# HYDROLYTIC EQUILIBRIA OF METALLIC IONS—III. THE HYDROLYSIS OF NI(II) ION IN NaClO₄ SOLUTIONS*

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**Abstract**—The first acidic ionization constant of Ni(II) ion as nickelous perchlorate has been determined be a potentiometric titration at constant ionic strength in sodium perchlorate solutions at temperatures ranging from 25 to 50°C. Ni(II) ion concentrations from 2 to $20 \times 10^{-3}$ M have been employed.

The assembled information indicates the first hydrolysis reaction of this ion is a mononuclear reaction where the complex NiOH⁺ is formed with $\Delta G^{'0}_{298} = 13.25 \pm 0.1$ kcal/mole and $\Delta H^{'0}_{298} = 7.76 \pm 1.0$ kcal/mole.

**Résumé**—La constante de la première ionisation acidique de l'ion Ni (II) sous la forme de perchlorate de nickel a été déterminée par titration potentiométrique en solution aqueuse de perchlorate de sodium, celles-ci constituant un milieu à force ionique constante.

Les données expérimentales ont été obtenues à des températures comprises entre 25 et 50°C. La concentration de l'ion Ni (II) était comprise entre 2 et $20 \times 10^{-3}$ M.

La première réaction d'hydrolyse de l'ion Ni (II) est une réaction mononucléaire où apparait le complexe NiOH⁺; les données thermodynamiques obtenues sont $\Delta G^{'0}_{298} = 13,25 \pm 0,1$ kcal/mole et $\Delta H^{'0}_{298} = 7,76 \pm 1,0$ kcal/mole.

**Zusammenfassung**—Die erste Ionisationskonstante von Nickel (II)-Perchlorat wurd durch elektrometrische Titration in Lösungen konstanter Ionenstärke bestimmt. Die Temperatur war 25–50°C, die Ni (II)-Konzentration betring 2 bis 20 mMol/L.

Aus den Ergebnissen geht hervor, dass die Hydrolyse-Reaktion des Ni (II)-ions mononuklear ist, wobei der Komplex NiOH¹ entsteht.

$$\Delta G^{'0}_{298} = 13,25 \pm 0,1 \text{ kcal/mol und} \quad \Delta H^{'0}_{298} = 7,76 \pm 1,0 \text{ kcal/mol.}$$

## INTRODUCTION

As a part of a systematic research on the hydrolysis of metallic ions in constant ionic medium, we have now also investigated the hydrolysis reaction of Ni(II) ion in the range of temperatures from 25 to 50°C. This reaction has been investigated by several authors and their results which were usually obtained at 25°C, are not coincident, as is the case for other metallic ions. The different figures have been grouped in Table 1. These data have been compiled by Bjerrum et al.[1]

TABLE 1

| $T$ (°C) | $pK_a$ | Ionic system | Author | Reference |
|---|---|---|---|---|
| 25 | 8·3 | NiSO₄ var. | Denham | 2 |
| 25 | 6·5 | NiCl₂ var. | Denham | 2 |
| 30 | 9·4 | $\mu = 0.1$ (KCl) | Chaberak et al. | 3 |
| 25 | 9·49–9·23 | variable | Ksandr and Hejtmanek | 4 |
| 20 | 8·94 | $\mu = 0$ (corr.) | Cuta et al. | 5 |
| 25 | 10·64 | $\mu = 0$ (corr.) | Gayer and Wootnter | 6 |
| 100 | 8·6 | dil. NiCl₂ | Kullgren | 7 |

## EXPERIMENTAL

Nickel perchlorate was prepared by a method similar to the one used earlier for cobaltous perchlorate[8]. Nickel metal was electrodeposited from a solution containing 4 g% nickel sulphate made strongly alkaline with ammonia. A.R. quality reagents were employed. Prior to the electrodeposition of nickel on a platinum cathode an electrolytic pretreatment of the solution at low current density was done to eliminate from it traces of interfering impurities. A weight of electrodeposited nickel was dissolved in a known volume of normal perchloric acid, at about 100°C, employing an all-glass reflux apparatus. The final nickel ion concentration was evaluated gravimetrically with dimethylglyoxime, following the usual procedure.

The rest of the solutions, i.e. sodium perchlorate, perchloric acid and sodium hydroxide solutions, were prepared employing a concentrated sodium perchlorate solution, as previously described.[8,9] Triple distilled water freed from carbon dioxide and air was used.

The potentiometric titrations were performed under a stream of purified nitrogen in a double wall titration cell thermostated within 0·05°C. Measurements were done with a Radiometer PHM-4 pH-meter. E.I.L. GHS-23 and Beckman type 41263 shielded glass electrodes previously calibrated with buffer solutions up to pH 9 were employed. Previous papers[8,9] give additional details of the experimental technique.

The cell can be represented as follows:

glass electrode | H$^+$, NaClO$_4$,Ni(ClO$_4$)$_2$ || NaClO$_4$, NaCl | calomel electrode
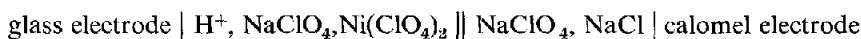
and the corresponding Nernst equation is

$$E = E' - \frac{2 \cdot 303\, RT}{F} \log h, \tag{1}$$

where $E$ is the e.m.f. of the cell and $E'$ is the normalized potential of the cell in V, including the liquid junction potentials. Each experiment comprised two parts. In the first one $E'$ was determined with buffer solutions and, previously to each run, by an acid–base titration, covering the proper range of pH. $E'$ is the sum of $E_{lj}$, the liquid junction potential and $E°$, the standard potential of the cell.

The equivalent point was determined at the same time by plotting the volume of alkaline solution added vs. $\Delta V/\Delta E$. This procedure was repeated by adding alkaline solution up to the end-point and adjusting the total volume of solution in the cell to 75·00 ml by adding inert electrolyte solution. Then 75·00 ml of the nickelous ion solution was added to the solution in the cell and titrated with the alkaline solution by adding simultaneously an equal volume of the nickelous ion solution in order to maintain the metallic ion concentration practically unchanged. The titration was continued until the precipitation of nickelous hydroxide became evident.

During the potentiometric titration each e.m.f. value was read when it reached a steady value, usually 20–30 min after the titrating solution had been added.

Experiments covered the range 25–50°C. Ni(II) ion concentration was varied from 2 to 20 mM/l, and sodium perchlorate concentration was varied from 250 to 1000 mM/l.

In Tables 2–5 typical results are reported. $C$ is the total Ni (II) ion concentration of the solution placed into the cell, in mM/l; $H$ is the hydrogen ion concentration in mM/l obtained by analysing the metal ion solution and assuming no hydrolysis

reaction to occur; $h$ is the hydrogen ion concentration in mM/l calculated from e.m.f. measurements with the glass–reference electrode pair; $x$ is the degree of hydrolysis and $K_a'$ and $pK_a'$ are the stoichiometric equilibrium constant for the hydrolysis reaction and $-\log K_a'$, respectively. The useful part of the titration covered a small range of pH, where $K_a'$ values were calculated.

TABLE 2

| $V$ (ml) | $E_g$ (mV) | $H \times 10^4$ | $h \times 10^4$ | $X \times 10^4$ | $K_a' \times 10^9$ | $pK_a'$ |
|---|---|---|---|---|---|---|
| 0·0 | −214·3 | 9900 | | | | |
| 19·00 | +35·5 | −267 | 0·303 | 50·88 | 0·154 | 9·81 |
| 19·25 | +42·0 | −373·5 | 0·235 | 71·21 | 0·167 | 9·80 |
| 19·50 | +47·0 | −479·3 | 0·194 | 91·41 | 0·177 | 9·75 |
| 19·75 | +50·0 | −584·7 | 0·172 | 101·5 | 0·192 | 9·71 |

Experiment no. 18, 25°C. Alkaline solution: NaOH: 10·06 mM/l; NaClO$_4$: 250 mM/l. Nickel (II) ion solution: Ni$^{2+}$: 10·482 mM/l; H$^+$: 1·9800 mM/l; ClO$_4^-$: 250 mM/l $E'$ from the previous acid–base titration: −231·8 mV. Electrode B.

TABLE 3

| $V$ (ml) | $E_g$ (mV) | $H \times 10^4$ | $h \times 10^4$ | $X \times 10^4$ | $K_a' \times 10^9$ | $pK_a'$ |
|---|---|---|---|---|---|---|
| 0·00 | −235·0 | 5700 | | | | |
| 9·60 | −2·2 | −312·9 | 0·660 | 31·4 | 0·207 | 9·68 |
| 9·80 | +4·0 | −420·1 | 0·520 | 42·1 | 0·219 | 9·66 |
| 10·00 | +9·0 | −526·8 | 0·430 | 52·7 | 0·227 | 9·64 |
| 10·20 | +11·8 | −632·9 | 0·386 | 63·3 | 0·244 | 9·61 |

Experiment no. 26, 30°C Alkaline solution: NaOH: 10·25 mM/l; NaClO$_4$: 1000 mM/l. Nickel (II) ion solution: Ni$^{2+}$: 19·998 mM/l.; H$^+$: 1·140 mM/l; ClO$_4^-$: 1000 mM/l $E'$ from the previous acid–base titration: −253·7 mV. Electrode D.

TABLE 4

| $V$ (ml) | $E_g$ (mV) | $H \times 10_4$ | $h \times 10^4$ | $X \times 10^4$ | $K_a' \times 10^9$ | $pK_a'$ |
|---|---|---|---|---|---|---|
| 0·00 | −236·5 | 5500 | | | | |
| 9·60 | −4·0 | −312·9 | 0·898 | 31·3 | 0·281 | 9·55 |
| 9·80 | +3·5 | −420·1 | 0·679 | 42·1 | 0·286 | 9·54 |
| 10·00 | +6·0 | −526·8 | 0·620 | 52·7 | 0·327 | 9·49 |
| 10·20 | +9·2 | 632·9 | 0·550 | 63·3 | 0·348 | 9·48 |

Experiment no. 42, 40°C. Alkaline solution: NaOH: 10·25 mM/l; NaClO$_4$: 1000 mM/l. Nickel (II) ion solution: Ni$^{2+}$: 19·998 mM/l; ClO$_4^-$: 1000 mM/l; H$^+$: 1·100 mM/l $E'$ from the previous acid–base titration: −255·5 mV. Electrode D.

TABLE 5

| $V$ (ml) | $E_g$ (mV) | $H \times 10^4$ | $h \times 10^4$ | $X \times 10^4$ | $K_a' \times 10^9$ | $pK_a'$ |
|---|---|---|---|---|---|---|
| 0·00 | −240·0 | 5500 | | | | |
| 9·8 | 3·2 | −420·1 | 1·017 | 42·2 | 0·429 | 9·37 |
| 10·0 | 0·0 | −526·8 | 0·906 | 52·8 | 0·478 | 9·32 |
| 10·2 | +1·0 | −632·9 | 0·874 | 63·4 | 0·554 | 9·26 |

Experiment no. 30, 50°C Alkaline solution: NaOH: 10·25 mM/l; NaClO$_4$: 1000 mM/l. Nickel (II) ion solutions Ni$^{-2}$: 19·998 mM/l; H$^+$: 1·100 mM/l; ClO$_4$: 1000 mM/l $E'$ from the previous acid–base titration: −259·2 mV. Electrode A.

## RESULTS AND DISCUSSION

*The first hydrolysis reaction of Ni(II) ion*

As was the case for the hydrolysis reaction of Fe(II) and Co(II) ions in sodium perchlorate solutions, the first hydrolysis reaction of Ni(II) was also interpreted with the same type of reaction, viz.

$$Ni^{2+}(aq) + H_2O\ (l) \rightleftharpoons NiOH^+(aq) + H^+)(aq)$$
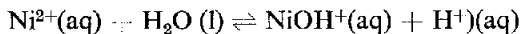
as previously done by other authors.[3,6]

Its stoichiometric equilibrium constant $K_a'$ is defined by

$$K_a' = \frac{[NiOH^+] \cdot [H^+]}{[Ni^{2+}]}.\tag{2}$$

$K_a'$ involves the thermodynamic equilibrium constant $K_a^\circ$, the activity coefficients of the reacting species and the activity of water. In the present case $K_a'$ is also to a first approximation, independent of the Ni(II) ion concentration; hence it can be concluded that the mononuclear reaction (I) represents the actual ionic equilibrium. Consequently the behaviour observed for Ni(II) ion in sodium perchlorate solutions is analogous to that previously found for the Co(II) and Fe(II) ions in the same ionic system. This is certainly the expected behaviour when the structures of the three aqueous ions are taken into account.

$pK_a'$ at 25°C is 9·76 and the free energy associated with reaction (I) is $\Delta G_{298}'^\circ = 13\cdot25 \pm 0\cdot1$ kcal/mole.

The first figure of $K_a'$ of each run has been used to obtain the average $pK_a'$ values. Nevertheless, the $K_a$'s show a small steady increase during the course of the titration, which is thought to be due, in part, to the colloidal nature of nickelous hydroxide, forming a basic salt containing precipitate.[4]

*The effect of temperature on $K_a'$*

Within the range of temperature investigated, the following experimental equation represents the dependence of $pK_a'$ with temperature,

$$pK_a' = \frac{1692}{T} + 4\cdot09,\tag{3}$$

where $T$ is the absolute temperature. Comparison between equation (3) and the average experimental results is given in Fig. 1.

No sensible dependence of $pK_a'$ with the total ionic strength could be observed and consequently no extrapolation to zero ionic strength could be done. We have used our value of $pK_a'$ to estimate the change of enthalpy of the reaction referred to a standard system of a fixed ionic composition as has been done with other cations studied in the same ionic medium. The evaluated change of enthalpy, obtained from equation (3), comes out $\Delta H_{298}'^\circ = 7\cdot76 \pm 1\cdot0$ kcal/mole.

*The second acidic ionization constant $K_{a2}'$*

The second acidic ionization constant $K_{a2}'$ corresponding to the reaction

$$NiOH^+(aq) + H_2O(l) \rightleftharpoons Ni(OH)_2(s) + H^+(aq)\tag{II}$$
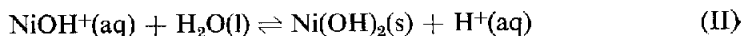
could be also estimated because it comes out from the relationship

$$K_{a2}' = \frac{Kw^2}{K_a' \cdot K_s}.$$ (4)

where $K_s$ is the solubility product of $Ni(OH)_2$ and $K_w$ the ionic product of water which is $1.01 \times 10^{-14}$ at $25°C$.

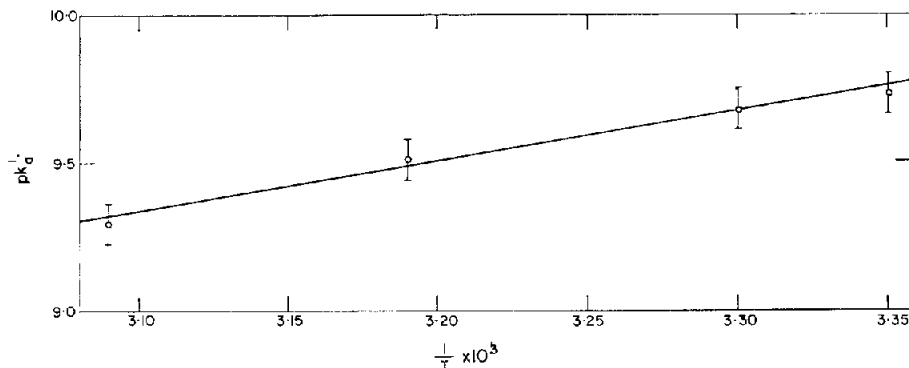The values of $K_s$ found in the literature at $25°C$ are comprised between $1.5 \times 10^{-14}$ [10]



Fig. 1. Dependence of $pK_a'$ with $1/T$.
Data at 25°C are averaged from 16 experiments
Data at 30°C are averaged from 10 experiments
Data at 40°C are averaged from 6 experiments
Data at 50°C are averaged from 4 experiments

and $6.5 \times 10^{-18}$.[11] Therefore the calculated figure for $K_{a2}'$ is placed between $2.7 \times 10^{-5}$ and $8.5 \times 10^{-3}$.

These values of $K_{a2}'$ for Ni(II) ion in sodium perchlorate medium, suggests that a disproportionation reaction of $NiOH^+$ complex ions is thermodynamically favoured as is the case for Co(II) and Fe(II ions.)

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