concentration of nickel ion |
| $b$ | Concentration of unhydrolyzed nickel ion |
| $Z$ | Average number of hydrogen ion 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 |
| $^*\beta_{pq}$ | Formation constant of the nickel hydroxo complex $Ni_q(OH)_p{}^{(2q-p)+}$, defined by Eq. (4) |
| [ ] | Concentration |
| $E$ | Emf |

## Experimental

The measurements were carried out at $25.00\pm0.02$ °C in a liquid paraffin bath set in a room thermostated at $25\pm1$ °C. Lithium perchlorate was used as an ionic medium to keep the perchlorate concentration at 3 M. The total concentration of nickel ion studied ranged from 0.02469 to 0.7891 M in water, 0.02488 to 0.7996 M in a 0.1 mole fraction (35.20% w/w) dioxane-water mixture, and 0.05170 to 0.9016 M in a 0.2 mole fraction (55.01% w/w) dioxane-water mixture. Some supplementary measurements were carried out in a 0.5 mole fraction (83.02% w/w) dioxane-water mixture and results obtained were compared with those in other solvent systems.

A slightly acid nickel(II) perchlorate solution in water or a mixed solvent was bubbled with nitrogen gas to remove carbon dioxide and then was mixed with a lithium hydroxide solution, which had been prepared by electrolysis, to form a small amount of precipitates. The turbid solution was stirred by bubbling with nitrogen gas for several days and filtered through G3 and G4 glass filters on which fine platinum powder was placed. A clear solution thus obtained was used as a test solution. The total concentration of nickel ion in a test solution was determined gravimetrically as its dimethylglyoximate.

The electric circuit for emf measurements was as follows.

G. E. | Solution | 3M $LiClO_4$ mixture |
3M $LiClO_4$ aq. soln | 0.01M $AgClO_4$ 2.99M $LiClO_4$ aq. soln | AgCl-Ag

Hydrogen ions were added coulometrically into the test solution during titrations. The circuit for coulometry was the same as that used in the preceding paper.[5] The emf reached a constant value within 15 minutes after coulometric generation of hydrogen ions and remained unchanged within $\pm0.2$ mV for more than several hours. The emf at equilibrium is written by the following equation.

$$E = E^{0*} + 59.15 \log h + 59.15 \log f_{\mathrm{H}} + E_{\mathrm{J}}(h, B) \qquad (5)$$

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[1] L. G. Sillén and A. E. Martell, "Stability Constants," Chem. Soc., London(1964), Supplement No. 1 (1971).

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

[3] H. Ohtaki and G. Biedermann, This Bulletin, **44**, 1822 (1971).

[4] B. Kennedy, S. C., Ph. D. Georgetown University, 1969.

[5] H. Ohtaki and T. Kawai, This Bulletin, **45**, 1735 (1972).

This equation is reasonably rewritten as Eq. (6) when only a small part of nickel ions hydrolyzes at a constant total concentration of nickel and the hydrogen ion concentration is $10^{-2} > h > 10^{-12}$ M.

$$E = E^\circ + 59.15 \log h \qquad (6)$$

where $E^\circ$ is a constant. Eq. (6) was used for determination of the concentration of hydrogen ion at equilibrium from emf data.

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

*Silver-Silver Chloride Electrodes* set in the "Wilhelm" type of the half cell[6] were prepared according to Brown.[7]

*A Coulometric Analyzer* (Leeds & Northrup Co., Philadelphia, Pa.) was used as a current source for generation of hydrogen ions in a solution during titration.

*Reagents.* *Nickel(II) Perchlorate*: Reagent grade nickel(II) nitrate was recrystallized twice from water and the crystals were heated under an infrared lamp and then in an electric oven at about 500 °C for several hours to decompose into nickel oxide. Nickel oxide thus prepared was dissolved in a little excess of about 30% hot perchloric acid solution and the solution was filtered through a G4 glass filter. Nickel(II) perchlorate was recrystallized twice from water. The crystals were dissolved into distilled water and a small amount of perchloric acid was added to keep pH of the solution at about 3 in order to prevent hydrolysis of the nickel ions. The concentration of nickel ion in the stock solution was determined by electrogravimetry, and that of hydrogen ion by potentiometry in combination with coulometry. The end point was detected according to Gran plot.[8]

*Lithium Perchlorate and Lithium Hydroxide* were prepared by the same procedures as described in the previous paper.[5]

*Dioxane* purified by an ordinary method[5] was stored in a refrigerator and melted just before preparation of a test solution.

The concentration of protolytic impurities in a 3 M lithium perchlorate solution was estimated from the deviation of a Gran plot at the end point of neutralization of perchloric acid in the solution in the absence of nickel ions. The total concentration of protolytic impurities was 75±10 μeq./l independent of solvent composition. Thus, it is very reasonable to conclude that most impurities had been contained in lithium perchlorate.

## Results and Discussion

The results obtained are summarized in Figs. 1—3 as $Z$ *vs.* $-\log h$ plots. These data have been corrected for the protolytic impurities on an assumption of the complete dissociation of the impurities[9] at pH where nickel(II) ions hydrolyze.

On the basis of the data shown in Figs. 1—3, $\log BZ$ was plotted against $-\log h$. The plots gave a set of straight lines with slope 4 in each solvent system. These results indicated that only homoligandic hydrolyzed species containing four hydroxyl groups were formed. A plot of ($\log BZ + 4\log h$) against $\log B$ yielded a straight line with a slope of 4. Therefore, it was concluded that the hydrolyezd species is $Ni_4(OH)_4^{4+}$ in dioxane–water mixed solvents at least to 0.2 mole fraction dioxane (55.01% w/w), as several investigators concluded so far in water.[2,3,4] Minor components such as $NiOH^+$ and $Ni_2OH^{3+}$ upon which some authors reported were not detected with reasonable

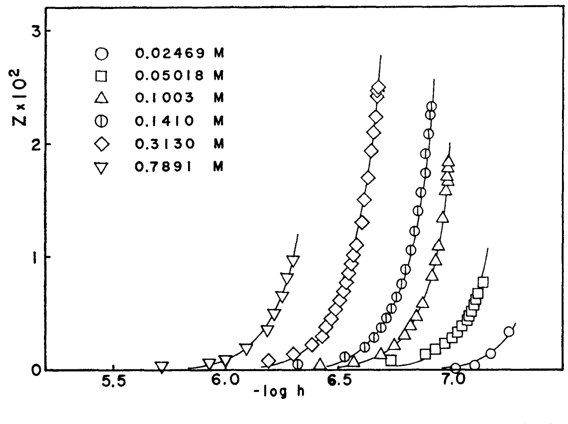

Fig. 1. Values of $Z$ *vs.* $-\log h$ in the aqueous solution. Solid lines show calculated curves of $Z$ with formation constant of $\log {}^*\beta_{44} = -27.32$.

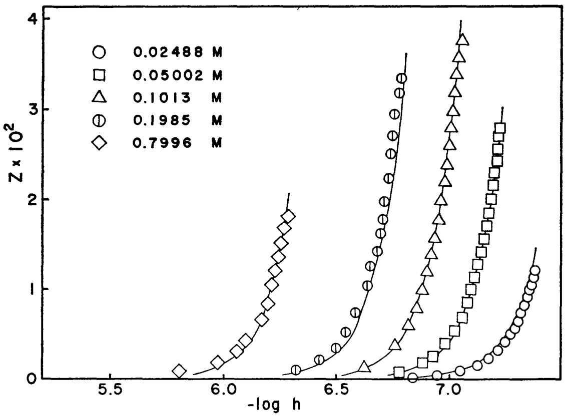

Fig. 2. Values of $Z$ *vs.* $-\log h$ in the solution of a 0.1 mole fraction dioxane-water mixture. Solid lines show calculated curves of $Z$ with formation constant of $\log {}^*\beta_{44} = -27.11$.

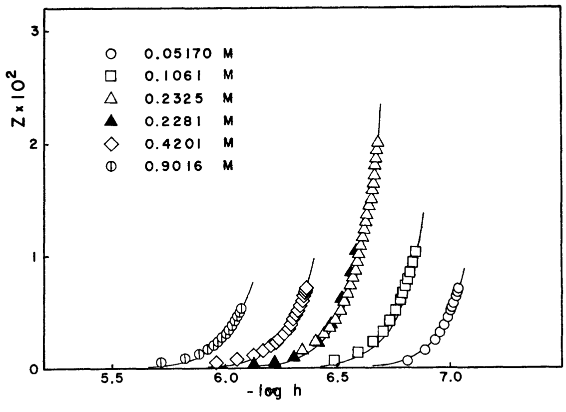

Fig. 3. Values of $Z$ *vs.* $-\log h$ in the solution of a 0.2 mole fraction dioxane-water mixture. Solid lines show calculated curves of $Z$ with formation constant of $\log {}^*\beta_{44} = -27.04$.

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

[7] A. S. Brown, *J. Amer. Chem. Soc.*, **56**, 646 (1934).

[8] G. Gran, *Analyst* (London), **77**, 661 (1952).

[9] G. Biedermann, L. Newman and H. Ohtaki, Proceedings on The Symposium on Trace Characterization-Chemical and Physical (1966), Gaithersburg, Maryland, U.S.A., p. 1.

certainties in this study. Solid lines in Figs. 1—3 indicate calculated values of $Z$ with formation constants given in each solvent system listed in Table 1.

Results obtained in a 0.5 mole fraction dioxane-water mixture were not sufficiently reliable because of low solubility of nickel(II) hydroxo complexes. The concentration of protolytic imputiries was almost comparable with that of nickel(II) hydroxo complexes present in the solution. However, the results were reasonably interpreted by the assumption of formation of the $Ni_4(OH)_4^{4+}$ complex with the formation constant of about $10^{-28\pm1}$.

Results are tabulated in Table 1 in the form of log $^*\beta_{44}$. These values were obtained after refinement by electronic computer calculations by means of a generalyzed least-squares method.

The composition of the complex formed remained unchanged with solvent composition over the wide range of the dioxane content, the same phenomenon having been found in the case of beryllium ion.[10] In the hydrolytic reaction of copper(II) ion[5] higher polymers gradually disappear with solvent composition, although formation constants of the complexes are not appreciably affected with solvent composition.

Table 1. Formation constants and solubility products

| | log* $\beta_{44}$ | log* $K_{s1}$ | log* $K_{s2}$ |
|---|---|---|---|
| Aqueous solution | −27.32±0.08 | 13.3±0.5 | 6.9±0.5 |
| 0.1 mole fraction mixt. | −27.11±0.08 | 14.1±0.5 | 7.4±0.5 |
| 0.2 mole fraction mixt. | −27.04±0.05 | 13.1±0.5 | 6.6±0.5 |
| 0.5 mole fraction mixt. | −28 ±1 | — | — |

*Solvent Effects on the Formation Constants of Complexes.* The authors previously found that the solvent effect of dioxane on the formation constants of hydrolysis of metal ions is much smaller than that expected in usual acid dissociation reactions.[11,12]

In order to test the relative change of formation constants with solvent composition, the following experiment was carried out. The method was first employed by Ohtaki and Kato[13] in their study of the solvent effect on hydrolysis of beryllium ion. We measured the change of emf on mixing two hydrolyzed solutions which had been prepared to have the same total concentration of nickel(II) ion and $Z$ value and the different solvent composition. The change of the liquid junction potential, $E_j$ in Eq. (5), with dioxane content was found to be negligible by using two reference cells. A salt bridge of one of the reference cells was composed of 3 M $LiClO_4$ aqueous solution and the other by 3 M $LiClO_4$ solution of a 0.2 mole fraction dioxane–water mixture. Negligible volume change was also found from the density measurements of 3 M $LiClO_4$ solution of dioxane–water mixtures. Then the following equation is reduced from Eq. (6).

$$\Delta \log h = (\Delta E - \Delta E^\circ)/59.15 \tag{7}$$

The change of $E^\circ$, $\Delta E^\circ$, was determined by similar measurements without nickel ions.[14]

If there is an appreciable amount of $Ni_4(OH)_4^{4+}$ in the solution, the following relations hold. From Eq. (2),

$$BZ = 4^*\beta_{44} b^4 h^{-4} \tag{8}$$

and

$$B = b + 4^*\beta_{44} b^4 h^{-4} = b + BZ$$

and therefore,

$$b = B(1-Z) \tag{9}$$

Insertion of Eq. (9) into Eq. (8) leads to

$$BZ = 4^*\beta_{44} B^4 (1-Z)^4 h^{-4} \tag{10}$$

Rearrangement of Eq. (10) gives rise to Eq. (11)

$$Z(1-Z)^{-4} = 4^*\beta_{44} B^3 h^{-4}$$

or

$$\log Z - 4\log(1-Z) = \log 4 + \log{}^*\beta_{44} + 3\log B - 4\log h \tag{11}$$

From the differeniation of Eq. (11) at constant $Z$ and $B$, Eq. (12) is obtained.

$$\partial \log{}^*\beta_{44} = 4\partial \log h \tag{12}$$

The change of the formation constant was determined from emf data with Eqs. (7) and (12), and results are given in Fig. 4. The formation constant first increases with dioxane concentration and then reaches a plateau.

*On the Solubility of Nickel(II) Hydroxo Complexes.* Approximate values of the solubility product of nickel(II) hydroxide precipitates were estimated from maximum values of $Z$ in various solvent systems.

The maximum value of $Z$, $Z_{max}$, increases with $B$ to reach a maximum and then decreases. This suggests that besides the nickel hydroxide the basic nickel perchlorate also precipitates as have been pointed out in the study of hydrolysis of nickel ion in the chloride system.[3]

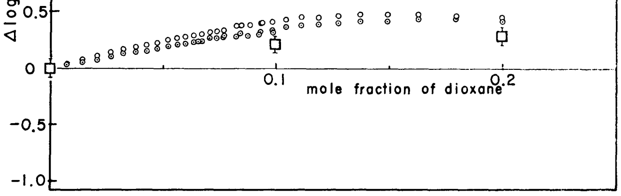

Fig. 4. $\Delta\log{}^*\beta_{44}$ from the value in aqueous solution for $Ni_4(OH)_4^{4+}$ complex in dioxane-water mixtures. Circles; points of continuous measurements, squares; points of individual determination with experimental uncertainties.

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[10] H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967). H. Ohtaki and H. Kato, *ibid.*, **6**, 1935 (1967).

[11] M. Paabo, R. G. Bates and R. A. Robinson, *J. Phys. Chem.*, **70**, 247 (1966).

[12] G. Douheret, *Bull Soc. Chim. France*, **1967**, 1942.

[13] H. Ohtaki and H. Kato, Abstracts of the Meeting of the Coordination Chemistry(Hiroshima), p. 111(1967).

[14] H. Ohtaki, Abstract of the Informal Meeting of the 10th ICCC (1967), Nikko, p. 43.

If the following equilibrium is assumed,

$$Ni(OH)_{2-x}(ClO_4)_x(s) + xH_2O$$
$$= k_{sx}Ni(OH)_2(s) + xClO_4^- + xH^+$$
$$k_{sx} = \frac{[Ni(OH)_2(s)][ClO_4^-]^x[H^+]^x}{[Ni(OH)_{2-x}(ClO_4)_x(s)]} = \frac{m(C_0h)^x}{1\text{-}m} \quad (13)$$

where (s) represents the solid phase and $C_0$ denotes the perchlorate ion concentration assumed to be constant (3M) and $m$ the mole fraction of $Ni(OH)_2$ in the solid phase with an assumption of unit activity coefficient, the mole fraction $m$ is obtained as follows:

$$m = \frac{k_{sx}}{k_{sx}+(C_0h)^x} \quad (14)$$

Solubility products of nickel hydroxide, $^*K_{s1}$, and basic nickel perchlorate, $^*K_{s2}$, respectively, are defined as follows.

$$^*K_{s1} = \frac{[Ni^{2+}][H^+]^{-2}}{[Ni(OH)_2(s)]} = \frac{bh^{-2}}{m} \quad (15)$$

$$^*K_{s2} = \frac{[Ni^{2+}][H^+]^{-(2-x)}[ClO_4^-]^x}{[Ni(OH)_{2-x}(ClO_4)_x(s)]} = \frac{b(C_0h)^xh^{-2}}{1-m} \quad (16)$$

Therefore,

$$k_{sx} = {}^*K_{s2}/{}^*K_{s1} \quad (17)$$

$$b = {}^*K_{s1}mh^2 = {}^*K_{s1}h^2\frac{k_{sx}}{k_{sx}+(C_0h)^x} \quad (18)$$

Thus $BZ_{\max}$ is represented as follows.

$$BZ_{\max} = 4{}^*\beta_{44}b^4h_{\max}^{-4} = \frac{4{}^*\beta_{44}{}^*K_{s1}^4k_{sx}^4h_{\max}^4}{\{k_{sx}+(C_0h_{\max})^x\}^4} \quad (19)$$

If we put $C_0h/k_{sx}^{1/x}=\omega$, we can compare Eq. (19) with Eq. (20)

$$y = \left[\frac{a\omega}{(1+\omega^x)}\right]^4;\ a=\{4{}^*\beta_{44}\}^{1/4}{}^*K_{s1}k_{sx}^{1/x}/C_0 \quad (20)$$

or

$$Y = \log\frac{\omega}{(1+\omega^x)} \quad (21)$$

Curve fitting of (log $BZ_{\max}$)/4 *vs.* log $h$ with $Y$ *vs.* log $\omega$ at various $x$ gives the values of $x$ about 1.0—1.3 in all solvent systems. A typical example is shown in Fig. 5. If we assume a stoichiometric composition of the basic nickel perchlorate taking into account the experimental uncertainties of $BZ_{\max}$ values and a simple assumption of ideal solid solution of the $Ni(OH)_2$–$Ni(OH)_{2-x}(ClO_4)_x$ mixture, the composition of the basic nickel perchlorate may be described as $NiOHClO_4$ ($x=1$). Under these assumptions the value of log with the known value of $^*\beta_{44}$. Results are given in $k_{sx}$ can be obtained from the abscissa and log $^*K_{s1}$, and thus log $^*K_{s2}$, from the ordinate Table 1. Solubility products of both hydroxide and basic perchlorate are fairly insensitive to the dioxane content as has been found in the case of copper(II) hydroxide.[5]

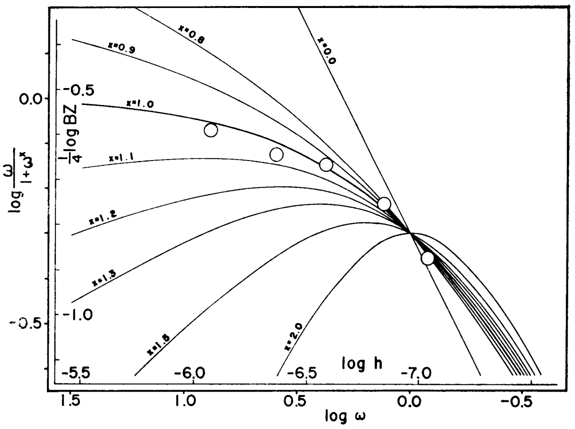

Fig. 5. A family of normalized curves of $Y=\log\frac{\omega}{(1+\omega^x)}$ *vs.* log $\omega$ at various $x$. Circles show values of (log $BZ_{\max}$)/4 obtained in a 0.2 mole fraction dioxane-water mixture.

The logarithmic values of solubility product of nickel hydroxide have been reported to be −13.8—−17.2 in aqueous solutions,[1] which correspond to $14._2$—10.8 in the log $^*K_{s1}$ scale. The value of log $^*K_{s1}=13.3$ in aqueous solution found in the present work can reasonably be compared with these literature values. No value has been found in literature for the solubility product of basic nickel salt.

It should be noted that the value of $k_{sx}$ was kept constant at $10^{-6.4}$—$10^{-6.6}$ independent of solvent composition, although the reaction is not isoelectric.

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