

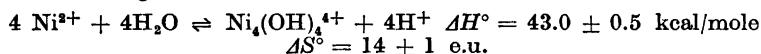
Thermochemical Studies of Hydrolytic Reactions

6. A Thermochemical Study of Hydrolysed NiCl₂ Solutions

ROBERT ARNEK

*Department of Inorganic Chemistry, The Royal Institute of Technology (KTH),
Stockholm 70, Sweden*

Enthalpy titrations have been performed with hydrolysed NiCl₂ solutions (25°C, 3 M (Na)Cl). The heat data have been interpreted using the hydrolysis mechanisms proposed by Burkov and Lilich¹ and by Biedermann and Ohtaki.² For the main hydrolysis reaction the following result was obtained



The heats of formation of proposed minor species are discussed.

During the last few years the hydrolysis equilibria of the nickel(II) ion have been investigated in different ionic media (3 M (Na)ClO₄, 3 M (Na)Cl, and 3 M (Na)NO₃) by workers in Leningrad and Stockholm using emf methods. Burkov and Lilich¹ and Biedermann and Ohtaki² investigated the hydrolysis of Ni(II) in 3 M (Na)Cl and obtained practically the same result with Ni₄(OH)₄⁴⁺ as the main complex. This complex was also found in 3 M (Na)ClO₄ by Burkov, Lilich and Sillén,³ whereas in 3 M (Na)NO₃ the main species according to Burkov and Lilich⁴ is Ni₃(OH)₃³⁺.

The hydrolysis mechanisms and equilibrium constants proposed in 3 M (Na)Cl are:

| Reaction | Biedermann, Ohtaki ² | Burkov, Lilich ¹ |
|--------------------------------------------------------------------------------------------------------|-------------------------------------|-----------------------------|
| $4\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni}_4(\text{OH})_4^{4+} + 4\text{H}^+$ | $\log \beta_{44} = -28.57 \pm 0.03$ | -28.42 ± 0.05 |
| $2\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Ni}_2(\text{OH})_2^{2+} + \text{H}^+$ | $\log \beta_{12} = -10.3 \pm 0.2$ | -9.3 ± 0.2 |
| $\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$ | $\log \beta_{11} = -10.5 \pm 0.1$ | — |

The concentration range studied by Biedermann and Ohtaki was 0.01–1 M Ni²⁺ and by Burkov and Lilich 0.2–1.4 M Ni²⁺; this might explain why they propose partly different hydrolysis mechanisms.

EXPERIMENTAL

The enthalpy titrations were performed using the calorimeter described earlier.⁵ A hydrolysed solution, S, of NiCl_2 contained in the calorimeter was titrated with an acid solution, T, from a thermostated buret.

A stock solution of nickel(II) chloride was prepared from commercial $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Riedel-De Haën *p.a.*). The nickel(II) content was determined by electrodeposition.

The nickel ion, Ni^{2+} , is very weakly hydrolysed in aqueous solution. As the hydrolysis takes place at $\log h < -5$ it is very important to avoid the introduction of protolysing impurities, such as CO_2 . The hydrolysed nickel(II) chloride solutions were prepared using a technique developed by Biedermann and Ohtaki.³ This technique has been described in an earlier work in this series,⁶ where it was used for the preparation of hydrolysed Cu(II) perchlorate solutions. In brief, a weak alkaline solution of NaOH (in 3 M NaCl), prepared by electrolysis, is added to an initially unhydrolysed NiCl_2 -solution until a precipitate of hydroxide is formed. The solution is left overnight with continuous nitrogen stirring, filtered through a glass filter and finally charged into the calorimeter vessel (which has been previously filled with nitrogen).

The analytical hydrogen ion excess concentration (a negative quantity) in the hydrolysed solution, $H_S = [\text{Cl}^-] - 2[\text{Ni(II)}] - [\text{Na}^+]$, was obtained directly from the enthalpy titrations as will be shown later.

The acid solutions, T, were prepared by mixing stock solutions of NiCl_2 and hydrochloric acid and adding the ionic medium.

The general composition of the solutions S and T was B M Ni(II), H M H^+ , $(3 - 2B - H)$ M Na^+ , and 3 M Cl^- . The total concentration of nickel, B , was kept practically constant in each experiment.

The values of B and H in the different experiments are given in Table 1, where H_S = initial value of H in the calorimeter solution; $H_T = \bar{H}$ of the buret solution; B_S = initial value of B in the calorimeter solution; $B_T = \bar{B}$ of the buret solution.

Table 1. Survey of titrations.

| Expt. No: | 1 | 2 | 3a,b | 4 | 5 | 6 |
|------------|-------|-------|-------|-------|-------|-------|
| B_S , mM | 56.85 | 107.5 | 194.7 | 342.6 | 667.5 | 742.3 |
| B_T , mM | 53.84 | 102.3 | 210.0 | 375.1 | 713.0 | 785.8 |
| H_S , mM | -1.02 | -1.65 | -2.64 | -3.80 | -3.27 | -4.60 |
| H_T , mM | 24.78 | 49.56 | 60.00 | 99.12 | 123.9 | 123.9 |

The heat experiments consist of titrations in which successive additions of v ml of the acid solution T are made, from a thermostated buret, to V_0 ml ($V_0 = 224.53$ ml) of the hydrolysed solution S contained in the calorimeter. The additions from the buret were continued till the heat evolved per addition had dropped to zero, *i.e.* when all hydrolysed Ni(II) had been converted to Ni^{2+} aq. In Fig. 1 $\sum Q$, the cumulative heat effect, during a typical experiment, is given as a function of v . The intersection of the two lines in Fig. 1 gives the volume at which all the hydrolysed Ni(II) has been converted

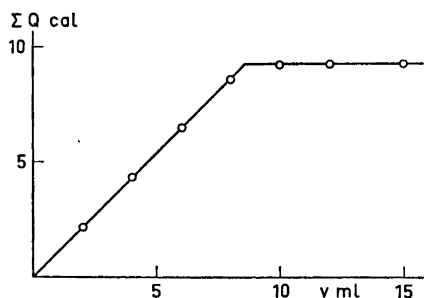


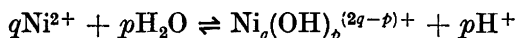
Fig. 1. $\sum Q$, the cumulative heat effect as a function of the added volume, v , during a typical experiment.

to Ni^{2+} aq. Since H_T is known from the preparation of the solution T, using $-H_S = v_e H_T / V_0$ we can directly calculate the analytical excess hydrogen ion concentration, H_S , in the initial solution from the value of v at the intersection point, v_e .

RESULTS AND CALCULATIONS

The data from the enthalpy titrations have been treated with the calorimeter version of the least squares computer program LETAGROPVRID.^{7,8} The principle by which the calorimeter data are treated using this program has been briefly described in earlier papers in this series (see, *e.g.*, Ref. 5). With LETAGROPVRID the computer searches for the set of unknown constants k_1, k_2, \dots which gives a minimum to the error square sum $U = \sum (Q_{\text{exp}} - Q_{\text{calc}})^2$, where Q is the heat effect. The result is a set of "best" constants with their standard deviations and also the standard deviation in the Q -measurements (σ_Q).

The reactions which have been studied are



for which we will write ΔH_{pq} for the enthalpy change and β_{pq} for the equilibrium constant. The values for the β_{pq} were taken from the emf measurements of Burkov and Lilich¹ and Biedermann and Ohtaki.²

In the present case we tried to find with LETAGROPVRID the enthalpies ΔH_{pq} that minimized the error square sum. In addition, possible small errors, δH_S , in the starting solution were also treated as variable parameter. The results of the LETAGROPVRID calculations are summarized in Table 2.

Table 2. Results of the LETAGROPVRID treatment.

| Calculation No: | a) $\Delta H_{pq} \pm \sigma(\Delta H_{pq})$, β_{pq} and σ_Q | | | |
|-----------------------------|----------------------------------------------------------------------------|------------------|------------------|------------------|
| | I | II | III | IV |
| ΔH_{44} , kcal/mole | 43.09 ± 0.14 | 42.98 ± 0.13 | 42.94 ± 0.13 | 42.97 ± 0.10 |
| ΔH_{12} , kcal/mole | 10.47 ± 0.16 | 3.8 ± 2.0 | 10 (not varied) | — |
| ΔH_{11} , kcal/mole | — | 15.4 ± 1.5 | 11.8 ± 1.0 | — |
| $10^{29} \beta_{44}$ | 3.8 | 2.7 | 2.7 | 2.7 |
| $10^{11} \beta_{12}$ | 50 | 5.0 | 5.0 | — |
| $10^{11} \beta_{11}$ | — | 3.2 | 3.2 | — |
| σ_Q , cal | 0.023 | 0.022 | 0.024 | 0.024 |

The deviations given in this table are σ , the standard deviation calculated by LETAGROPVRID. In calculation I in the table, the equilibrium constants given by Burkov and Lilich were used; in the other calculations (II, III, IV) the constants given by Biedermann and Ohtaki were used.

DISCUSSION

As can be seen from Table 2 a ΔH value of about 43 kcal/mole is obtained for the formation of the main hydrolysis product $\text{Ni}_4(\text{OH})_4^{4+}$, irrespective of which assumptions are made about the minor species. We have chosen as

the best value $\Delta H_{44} = 43.0 \pm 0.5$ kcal/mole (with 3σ). Using the equilibrium constant given by Burkov and Lilich for the formation of the species $\text{Ni}_2\text{OH}^{3+}$ we obtain $\Delta H_{12} = 10.5 \pm 0.5$ kcal/mole (3σ) (calculation I, Table 2). When the heat data are interpreted using the equilibrium constants β_{44} , β_{12} , and β_{11} given by Biedermann and Ohtaki, very uncertain values for ΔH_{11} and ΔH_{12} are obtained (calc. II, Table 2). This situation arises from the fact that the minor species give only a very small contribution (of the order of a few percent) to the measured heat effect. If the minor species are neglected (calc. IV, Table 2) ΔH_{44} remains practically unchanged and the fit is only slightly worse. If a value 10 kcal/mole is assigned to ΔH_{12} , then ΔH_{11} is found to be 11.8 ± 1.0 kcal/mole (calc. III, Table 2). It is thus obvious that the accuracy of the calorimeter data is not sufficient for the determination of ΔH_{11} and ΔH_{12} . In Table 3 the experimental data (v, Q) and the difference ($Q_{\text{calc}} - Q_{\text{exp}}$)

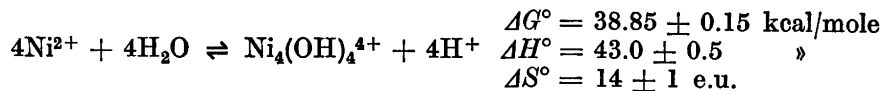
Table 3. Survey of measurements.

Values of v [ml], Q_{exp} [cal], ($Q_{\text{calc}} - Q_{\text{exp}}$) [cal]

| |
|-------------------------------------------------------------------------------------------------------------------------------------|
| Expt. 1. $B_S = 56.85$ mM, $H_S = -(1.02 \pm 0.04)$ mM |
| 2.00, 0.55, -0.01; 4.00, 0.61, -0.07; 6.00, 0.56, -0.02; 8.00, 0.54, 0.01; 10.00, 0.33, 0.01; 12.00, 0.00, 0.00; |
| Expt. 2. $B_S = 107.5$ mM, $H_S = -(1.64 \pm 0.02)$ mM |
| 2.00, 1.06, 0.01; 4.00, 1.10, -0.03; 6.00, 1.08, -0.01; 8.00, 0.77, 0.01; 10.00, 0.03, -0.03; 12.00, 0.00, 0.00; |
| Expt. 3a. $B_S = 194.7$ mM, $H_S = -(2.64 \pm 0.02)$ mM |
| 3.00, 1.96, -0.02; 5.00, 1.30, -0.01; 7.00, 1.29, 0.00; 9.00, 1.33, -0.03; 11.00, 0.59, 0.01; 13.00, 0.00, 0.00; |
| Expt. 3b. $B_S = 194.7$ mM, $H_S = -(2.64 \pm 0.02)$ mM |
| 2.00, 1.29, 0.00; 4.00, 1.31, -0.02; 6.00, 1.30, -0.01; 8.00, 1.30, 0.00; 10.00, 1.25, 0.01; 12.00, 0.00, 0.00; 14.00, 0.00, 0.00; |
| Expt. 4. $B_S = 342.6$ mM, $H_S = -(3.80 \pm 0.03)$ mM |
| 2.00, 2.14, -0.01; 4.00, 2.14, -0.01; 6.00, 2.18, -0.05; 8.00, 2.13, 0.00; 10.00, 0.65, 0.00; 12.00, 0.00, 0.00; 15.00, 0.00, 0.00; |
| Expt. 5. $B_S = 667.5$ mM, $H_S = -(3.28 \pm 0.04)$ mM |
| 2.00, 2.61, 0.05; 4.00, 2.68, -0.02; 6.00, 2.58, -0.01; 8.00, 0.00, 0.00; 12.00, 0.00, 0.00; |
| Expt. 6. $B_S = 742.3$ mM, $H_S = -(4.59 \pm 0.04)$ mM |
| 2.00, 2.66, 0.00; 4.50, 3.28, 0.04; 7.00, 3.27, 0.05; 9.00, 1.73, -0.01; 12.00, 0.00, 0.00; 15.00, 0.00, 0.00; |

are given. The values of Q_{calc} were taken from calculation II, Table 2. No systematic deviations seem to be present and the agreement between experimental and calculated values ($\sigma_Q = 0.02$ cal) is what could be expected from the accuracy of the calorimeter. The concentrations H_S , estimated by the computer, together with their deviations (3σ) are given in Table 3 for each experiment. The H_S values obtained agree very well with those determined graphically (Table 1).

For the main hydrolysis reaction of Ni^{2+} ion in 3 M (Na)Cl medium at 25°C the following thermochemical data were obtained. The zero superscripts when used with ΔG , ΔH , and ΔS mean that the standard states are hypothetical ideal one molar solutions of the solutes in 3 M NaCl as solvent



At present we will not make a comparison with data for other systems (*e.g.* Cd(II) and Pb(II)) where the corresponding species (4,4) have been found. This will be done in a forthcoming publication in which data for some other systems will be also discussed.

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