# Metal Complexes with Mixed Ligands. 10. A Potentiometric Study of Nickel(II) Imidazoles and Nickel(II) Hydroxo-imidazoles in 3.0 M (Na)ClO$_4$ and 3.0 M (Na)Cl

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Three component equilibria between nickel(II), imidazole ($C_3H_4N_2$) and $OH^-$ have been studied by means of emf titrations at 25 °C in two media 3.0 M (Na)ClO$_4$ and 3.0 M (Na)Cl using a glass electrode. The total nickel, $B$, and the total imidazole, $C$, have been varied within the limits $0.0025 \leq B \leq 0.090$ M and $0.0035 \leq C \leq 0.270$ M and the ratios $C/B$ between $0.25 \leq C/B \leq 12$. At the highest $C/B$-ratios, data can be explained solely with stepwise metal complexes $Ni(C_3H_4N_2)_n{}^{2+}$, $n=1,2,3,4$ and the following log $(\beta \pm 3\sigma)$ could be determined: log $\beta_1 = 3.344 \pm 0.005$, log $\beta_2 = 6.087 \pm 0.008$, log $\beta_3 = 8.31 \pm 0.01$ and log $\beta_4 = 9.92 \pm 0.03$ in 3.0 M (Na)ClO$_4$ and log $\beta_1 = 3.250 \pm 0.004$, log $\beta_2 = 5.852 \pm 0.006$ log $\beta_3 = 7.86 \pm 0.02$ and log $\beta_4 = 9.08 \pm 0.06$ in 3.0 M (Na)Cl. At the lowest $C/B$-ratios also a ternary hydroxo-imidazole $Ni(OH)C_3H_4N_2{}^+$ with log $K$ ($Ni^{2+} + C_3H_4N_2 \rightleftharpoons Ni(OH)C_3H_4N_2{}^+ + H^+$) $= -5.85 \pm 0.05$ in 3.0 M (Na)ClO$_4$ and $-6.04 \pm 0.04$ in 3.0 M (Na)Cl seems to be formed.

In part 7 of this series Sjöberg[7] investigated the three component equilibria in the system copper(II)-imidazole-$OH^-$ in 3.0 M (Na)ClO$_4$, 3.0 M (Na)Cl, and 5.0 M (Na)Cl using a glass electrode at 25° C. It was found that at $C/B > 8$ ($B$ and $C$ are the total copper and imidazole concentrations, respectively) only stepwise metal complexes were formed. At the lower $C/B$-ratios, data indicated that hydroxo-imidazoles must also be formed and the complexes $Cu_2(OH)_2(C_3H_4N_2)_2{}^{2+}$, $Cu_2(OH)_2(C_3H_4N_2)_4{}^{2+}$, and $Cu(OH)C_3H_4N_2{}^+$ were proposed. In equilibrium solutions of these lower $C/B$-ratios the binary hydroxo complexes $Cu_2(OH)_2{}^{2+}$ and $CuOH^+$ are also present. It therefore seems likely that the

hydroxo-imidazoles formed result from complex formation between these ions and imidazole molecules.

The purpose of the present investigation is to determine whether similar behaviour is obtained in the nickel(II)-imidazole-$OH^-$ system. The binary hydroxo complexes are in this case $Ni_4(OH)_4{}^{4+}$, $Ni_2OH^{3+}$ and $NiOH^+$. One would then expect hydroxo-imidazoles of the types $Ni_4(OH)_4(C_3H_4N_2)_x{}^{4+}$, $Ni_2(OH)(C_3H_4N_2)_y{}^{3+}$ and $NiOH(C_3H_4N_2)_z{}^+$. Previous studies of nickel(II)-imidazole complexes indicate that solely $Ni(C_3H_4N_2)_n{}^{2+}$-complexes with $n = 1, \cdots 6$, should be formed (see Table 1). However, these conclusions are based on rather few data with small variations in concentrations and no experimental attempts seem to have been made to try to find hydroxo-imidazoles.

## EXPERIMENTAL

*Chemicals and analysis.* Stock solutions of *sodium perchlorate* were prepared by neutralizing concentrated perchloric acid (Merck *p.a.*) with solid Na$_2$CO$_3$ (Merck *p.a.*) After the acid had been neutralized, a slight excess of sodium carbonate was added. This slightly alkaline solution ($pH \approx 8$) was then allowed to stand for about a week. If Fe-, Al-, and Si-impurities were present, they usually precipitated during this time as silicates or hydroxides. These precipitated impurities were filtered off, using a Jena G4 glass filter. The filtered solution was acidified with a slight excess of perchloric acid and then boiled to expel the carbonate as $CO_2$. After boiling, the solution was neutralized to $pH \approx 6$. Neither $Cl^-$ nor $CO_3{}^{2-}$ or $Fe^{3+}$ could be detected in the solution prepared in this

*Table 1.* Earlier studies on nickel(II) imidazoles.

| Ref. | Temp | Medium | Method | $pK_a$ | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ | $\log K_5$ | $\log K_6$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 25 | 0.135M KCl | pot. | 7.09 | 2.94 | 2.41 | 1.99 | 1.3 | | |
| 14 | 25 | 0.15M KNO₃ | pol., pot. | 7.12 | 3.27 | 2.68 | 2.15 | 1.65 | 1.12 | 0.52 |
| 16 | 25 | 0.16M KNO₃ | pot. | 7.11 | 3.09 | 2.47 | 2.00 | 1.54 | 1.1 | 0.5 |
| 15 | 25 | 0.5M NH₄NO₃ | pot., pol. | | 2.933 | 2.27 | 1.82 | 0.76 | 0.97 | |
| | Present work | | | | | | | | | |
| | 25 | 3M (Na)Cl | pot. | 7.637 | 3.25 | 2.60 | 2.01 | 1.22 | | |
| | 25 | 3M (Na)ClO₄ | pot. | 7.913 | 3.34 | 2.75 | 2.22 | 1.61 | | |

way. The sodium perchlorate stock was analysed for $NaClO_4$ by evaporating a known weight of solution at 120° C and then drying to constant weight.

The dilute *perchloric acids* and *hydrochloric acids* were standardized against tris(hydroxymethyl)aminomethane (TRISMA-base).

Dilute *sodium hydroxide* was prepared from "oljelut" (50 % NaOH and 50 % $H_2O$) and standardized against acid or hydrazine sulfate.

*Imidazole*, $C_3H_4N_2$, (Merck *p.a.*) with melting point 88−90 °C (lit. 90 °C) was used without further purification after drying. In some stock solutions it was, however, recrystallized from benzene.

Stock solutions of $C_3H_5N_2^+$ were prepared by dissolving $C_3H_4N_2$ in $HClO_4$ or HCl. The $C_3H_5N_2^+$-content was determined potentiometrically using the Gran[3] extrapolation method. The titrated amount was always a little higher than that expected from the weighed amount (∼0.4 %). The value from titration has been assumed to be correct.

Stock solutions of *nickel perchlorate* were prepared by dissolving solid $NiCO_3$ (Baker, Reagent Grade) in perchloric acid, boiling and recrystallizing as $Ni(ClO_4)_2.6H_2O$ from distilled water several times.

*Nickel chloride* $NiCl_2.6H_2O$ (Baker, Reagent Grade) was recrystallized from water and dissolved in distilled water in order to prepare a stock solution of nickel chloride.

The Ni(II)-content ($\approx 0.75-0.9$ M) of the stock solutions was determined by precipitation with dimethylglyoxime according to Vogel[2] and by indirect titration with EDTA-Pb(NO₃)₂ (Indicator: Xylenolorange). The difference in [$Ni^{2+}$] obtained by the two methods was less than 0.2 %.

The different $Ni^{2+}$-solutions used in the titrations were prepared from different stock solutions in order to detect possible systematic errors caused by impurities and analytical errors.

Stock solutions of *sodium chloride* were prepared by drying solid NaCl (Merck *p.a.*) for one day at about 200 °C in an electric oven, weighing and then dissolving in distilled water. All solutions were prepared using distilled water.

*Apparatus.* All emf measurements were carried out at 25.00 ± 0.05 °C. The salt bridge was of the "Wilhelm" type, described by Forsling, Hietanen and Sillén.[5] The cell arrangement was immersed in an oil thermostat (The oil thermostat and the burettes with NaOH- and Ni(II)-solutions were kept in a thermostated room at 25.0 ± 0.2 °C.)

During the experiments a stream of nitrogen was bubbled through the solution for stirring and for maintaining an inert atmosphere. Nitrogen from a cylinder was purified from acid and alkaline impurities by bubbling through solutions of 10 % NaOH and 10 % $H_2SO_4$. Finally, before the gas came into contact with the equilibrium solution, it was passed through pure ionic medium.

The potentiometric titrations were performed with an automatic system for precise emf titrations, a system constructed and built at this institute by O. Ginstrup.[6] The Ag, AgCl electrodes were prepared according to Brown.[10] Glass electrodes, Beckman type 40498 and Ingold type 201-NS were employed, giving constant and reproducible potentials within ± 0.2 mV.

The free $H^+$-concentration, $h$, was determined by measuring the emf of the cell

(A)  $-$Re||equilibrium solution |GE$+$

where GE denotes a glass electrode and RE$=$ Ag, AgCl|3 M NaCl saturated with AgCl||3 M NaCl and RE$=$Ag, AgCl/0.01 M NaCl, 2.99 M NaClO$_4$||3 M NaClO$_4$ respectively. The emf of cell (A) can be written at 25 °C as

$$E = E° + 59.157 \log h + E_j \qquad (1)$$

where $E°$ is a constant determined at each titration in the acidic range ($-\log h < 3$) where $h$ is known from a Gran [3] plot. For the liquid junction potentials we have used in 3.0 M (Na)Cl $E_j = -17.0h + 8.0 k_w h^{-1}$ mV and in 3.0 M (Na)ClO$_4$ $E_j = -16.3 h + 8.0 k_w h^{-1}$ mV where $k_w = 9.33 \times 10^{-15}$ M$^2$ and $k_w = 6.03 \times 10^{-15}$ M$^2$ are the ionic products of water in 3.0 M (Na)Cl and 3.0 M (Na)ClO$_4$, respectively. However, in most of our titrations the correction for the $E_j$ terms could be neglected.

## METHOD

The titration procedures used were similar to those earlier described by Sjöberg.[7] During the titrations the total concentrations of nickel, $B$, and imidazole, $C$, were kept either constant or varied. In general each titration was performed at a constant $C/B$-ratio. The free hydrogen ion concentration, $h$, was varied by adding hydroxide ions or hydrogen ions, and was measured with a glass electrode. In order to avoid activity coefficient variations, a constant ionic medium of 3.0 M (Na)ClO$_4$ or 3.0 M (Na)Cl was used. The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\log h$) and backward (decreasing $-\log h$) titrations. Dilution experiments at constant $Z$-values were also carried out to test the reversibility, especially at low $C/B$-quotients. Special efforts were made to cover as great part of the concentration range as possible and at the same time to try to cover the most interesting $C/B$ ratios as well as possible. Due to the formation of precipitates, the available $-\log h$ range was restricted to an upper limit of $6.5-9$. The crystalline precipitate with a composition of Ni(C$_3$H$_4$N$_2$)$_6$(ClO$_4$)$_2$ in 3.0 M (Na)ClO$_4$ has been X-ray investigated by Ivarsson.[21] However, at $C/B < 4$ a voluminous nickel-hydroxoprecipitate was always formed. The total concentrations (initial concentrations) of $B$ and $C$ were varied within the limits $0.0025 \leq B \leq 0.090$ M and $0.0035 \leq C \leq 0.270$ M. The following quotients

$C/B$ were thereby studied: 0.25, 0.5, 1, 1.4, 2, 3, 4, 5, 8, 10, and 12.

Most of the titrations were started with a calibration of the glass electrode (determination of $E°$ and $E_j$) using those acidic points where hydrolysis and complex formation can be neglected. In the range of complex formation the [H$^+$]$=h$ can then be obtained for each point from the measured emf using eqn. 1. Since $B$, $C$, and $H$ are known from analysis we can calculate for each point in a titration either
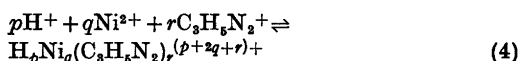
$$Z_B = (h-H)/B \qquad (2)$$

or

$$Z_C = (h-H)/C \qquad (3)$$

which are the average numbers of OH$^-$ reacted per $B$ and $C$, respectively. The experiments thus provide sets of data $Z_B$ (log $h$) and/or $Z_C$ (log $h$) at constant $B$, $C$ or $C/B$.

We will assume the presence of three component equilibria of the general type

$$p\text{H}^+ + q\text{Ni}^{2+} + r\text{C}_3\text{H}_5\text{N}_2{}^+ \rightleftharpoons$$
$$\text{H}_p\text{Ni}_q(\text{C}_3\text{H}_5\text{N}_2)_r{}^{(p+2q+r)+} \qquad (4)$$

Applying the law of mass action to these equilibria the conditions for the total concentrations then give:

$$B = b + \sum_{pqr} q \beta_{pqr} h^p b^q c^r \qquad (5)$$

$$C = c + K_a h^{-1} c + \sum_{pqr} r \beta_{pqr} h^p b^q c^r \qquad (6)$$

$$H = h - K_a h^{-1} c + \sum_{pqr} p \beta_{pqr} h^p b^q c^r \qquad (7)$$

where $b = $[Ni$^{2+}$] and $c = $[C$_3$H$_5$N$_2{}^+$]. The calculational problem is then to find the model (sets of $pqr$ and $\beta_{pqr}$) that best can explain the experimental data. The search for "best" model was performed by using the least squares computer program LETAGROPVRID [11] (version ETITR [12]). As "best" model or models we will consider those giving the lowest error squares sum $U = \sum[Z_C - Z_C(\text{calc})]^2$. The Letagrop calculations also give standard deviations $\sigma(Z_C)$, $\sigma(\beta_{pqr})$ and/or $\sigma(\log \beta_{pqr})$. For the definitions of these errors the reader is referred to the Letagrop paper I.[13]

Concerning the binary proton imidazole equilibrium

$$\text{C}_3\text{H}_5\text{N}_2{}^+ \rightleftharpoons \text{C}_3\text{H}_4\text{N}_2 + \text{H}^+ \qquad (8)$$
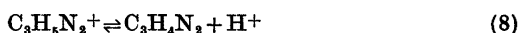
we will make use of the result obtained by Sjöberg[7] and for binary hydrolysis equilibria

$$p\mathrm{H}^+ + q\mathrm{Ni}^{2+} \rightleftharpoons \mathrm{Ni}_q\mathrm{H}_p^{(p+2q)+} \qquad (9)$$
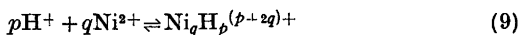
the results obtained by Ohtaki-Biedermann[8] (3 M (Na)Cl) and Burkov-Sillén[17] (3 M (Na)ClO$_4$). For reaction (3), Sjöberg[7] reported log $(K_a \pm 3\sigma)$ to be $-7.637 \pm 0.001$ in 3 M (Na)Cl and $-7.913 \pm 0.002$ in 3 M (Na)ClO$_4$. Concerning equilibria (4) the investigations both of Ohtaki-Biedermann and of Burkov-Sillén clearly show that the main species in a hydrolyzed Ni$^{2+}$ solution is a tetramer Ni$_4$(OH)$_4^{4+}$ and the following log $\beta_{-404}$ values were reported $-28.5$ (3.0 M (Na)Cl) and $-27.37$ (3.0 M (Na)ClO$_4$). Only minor amounts of the complexes NiOH$^+$ and Ni$_2$OH$^{3+}$ were found in the concentration ranges studied.

From separate experiments the results of these binary equilibria were carefully tested and we found excellent agreement with the result earlier reported. We will therefore assume these binary equilibria to be exactly known, and all effects above this level will be treated as being caused by ternary species. Note that complexes Ni(C$_3$H$_4$N$_2$)$_n^{2+}$ in the following will be regraded as ternary species, where $p = -r$.

## DATA, CALCULATIONS AND RESULTS

The mathematical analysis of data was started by making a Bjerrum plot, $\bar{n}$(log [C$_3$H$_4$N$_2$]). The plot is shown in Fig. 1. It is seen from the plot that for quotients $C/B > 4$ and $B > 0.01$ M the function $\bar{n}$(log[C$_3$H$_4$N$_2$]) seems to be independent of $B$ and $C$ thus indicating formation of a series of stepwise mononuclear complexes Ni(C$_3$H$_4$N$_2$)$_n^{2+}$. Data fulfilling these conditions will in the following be denoted Data 0.

However, at quotients $C/B < 4$ and $C < 0.01$ M the function $\bar{n}$(log[C$_3$H$_4$N$_2$]) is not independent of $B$ and $C$ (Fig. 2a, b). This would indicate that ternary hydrolytic species of the type Ni$_q$(OH)$_p$(C$_3$H$_4$N$_2$)$_r^{(2q-p)+}$ are probably formed. These data will below be denoted as Data 1. It may be mentioned that data at very high $C/B$-ratios. $12 < C/B < 80$, have also been collected. These $\bar{n}$(log[C$_3$H$_4$N$_2$]) functions are dependent on $B$ and $C$ as well.

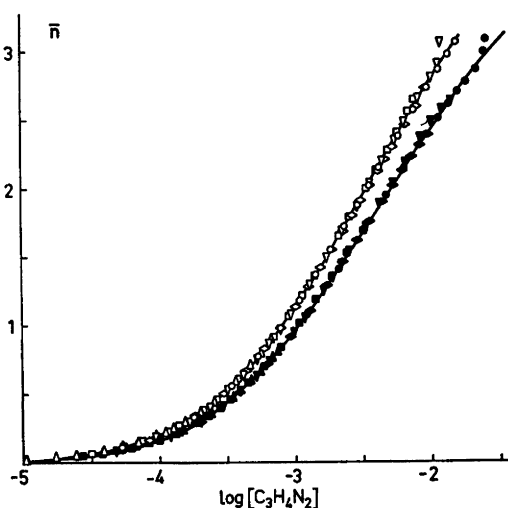A preliminary analysis of these data in-



*Fig. 1.* Experimental data plotted as curves $\bar{n}$(log [C$_3$H$_4$N$_2$]) for $C/B$ ratios 1,2,3,4,8 and high $B/C$ concentrations. Open symbols mark titrations in 3 M (Na)ClO$_4$ and dark symbols 3 M (Na)Cl. The figure also gives a comparison between the strength of complexation in the two media. The symbols stand for the following $B$ and $C$ in mM (start concentrations). ○●, 10−80; ◇◆, 10−40; △▲, 40−40; ▽▼, 20−80; □, 90−270; ■, 80−160. In order to make the figure clear only a few titrations have been plotted. The full curves have been calculated with the set of proposed constants in Table 3.

dicates formation of acidic ternary complexes of the type Ni(C$_3$H$_4$N$_2$)$_x$(C$_3$H$_5$N$_2$)$_y^{(2+y)+}$. However, the results and discussion of these complexes will be given in a forthcoming paper.

*Data 0.* A Letagrop analysis showed that these data could well be explained with the complexes Ni(C$_3$H$_4$N$_2$)$^{2+}$, Ni(C$_3$H$_4$N$_2$)$_2^{2+}$, Ni(C$_3$H$_4$N$_2$)$_3^{2+}$, and Ni(C$_3$H$_4$N$_2$)$_4^{2+}$ for both the NaCl and for the NaClO$_4$ media. The analysis ended at a $\sigma(Z)$ of 0.003 in 3.0 M (Na)ClO$_4$ and a $\sigma(Z) = 0.002$ in 3.0 M (Na)Cl, which must be considered as a very good explanation. The data included in the analysis consist of around 350 experimental points distributed over 15 $BC$-combinations. The "best" equilibrium constants with corresponding standard deviations obtained in these analyses, are given in Table 3, calculation denoted 1. The residuals $\Delta Z = Z_C - Z_C$(calc) after "best" fit are given together with experimental data in Table 5.

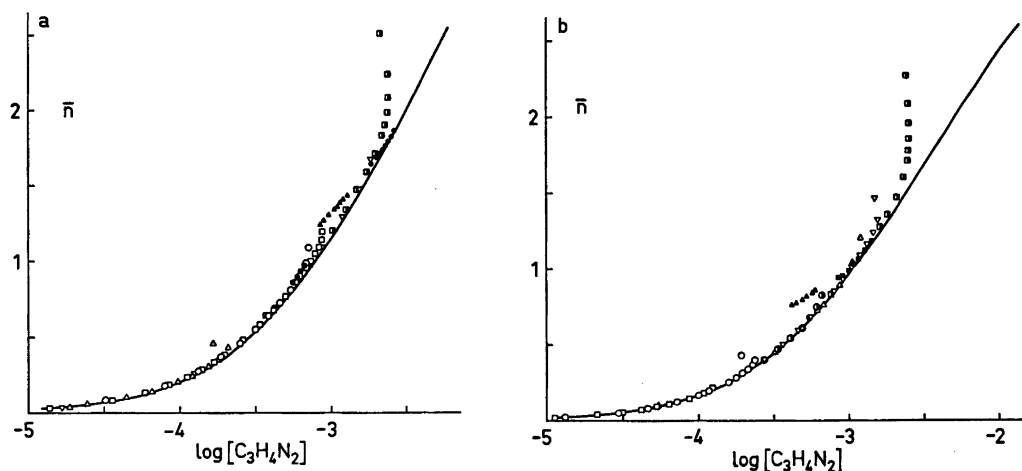*Data 1.* These data cover the ranges

*Fig. 2.* Experimental data plotted as curves $\bar{n}(\log [C_3H_4N_2])$ for $C/B$ ratios 0.25, 0.5, 1, 1.4, 2, 4 and low $B,C$ concentrations. Dark symbols mark back titrations with pure ionic media. The symbols stand for the following $B$ and $C$ in mM (start concentrations). *a.* 3 M (Na)ClO$_4$-medium. O, 4.5 − 6.5; □, 9 − 13; △, 10 − 15; ▽, 10 − 20; ◥, 2.5 − 10; ■, 4.2 − 6; ●, 4.2 − 12; ▲, 4.6 − 9.2. *b.* 3 M (Na)Cl-medium. O, 26.8 − 12.1; □, 53.6 − 12.1; △, 2.5 − 5; ▽, 5 − 10; ◑, 10 − 10; ◥, 2.5 − 10; ■; 3.3 − 6.6; ▲, 6.4 − 6.6. Only a few titrations have been plotted. The full curves have been calculated with the set of proposed constants (not $-\log \beta_{-2,1,1}$) in Table 3.

$0.0025 \leq B \leq 0.08$ M, $0.003 \leq C < 0.08$ M, $1 \leq -\log h \leq 9$ and the quotients $C/B \leq 5$. The $C/B$-ratios studied were, in 3.0 M (Na)ClO$_4$, 0.5, 1, 1.4, 2, 3, and 4 in 3.0 M (Na)Cl, 0.25, 0.5, 1, 2, 5.

In the search for the ternary hydrolytic species it was assumed that the binary complexes were known and that the equilibrium constants had the values given above. The search was started with a *pqr*-analysis (systematic testing of different *pqr*-complexes). The result of the analysis is given in Fig. 3

and Table 3. It is seen from these calculations that the lowest error squares sum, in both media, is obtained for the complex Ni(OH)C$_3$H$_4$N$_2^+$. In 3 M (Na)Cl medium data could be fairly well explained by the complex NiOH$^+$. However, the value of the formation constant obtained, $\log \beta_{11} = -9.22$, is quite different from the value $-10.5$, obtained and proposed by Ohtaki-Biedermann in their binary investigation, and therefore an explanation with the ternary complex Ni(OH)C$_3$H$_4$N$_2^+$ appears more likely. Furthermore, in the

*Table 2.* The material, which has been used in the LETAGROP calculations, 73 points, is chosen to cover the range where the amount of the ternary complex is high.

| Number of points | $\sigma(Z)$ | $\log K_a \pm 3\sigma$ | $\log \beta_{-211} \pm 3\sigma$ | $U$ |
|---|---|---|---|---|
| 73 | 0.003 | $-6.52 \pm 0.03$[a] | – | 444 |
| 73 | 0.002 | – | $-13.68 \pm 0.02$ | 259 |
| 73 | 0.0003 | $-7.44 \pm 0.16$[b] | $-13.44 \pm 0.02$ | 11 |

[a] The amount of the impurity acid was about 0.1 mM. [b] The impurity acid obtained negative concentrations.

*Table 3.* Results of the final covariations of binary and ternary constants in the two media investigated. When no $3\sigma(\log \beta_{pqr})$ is given the formation constant has not been varied. To illustrate the difficulties in determining formation constants of complexes in the buffer range of imidazole, we have shown the change of $\log \beta_{-313}$ and $\log \beta_{-414}$ when $\log \beta_{-101}$ is changed 0.02 logarithmic units. The variation in $\log \beta_{-414}$ is big, but the change in $\log \beta_{-313}$ is negligible (as the change in $\log \beta_{-212}$ and $\log \beta_{-111}$).

| | Method | Medium | Number of points | $\log \beta_{-101}$ | $\sigma(z)$ | $\log \beta_{-111}$ $\pm 3\sigma$ | $\log \beta_{-212}$ $\pm 3\sigma$ | $\log \beta_{-313}$ $\pm 3\sigma$ | $\log \beta_{-414}$ $\pm 3\sigma$ | $\log \beta_{-211}$ $\pm 3\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Emf. | 3M(Na)Cl | 353 | −7.637 | 0.002 | −4.387 $\pm 0.004$ | −9.422 $\pm 0.006$ | −15.053 $\pm 0.018$ | −21.469 $\pm 0.056$ | |
| 2 | Emf. | 3M(Na)Cl | 327 | −7.637 −7.657 | 0.004 | −4.387 −4.387 | −9.422 −9.422 | −15.053 −15.050 $\pm 0.013$ | −21.469 −21.236 $\pm 0.037$ | −13.684 $\pm 0.035$ |
| 1 | Emf. | 3M(Na)ClO$_4$ | 326 | −7.913 | 0.003 | −4.569 $\pm 0.005$ | −9.739 $\pm 0.008$ | −15.429 $\pm 0.012$ | −21.728 $\pm 0.032$ | |
| 2 | Emf. | 3M(Na)ClO$_4$ | 387 | −7.913 | 0.005 | −4.569 | −9.739 | −15.429 | −21.728 | −13.763 $\pm 0.048$ |

3 M (Na)ClO$_4$ medium it was not possible to explain data with NiOH$^+$.

In order to visualize the amounts of Ni(OH)C$_3$H$_4$N$_2^+$ at some typical concentrations and $C/B$-ratios, we have calculated a set of distribution diagrams, which are shown in Fig. 4. It can be seen from the diagrams that the maximum amounts of Ni(OH)C$_3$H$_4$N$_2^+$ are obtained at around $-\log h = 8.5$, where about $5-10$ % of the total nickel is present as Ni(OH)C$_3$H$_4$N$_2^+$. However, the total concentrations of the species are always rather low, mainly due to the fact that the necessary $-\log h$ values can be reached solely at low total nickel concentrations. Since the Ni(OH)C$_3$H$_4$N$_2^+$ concentrations are obviously rather low, it seems worthwhile to test whether the complex can be explained equally well with an impurity acid. A Letagrop calculation

showed, however, that the "Ni(OH)C$_3$H$_4$N$_2^+$-effect" could not be explained with an impurity acid. The results of these calculations are collected in Table 2. Thus there appears to be good evidence that the complex Ni(OH)C$_3$H$_4$N$_2^+$ really exists. As stated in the introduction we had hoped to find some polynuclear complexes related to the species Ni$_4$OH$_4^{4+}$, but no indications in this direction could be found. This finding was tested and settled by performing experiments at constant $Z$, where hydrolyzed solutions of nickel chloride were titrated with nickel imidazole solutions. No effects due to complexes other than those given in Table 3 were found.

For complex formation in the chloride medium, the formation of chloro complexes must be taken into consideration. Many workers have reported that nickel(II) ions

*Table 4.* "Conditional stability constants" $\beta'_{pqr}$ defined according to $p\mathrm{H}^+ + q\mathrm{Ni}^{2+} + r\mathrm{C}_3\mathrm{H}_4\mathrm{N}_2 \rightleftharpoons$ $(\mathrm{H}^+)_p(\mathrm{Ni}^{2+})_q(\mathrm{C}_3\mathrm{H}_4\mathrm{N}_2)_r$ and calculated from the relation $\beta'_{pqr} = \beta_{pqr}(1 + \beta_{010})^q$. The values of $\beta_{pqr}$ are calculated from constants given in Table 1. Approximate values of $\beta_{010}$ have been calculated (see eqn. 10) by assuming $\log K(\mathrm{NiCl}^+) = -0.48$ and $[\mathrm{Cl}^-] = 3$ M.

| Medium | NiL$^{2+}$ $\log \beta'_{011}$ | NiL$_2^{2+}$ $\log \beta'_{012}$ | NiL$_3^{2+}$ $\log \beta'_{013}$ | NiL$^{2+}$ $\log \beta'_{014}$ | Ni(OH)L$^+$ $\log \beta'_{-111}$ |
|---|---|---|---|---|---|
| 3.0 M (Na)Cl | 3.55 | 6.15 | 8.16 | 9.38 | −5.64 |
| 3.0 M (Na)ClO$_4$ | 3.34 | 6.09 | 8.31 | 9.94 | −5.85 |

form weak complexes with chloride ions. The dominating complex seems to be NiCl$^+$ and formation constants of other complexes are so small and erroneous that only this species is taken into account in the following discussion.

Assuming the equilibrium Ni$^{2+}$ + Cl$^-$ $\rightleftharpoons$ NiCl$^+$ to be known with log $K_1 = -0.48$ (an average value) it is possible to calculate a new conditional constant $\beta'_{pqr}$ which is corrected for the equilibrium through the relation

*Table 5.* Experimental data $Z$ (log $h$) at different $B$ and $C$ concentrations (initial concentrations) (3.0 M (Na)ClO$_4$ medium). For each point the quantities, $H$ (in mM), log $h$, $Z$, $\Delta Z_0$ and $\Delta Z_1$ are given. $\Delta Z$ is the residual $(Z_{exp} - Z_{calc}) \times 1000$ and the indices 0 and 1 refer to the assumptions 0, Binary complexes Ni(C$_3$H$_4$N$_2$)$_n^{2+}$ only with constants given in Table 3 together with hydrolysis species Ni$_4$OH$_4^{4+}$ with constants proposed by Burkov *et al.*;[17] 1, Binary complexes and proposed ternary complex with equilibrium constants given in Table 3.

SATS 1    B = 0.01000    C = 0.01000

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.30 | -5.084 | 0.033 | 2.08 | 2.07 |
| -0.71 | -5.485 | 0.076 | 3.64 | 3.61 |
| -0.91 | -5.612 | 0.098 | 4.31 | 4.27 |
| -1.50 | -5.888 | 0.164 | 5.97 | 5.86 |
| -1.70 | -5.960 | 0.186 | 6.48 | 6.33 |
| -1.89 | -6.028 | 0.207 | 6.71 | 6.51 |
| -2.08 | -6.090 | 0.229 | 7.17 | 6.93 |
| -2.27 | -6.148 | 0.251 | 7.64 | 7.35 |
| -2.45 | -6.204 | 0.273 | 7.77 | 7.42 |
| -2.64 | -6.258 | 0.295 | 8.04 | 7.63 |
| -3.18 | -6.406 | 0.361 | 9.16 | 8.51 |
| -3.72 | -6.544 | 0.426 | 9.72 | 8.76 |
| -4.23 | -6.679 | 0.492 | 9.57 | 8.18 |
| -4.74 | -6.811 | 0.558 | 10.06 | 8.12 |
| -5.23 | -6.948 | 0.623 | 10.05 | 7.35 |
| -5.71 | -7.092 | 0.689 | 9.84 | 6.03 |
| -6.18 | -7.250 | 0.754 | 9.82 | 4.33 |
| -6.48 | -7.369 | 0.798 | 9.89 | 2.68 |
| -6.63 | -7.435 | 0.820 | 9.87 | 1.51 |
| -6.78 | -7.506 | 0.842 | 9.87 | 0.05 |
| -6.93 | -7.584 | 0.864 | 9.88 | -1.84 |
| -7.08 | -7.671 | 0.886 | 10.12 | -4.12 |

SATS 2    B = 0.02000    C = 0.04000

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.23 | -4.283 | 0.009 | -0.15 | -0.15 |
| -0.95 | -4.830 | 0.029 | 0.29 | 0.29 |
| -1.64 | -5.095 | 0.051 | 0.59 | 0.58 |
| -2.31 | -5.274 | 0.073 | 0.98 | 0.97 |
| -2.96 | -5.415 | 0.095 | 1.20 | 1.18 |
| -3.59 | -5.532 | 0.117 | 1.29 | 1.26 |
| -4.20 | -5.634 | 0.138 | 1.43 | 1.38 |
| -4.79 | -5.725 | 0.160 | 1.43 | 1.36 |
| -5.36 | -5.807 | 0.182 | 1.65 | 1.56 |
| -5.92 | -5.884 | 0.204 | 1.78 | 1.66 |
| -6.46 | -5.957 | 0.226 | 1.78 | 1.64 |
| -6.99 | -6.025 | 0.248 | 1.68 | 1.51 |
| -7.50 | -6.090 | 0.270 | 1.65 | 1.65 |
| -8.00 | -6.153 | 0.292 | 2.03 | 1.79 |
| -8.48 | -6.213 | 0.314 | 2.06 | 1.78 |
| -8.96 | -6.274 | 0.336 | 1.35 | 1.03 |
| -9.42 | -6.333 | 0.357 | 0.79 | 0.42 |
| -9.86 | -6.390 | 0.379 | 0.49 | 0.07 |
| -10.30 | -6.445 | 0.401 | 0.58 | 0.11 |
| -10.72 | -6.500 | 0.423 | 0.40 | -0.13 |
| -11.14 | -6.554 | 0.445 | 0.18 | -0.42 |
| -11.54 | -6.608 | 0.467 | -0.09 | -0.76 |
| -11.94 | -6.662 | 0.489 | -0.42 | -1.16 |
| -12.32 | -6.715 | 0.511 | -0.27 | -1.08 |
| -12.70 | -6.768 | 0.533 | -0.42 | -1.32 |
| -13.06 | -6.822 | 0.555 | -0.43 | -1.43 |

SATS 3    B = 0.01000    C = 0.02000

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.39 | -4.896 | 0.023 | 3.45 | 3.45 |
| -2.43 | -5.823 | 0.137 | 8.34 | 8.26 |
| -4.43 | -6.206 | 0.253 | 11.12 | 10.86 |
| -6.40 | -6.500 | 0.368 | 11.09 | 10.55 |
| -8.34 | -6.762 | 0.483 | 10.79 | 9.84 |
| -10.24 | -7.022 | 0.599 | 8.99 | 7.44 |
| -12.11 | -7.303 | 0.714 | 6.55 | 3.96 |
| -13.95 | -7.646 | 0.830 | 4.80 | -0.23 |
| -15.75 | -8.212 | 0.945 | 5.87 | -10.81 |

SATS 4    B = 0.01976    C = 0.01977

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.21 | -4.459 | 0.014 | 0.36 | 0.36 |
| -1.06 | -5.166 | 0.063 | 0.44 | 0.43 |
| -1.87 | -5.469 | 0.113 | 0.33 | 0.30 |
| -2.63 | -5.676 | 0.164 | 0.28 | 0.21 |
| -3.37 | -5.841 | 0.214 | 0.33 | 0.20 |
| -4.06 | -5.979 | 0.265 | 1.81 | 1.60 |
| -4.73 | -6.106 | 0.316 | 2.12 | 1.81 |
| -5.37 | -6.223 | 0.366 | 3.00 | 2.56 |
| -5.98 | -6.336 | 0.417 | 3.06 | 2.45 |
| -6.56 | -6.444 | 0.467 | 3.60 | 2.80 |
| -7.12 | -6.551 | 0.518 | 3.85 | 2.79 |
| -7.66 | -6.659 | 0.569 | 4.29 | 2.90 |
| -8.17 | -6.769 | 0.619 | 4.73 | 2.92 |
| -8.67 | -6.883 | 0.670 | 4.85 | 2.48 |
| -9.14 | -7.005 | 0.720 | 5.22 | 2.07 |
| -9.60 | -7.139 | 0.771 | 5.11 | 0.83 |
| -9.75 | -7.187 | 0.788 | 5.48 | 0.71 |
| -10.04 | -7.292 | 0.822 | 5.19 | -0.86 |
| -10.33 | -7.409 | 0.855 | 5.55 | -2.35 |
| -10.47 | -7.477 | 0.872 | 5.24 | -3.96 |

SATS 5    B = 0.004189    C = 0.005960

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -4.73 | -7.648 | 0.794 | 15.97 | 6.29 |
| -4.58 | -7.650 | 0.791 | 16.04 | 6.32 |
| -4.31 | -7.653 | 0.786 | 15.73 | 5.91 |
| -4.06 | -7.655 | 0.780 | 15.42 | 5.53 |
| -3.83 | -7.656 | 0.774 | 15.01 | 5.47 |
| -3.63 | -7.657 | 0.768 | 15.01 | 5.03 |
| -3.44 | -7.657 | 0.762 | 14.77 | 4.78 |
| -3.27 | -7.657 | 0.756 | 14.47 | 4.46 |
| -3.11 | -7.656 | 0.750 | 14.31 | 4.32 |
| -2.97 | -7.654 | 0.745 | 14.47 | 4.52 |
| -2.84 | -7.652 | 0.739 | 14.35 | 4.43 |

SATS 6    B = 0.009081    C = 0.01292

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -1.81 | -5.890 | 0.151 | 5.60 | 5.50 |
| -2.97 | -6.195 | 0.249 | 6.52 | 6.23 |
| -4.12 | -6.433 | 0.346 | 6.47 | 5.89 |
| -5.26 | -6.648 | 0.444 | 4.59 | 3.57 |
| -6.39 | -6.850 | 0.542 | 4.35 | 2.71 |
| -7.51 | -7.054 | 0.640 | 6.33 | 3.76 |
| -8.62 | -7.284 | 0.738 | 5.77 | 1.56 |
| -9.72 | -7.556 | 0.835 | 9.20 | 1.62 |

SATS 7    B = 0.009081    C = 0.01292

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| 0.14 | -3.804 | 0.002 | 0.40 | 0.40 |
| -0.27 | -5.027 | 0.026 | 3.39 | 3.38 |
| -0.68 | -5.460 | 0.063 | 5.63 | 5.61 |
| -1.09 | -5.701 | 0.100 | 6.86 | 6.81 |
| -1.49 | -5.875 | 0.138 | 7.54 | 7.45 |
| -1.89 | -6.014 | 0.176 | 8.27 | 8.12 |
| -2.29 | -6.136 | 0.213 | 7.90 | 7.67 |
| -2.68 | -6.240 | 0.251 | 8.82 | 8.50 |
| -3.07 | -6.336 | 0.288 | 9.22 | 8.79 |
| -3.45 | -6.427 | 0.326 | 9.42 | 8.86 |
| -3.83 | -6.512 | 0.363 | 9.69 | 8.98 |
| -4.21 | -6.592 | 0.401 | 10.92 | 10.04 |
| -4.59 | -6.671 | 0.439 | 11.24 | 10.17 |
| -5.33 | -6.828 | 0.514 | 11.63 | 10.08 |
| -5.70 | -6.907 | 0.551 | 10.87 | 9.00 |
| -6.07 | -6.986 | 0.589 | 10.92 | 8.68 |
| -6.43 | -7.066 | 0.627 | 11.25 | 8.59 |

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -6.79 | -7.149 | 0.664 | 11.56 | 8.38 |
| -7.14 | -7.236 | 0.702 | 11.39 | 7.54 |
| -7.50 | -7.328 | 0.739 | 11.33 | 6.64 |
| -7.85 | -7.427 | 0.777 | 11.49 | 5.70 |
| -8.19 | -7.536 | 0.815 | 11.59 | 4.27 |
| -8.54 | -7.659 | 0.852 | 11.88 | 2.29 |
| -8.88 | -7.807 | 0.890 | 12.01 | -1.22 |
| -9.22 | -7.992 | 0.927 | 12.83 | -7.02 |

SATS 8    B = 0.005000    C = 0.01000

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.65 | -5.718 | 0.068 | 3.55 | 3.51 |
| -2.13 | -6.385 | 0.226 | 6.96 | 6.60 |
| -3.59 | -6.778 | 0.384 | 8.16 | 7.14 |
| -5.04 | -7.117 | 0.542 | 8.70 | 6.60 |
| -6.47 | -7.470 | 0.699 | 8.04 | 3.91 |
| -7.88 | -7.901 | 0.857 | 15.13 | 5.30 |

SATS 9    B = 0.004155    C = 0.01254

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -10.59 | -8.108 | 0.858 | 2.15 | -3.92 |
| -10.30 | -8.115 | 0.858 | 2.02 | -4.25 |
| -10.02 | -8.121 | 0.858 | 2.04 | -4.40 |
| -9.76 | -8.127 | 0.858 | 1.93 | -4.71 |
| -9.51 | -8.133 | 0.858 | 1.90 | -4.92 |
| -9.27 | -8.139 | 0.858 | 1.86 | -5.14 |
| -9.05 | -8.145 | 0.858 | 1.69 | -5.50 |
| -8.83 | -8.150 | 0.858 | 1.61 | -5.77 |
| -8.63 | -8.155 | 0.858 | 1.71 | -5.84 |
| -8.43 | -8.160 | 0.858 | 1.72 | -6.00 |
| -8.25 | -8.164 | 0.858 | 1.92 | -5.97 |
| -8.07 | -8.169 | 0.858 | 1.91 | -6.16 |
| -7.90 | -8.173 | 0.858 | 2.00 | -6.24 |
| -7.73 | -8.178 | 0.858 | 1.96 | -6.45 |
| -7.58 | -8.182 | 0.858 | 2.03 | -6.56 |
| -7.43 | -8.186 | 0.858 | 2.03 | -6.72 |
| -7.28 | -8.189 | 0.858 | 2.22 | -6.69 |
| -7.14 | -8.193 | 0.858 | 2.30 | -6.77 |
| -7.01 | -8.196 | 0.858 | 2.43 | -6.79 |
| -6.88 | -8.200 | 0.858 | 2.55 | -6.83 |
| -6.75 | -8.203 | 0.858 | 2.64 | -6.90 |
| -6.63 | -8.206 | 0.858 | 2.84 | -6.84 |
| -6.52 | -8.209 | 0.858 | 2.94 | -6.91 |
| -6.40 | -8.212 | 0.858 | 3.14 | -6.85 |
| -6.30 | -8.215 | 0.858 | 3.28 | -6.85 |
| -6.19 | -8.218 | 0.858 | 3.41 | -6.88 |
| -6.09 | -8.220 | 0.858 | 3.65 | -6.78 |
| -5.99 | -8.223 | 0.858 | 3.69 | -6.89 |
| -5.90 | -8.226 | 0.858 | 3.65 | -6.87 |
| -5.81 | -8.229 | 0.858 | 3.72 | -7.16 |
| -5.72 | -8.232 | 0.858 | 3.89 | -7.12 |
| -5.63 | -8.234 | 0.858 | 4.14 | -7.01 |
| -5.55 | -8.236 | 0.858 | 4.24 | -7.05 |
| -5.47 | -8.239 | 0.858 | 4.32 | -7.11 |
| -5.39 | -8.241 | 0.858 | 4.43 | -7.13 |
| -5.31 | -8.244 | 0.858 | 4.26 | -7.47 |
| -5.23 | -8.246 | 0.858 | 4.44 | -7.42 |
| -5.16 | -8.248 | 0.858 | 4.74 | -7.24 |

SATS10    B = 0.004505    C = 0.01802

| H | log h | Z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -11.48 | -7.557 | 0.637 | 1.37 | 0.52 |
| -11.17 | -7.563 | 0.637 | 1.33 | 0.44 |
| -10.87 | -7.570 | 0.637 | 1.27 | 0.35 |
| -10.58 | -7.576 | 0.637 | 1.26 | 0.31 |
| -10.32 | -7.582 | 0.637 | 1.10 | 0.12 |
| -10.06 | -7.588 | 0.637 | 0.87 | -0.15 |
| -9.82 | -7.594 | 0.637 | 0.77 | -0.28 |

*Table 5. Continued.*

| | | | | |
|---|---|---|---|---|
| -9.59 | -7.600 | 0.637 | 0.67 | -0.41 |
| -9.37 | -7.605 | 0.637 | 0.44 | -0.68 |
| -9.16 | -7.611 | 0.637 | 0.42 | -0.73 |
| -8.96 | -7.616 | 0.637 | 0.35 | -0.84 |
| -8.76 | -7.621 | 0.637 | -0.06 | -1.29 |
| -8.58 | -7.626 | 0.637 | 0.11 | -1.15 |
| -8.40 | -7.631 | 0.637 | -0.13 | -1.42 |
| -8.23 | -7.636 | 0.637 | -0.34 | -1.67 |
| -8.07 | -7.640 | 0.637 | -0.39 | -1.75 |
| -7.91 | -7.644 | 0.637 | -0.41 | -1.80 |
| -7.76 | -7.648 | 0.637 | -0.47 | -1.90 |
| -7.62 | -7.652 | 0.637 | -0.43 | -1.90 |
| -7.48 | -7.656 | 0.637 | -0.29 | -1.78 |
| -7.34 | -7.659 | 0.637 | -0.11 | -1.64 |
| -7.21 | -7.662 | 0.637 | 0.18 | -1.38 |
| -7.09 | -7.666 | 0.637 | 0.07 | -1.52 |
| -6.96 | -7.670 | 0.637 | 0.07 | -1.56 |
| -6.85 | -7.673 | 0.637 | 0.26 | -1.40 |
| -6.73 | -7.676 | 0.637 | 0.34 | -1.35 |
| -6.63 | -7.679 | 0.637 | 0.25 | -1.48 |
| -6.52 | -7.683 | 0.637 | 0.27 | -1.49 |

**SATS11**   $B = 0.005000$   $\sigma = 0.02000$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -2.47 | -6.126 | 0.132 | 2.71 | 2.59 |
| -3.63 | -6.381 | 0.195 | 2.75 | 2.54 |
| -4.78 | -6.587 | 0.258 | 3.19 | 2.87 |
| -5.92 | -6.768 | 0.321 | 3.76 | 3.33 |
| -7.05 | -6.938 | 0.384 | 2.93 | 2.41 |
| -8.18 | -7.096 | 0.448 | 3.02 | 2.43 |
| -9.29 | -7.252 | 0.511 | 1.70 | 1.05 |
| -10.39 | -7.405 | 0.574 | 0.84 | 0.10 |
| -11.48 | -7.557 | 0.637 | 1.33 | 0.48 |

**SATS12**   $B = 0.004598$   $\sigma = 0.009196$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -7.88 | -7.901 | 0.857 | 15.10 | 5.27 |
| -7.61 | -7.911 | 0.857 | 15.35 | 5.24 |
| -7.36 | -7.921 | 0.857 | 15.39 | 4.99 |
| -7.13 | -7.930 | 0.857 | 15.51 | 4.83 |
| -6.91 | -7.938 | 0.857 | 15.76 | 4.82 |
| -6.70 | -7.946 | 0.857 | 15.96 | 4.76 |
| -6.51 | -7.954 | 0.857 | 16.12 | 4.65 |
| -6.33 | -7.961 | 0.857 | 16.53 | 4.82 |
| -6.15 | -7.969 | 0.857 | 16.58 | 4.60 |
| -5.99 | -7.975 | 0.857 | 16.78 | 4.56 |
| -5.83 | -7.983 | 0.857 | 16.87 | 4.39 |
| -5.69 | -7.989 | 0.857 | 17.04 | 4.32 |
| -5.54 | -7.996 | 0.857 | 17.14 | 4.17 |
| -5.41 | -8.001 | 0.857 | 17.71 | 4.54 |
| -5.28 | -8.006 | 0.857 | 18.03 | 4.65 |
| -5.16 | -8.012 | 0.857 | 18.16 | 4.54 |
| -5.05 | -8.017 | 0.857 | 18.42 | 4.59 |
| -4.94 | -8.022 | 0.857 | 18.64 | 4.59 |
| -4.73 | -8.033 | 0.857 | 18.75 | 4.33 |
| -4.54 | -8.044 | 0.857 | 18.96 | 4.01 |
| -4.36 | -8.053 | 0.857 | 19.26 | 3.90 |
| -4.20 | -8.062 | 0.857 | 19.62 | 3.86 |
| -4.05 | -8.070 | 0.857 | 19.99 | 3.85 |
| -3.90 | -8.078 | 0.857 | 20.19 | 3.65 |
| -3.65 | -8.093 | 0.857 | 20.70 | 3.42 |
| -3.43 | -8.108 | 0.857 | 20.96 | 2.96 |
| -3.23 | -8.120 | 0.857 | 21.38 | 2.70 |
| -3.05 | -8.132 | 0.857 | 21.74 | 2.41 |

**SATS13**   $B = 0.008841$   $\sigma = 0.008841$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -6.69 | -7.234 | 0.757 | 6.66 | 1.37 |
| -6.53 | -7.239 | 0.755 | 6.61 | 1.26 |
| -6.24 | -7.248 | 0.752 | 6.43 | 0.96 |
| -5.97 | -7.257 | 0.749 | 6.38 | 0.81 |
| -5.71 | -7.264 | 0.746 | 6.35 | 0.69 |
| -5.48 | -7.272 | 0.743 | 6.23 | 0.48 |
| -5.27 | -7.279 | 0.740 | 6.25 | 0.41 |
| -5.06 | -7.284 | 0.737 | 6.34 | 0.43 |
| -4.88 | -7.290 | 0.734 | 6.32 | 0.34 |
| -4.70 | -7.296 | 0.731 | 6.27 | 0.22 |
| -4.54 | -7.300 | 0.728 | 6.34 | 0.23 |
| -4.38 | -7.305 | 0.725 | 6.26 | 0.09 |
| -4.24 | -7.309 | 0.722 | 6.18 | -0.05 |
| -4.10 | -7.313 | 0.719 | 6.11 | -0.17 |
| -3.97 | -7.317 | 0.716 | 6.13 | -0.19 |
| -3.85 | -7.321 | 0.713 | 6.02 | -0.34 |
| -3.73 | -7.324 | 0.710 | 5.88 | -0.52 |
| -3.62 | -7.327 | 0.707 | 5.78 | -0.66 |
| -3.51 | -7.330 | 0.704 | 5.65 | -0.83 |
| -3.41 | -7.332 | 0.701 | 5.64 | -0.86 |
| -3.32 | -7.335 | 0.698 | 5.54 | -0.99 |
| -3.23 | -7.337 | 0.695 | 5.36 | -1.20 |
| -3.14 | -7.339 | 0.692 | 5.39 | -1.18 |
| -3.06 | -7.340 | 0.689 | 5.34 | -1.25 |
| -2.98 | -7.342 | 0.686 | 5.22 | -1.39 |
| -2.90 | -7.344 | 0.683 | 4.94 | -1.68 |
| -2.83 | -7.345 | 0.680 | 4.98 | -1.65 |

**SATS14**   $B = 0.008181$   $\sigma = 0.01164$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -9.72 | -7.556 | 0.835 | 9.17 | 1.61 |
| -9.39 | -7.562 | 0.834 | 9.24 | 1.56 |
| -9.09 | -7.567 | 0.832 | 9.41 | 1.61 |
| -8.80 | -7.572 | 0.830 | 9.68 | 1.78 |
| -8.52 | -7.577 | 0.828 | 9.74 | 1.74 |
| -8.27 | -7.582 | 0.827 | 9.82 | 1.72 |
| -8.02 | -7.587 | 0.825 | 9.75 | 1.55 |
| -7.79 | -7.592 | 0.823 | 9.65 | 1.34 |
| -7.37 | -7.600 | 0.820 | 9.52 | 1.04 |
| -6.98 | -7.608 | 0.817 | 9.21 | 0.55 |
| -6.63 | -7.615 | 0.813 | 9.08 | 0.25 |
| -6.31 | -7.622 | 0.810 | 8.75 | -0.23 |
| -6.02 | -7.627 | 0.806 | 8.42 | -0.70 |
| -5.75 | -7.632 | 0.803 | 8.29 | -0.95 |
| -5.51 | -7.636 | 0.800 | 8.33 | -1.01 |
| -5.28 | -7.640 | 0.796 | 8.13 | -1.31 |
| -4.97 | -7.644 | 0.791 | 7.99 | -1.57 |
| -4.69 | -7.648 | 0.786 | 7.78 | -1.90 |

**SATS15**   $B = 0.04000$   $\sigma = 0.02000$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.64 | -4.609 | 0.038 | -0.12 | -0.13 |
| -1.58 | -5.031 | 0.092 | 0.64 | 0.63 |
| -2.48 | -5.275 | 0.146 | 1.17 | 1.14 |
| -3.34 | -5.458 | 0.201 | 1.26 | 1.20 |
| -4.17 | -5.607 | 0.256 | 1.76 | 1.66 |
| -4.97 | -5.740 | 0.310 | 1.85 | 1.69 |
| -5.73 | -5.861 | 0.365 | 1.97 | 1.73 |
| -6.78 | -6.011 | 0.438 | 2.56 | 2.19 |
| -7.40 | -6.122 | 0.493 | 1.95 | 1.45 |
| -8.07 | -6.232 | 0.548 | 1.89 | 1.20 |
| -8.72 | -6.343 | 0.602 | 2.09 | 1.17 |
| -9.34 | -6.458 | 0.657 | 2.40 | 1.17 |
| -9.94 | -6.582 | 0.712 | 2.29 | 0.60 |
| -10.52 | -6.719 | 0.767 | 2.20 | -0.15 |
| -11.09 | -6.876 | 0.822 | 2.70 | -0.73 |
| -11.45 | -6.998 | 0.858 | 3.60 | -0.97 |
| -11.63 | -7.069 | 0.876 | 3.82 | -1.57 |
| -11.81 | -7.148 | 0.895 | 3.85 | -2.63 |
| -11.98 | -7.237 | 0.913 | 4.15 | -3.80 |
| -12.16 | -7.336 | 0.931 | 4.64 | -5.35 |
| -12.33 | -7.438 | 0.949 | 6.23 | -6.34 |

**SATS16**   $B = 0.02008$   $\sigma = 0.01000$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.45 | -4.987 | 0.049 | 1.25 | 1.24 |
| -1.05 | -5.397 | 0.114 | 3.10 | 3.07 |
| -1.63 | -5.640 | 0.179 | 4.57 | 4.49 |
| -2.20 | -5.825 | 0.245 | 5.43 | 5.27 |
| -2.76 | -5.981 | 0.310 | 5.65 | 5.38 |
| -3.12 | -6.075 | 0.354 | 6.43 | 6.06 |
| -3.30 | -6.120 | 0.376 | 6.79 | 6.37 |
| -3.48 | -6.164 | 0.398 | 6.91 | 6.43 |
| -3.65 | -6.287 | 0.420 | 7.14 | 6.59 |
| -3.83 | -6.250 | 0.442 | 7.14 | 6.52 |
| -4.34 | -6.378 | 0.507 | 6.92 | 6.01 |
| -5.00 | -6.546 | 0.595 | 7.84 | 6.40 |
| -5.48 | -6.680 | 0.660 | 7.81 | 5.77 |
| -5.96 | -6.824 | 0.726 | 8.32 | 5.40 |
| -6.42 | -6.988 | 0.792 | 8.71 | 4.35 |
| -6.72 | -7.119 | 0.836 | 8.41 | 2.47 |
| -6.86 | -7.193 | 0.857 | 8.25 | 1.17 |
| -7.01 | -7.277 | 0.879 | 7.99 | -0.61 |
| -7.16 | -7.371 | 0.901 | 8.05 | -2.63 |
| -7.30 | -7.478 | 0.923 | 8.28 | -5.37 |
| -7.45 | -7.590 | 0.945 | 9.85 | -7.73 |

**SATS17**   $B = 0.01000$   $\sigma = 0.005000$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.15 | -5.024 | 0.033 | 4.58 | 4.58 |
| -0.36 | -5.438 | 0.075 | 6.55 | 6.53 |
| -0.57 | -5.674 | 0.119 | 7.49 | 7.43 |
| -0.78 | -5.845 | 0.162 | 7.66 | 7.55 |
| -0.98 | -5.982 | 0.206 | 7.75 | 7.56 |
| -1.18 | -6.100 | 0.250 | 7.73 | 7.44 |
| -1.38 | -6.204 | 0.293 | 7.68 | 7.26 |
| -1.58 | -6.300 | 0.337 | 7.68 | 7.10 |
| -1.78 | -6.390 | 0.381 | 7.54 | 6.77 |
| -1.98 | -6.475 | 0.425 | 7.94 | 6.93 |
| -2.17 | -6.558 | 0.468 | 8.46 | 7.17 |
| -2.36 | -6.640 | 0.512 | 8.58 | 6.95 |
| -2.55 | -6.722 | 0.556 | 8.85 | 6.80 |
| -2.74 | -6.806 | 0.600 | 9.08 | 6.51 |
| -2.93 | -6.892 | 0.644 | 9.16 | 5.93 |

| | | | | |
|---|---|---|---|---|
| -3.11 | -6.082 | 0.687 | 9.54 | 5.48 |
| -3.29 | -7.079 | 0.731 | 9.58 | 4.41 |
| -3.48 | -7.186 | 0.775 | 9.44 | 2.75 |
| -3.66 | -7.305 | 0.819 | 9.80 | 0.90 |
| -3.83 | -7.443 | 0.862 | 10.66 | -1.65 |
| -4.01 | -7.611 | 0.906 | 12.33 | -5.80 |
| -4.19 | -7.791 | 0.950 | 19.40 | -7.79 |

**SATS18**   $B = 0.004541$   $\sigma = 0.006460$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.82 | -6.111 | 0.140 | 10.87 | 10.71 |
| -1.26 | -6.371 | 0.215 | 10.67 | 10.30 |
| -1.69 | -6.570 | 0.290 | 10.83 | 10.12 |
| -2.12 | -6.744 | 0.365 | 9.77 | 8.59 |
| -2.54 | -6.901 | 0.440 | 10.31 | 8.54 |
| -2.96 | -7.055 | 0.515 | 9.79 | 7.21 |
| -3.37 | -7.206 | 0.590 | 10.34 | 6.67 |
| -3.79 | -7.361 | 0.665 | 12.00 | 6.81 |
| -4.20 | -7.532 | 0.740 | 13.08 | 5.54 |
| -4.60 | -7.728 | 0.815 | 15.27 | 3.72 |
| -5.00 | -7.973 | 0.890 | 19.42 | -0.32 |

**SATS19**   $B = 0.002500$   $\sigma = 0.01000$

| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.06 | -4.891 | 0.009 | 3.50 | 3.50 |
| -0.59 | -6.066 | 0.074 | 7.92 | 7.86 |
| -1.11 | -6.441 | 0.141 | 8.73 | 8.52 |
| -1.61 | -6.694 | 0.207 | 8.80 | 8.37 |
| -2.09 | -6.896 | 0.274 | 9.25 | 8.56 |
| -2.56 | -7.073 | 0.341 | 8.60 | 7.66 |
| -3.02 | -7.234 | 0.408 | 7.93 | 6.71 |
| -3.24 | -7.310 | 0.441 | 7.66 | 6.30 |
| -3.47 | -7.384 | 0.474 | 7.44 | 5.92 |
| -3.68 | -7.457 | 0.508 | 7.38 | 5.70 |
| -3.90 | -7.529 | 0.541 | 7.50 | 5.63 |
| -4.11 | -7.600 | 0.574 | 7.90 | 5.82 |
| -4.31 | -7.672 | 0.608 | 8.19 | 5.88 |
| -4.52 | -7.745 | 0.641 | 8.36 | 5.76 |
| -4.72 | -7.819 | 0.675 | 9.04 | 6.09 |
| -4.92 | -7.896 | 0.708 | 9.60 | 6.22 |
| -5.12 | -7.976 | 0.741 | 10.49 | 6.57 |
| -5.31 | -8.061 | 0.775 | 11.30 | 6.68 |
| -5.50 | -8.151 | 0.808 | 12.50 | 6.96 |
| -5.69 | -8.252 | 0.841 | 13.57 | 6.74 |

**SATS20**   $B = 0.004550$   $\sigma = 0.01331$

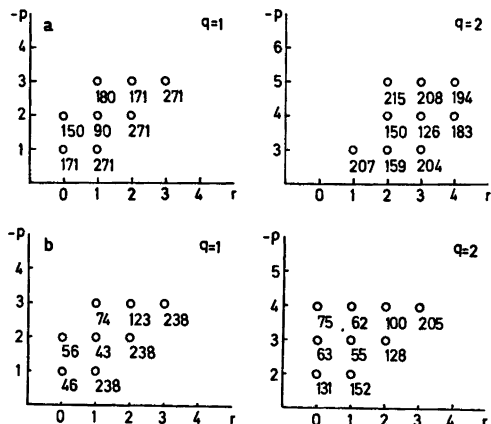| H | log h | z | $\Delta Z_0$ | $\Delta Z_1$ |
|---|---|---|---|---|
| -0.13 | -4.848 | 0.012 | 3.75 | 3.75 |
| -0.98 | -5.885 | 0.083 | 5.63 | 5.58 |
| -1.82 | -6.248 | 0.155 | 5.21 | 5.03 |
| -2.64 | -6.561 | 0.227 | 4.38 | 4.01 |
| -3.45 | -6.708 | 0.299 | 3.53 | 2.94 |
| -4.24 | -6.893 | 0.370 | 2.32 | 1.47 |
| -5.02 | -7.064 | 0.442 | 1.62 | 0.48 |
| -5.79 | -7.228 | 0.514 | 1.19 | -0.27 |
| -6.55 | -7.392 | 0.586 | 0.93 | -0.92 |
| -7.29 | -7.558 | 0.658 | 1.33 | -1.06 |
| -8.02 | -7.735 | 0.730 | 2.46 | -0.75 |
| -8.74 | -7.934 | 0.802 | 4.61 | -0.02 |
| -9.45 | -8.175 | 0.874 | 8.13 | 0.58 |
| -10.14 | -8.535 | 0.946 | 12.64 | -3.47 |

*Fig. 3.* LETAGROP-search for ternary $H_pNi_q(C_3H_5N_2)_r^{(2q+p+r)}$-complexes. The diagrams give error square sums $U(pr)_q \times 10^{-2}$ assuming only one complex. In the calculations the species $Ni_4OH_4^+$, $Ni(C_3H_4N_2)_n^{2+}$, ($n = 1, 2, 3, 4$) have been assumed to be known. a, shows the calculations in 3 M (NaClO$_4$ (387 points) and b, shows the calculations in 3 M (Na)Cl (327 points).

$$\beta'_{pqr} = \beta_{pqr}(1 + \beta_{010})^q \qquad (10)$$

where $\beta_{010} = K_1[Cl^-]$,           (11)

$\beta_{010}$ is constant provided [Cl$^-$] remains constant during the titration.

The values of $\beta'_{pqr}$ from the chloride medium are given in Table 4. As is seen from this table the values of the $\beta'_{pqr}$ constants are (usually) greater than those in the perchlorate medium indicating that $(H^+)_p(Ni^{2+})_q(C_3H_5N_2^+)_r(Cl^-)_s$ complexes are also formed.

## DISCUSSION

The present emf investigation has given clear evidence for the existence of a hydrolyzed nickel imidazole complex. $Ni(OH)C_3H_4N_2^+$, together with a series of stepwise metal complexes $Ni(C_3H_4N_2)_n^{2+}$, $n = 1,2,3,4$. No evidence for the formation of any polynuclear ternary complexes $Ni_q(OH)_p(C_3H_4N_2)_r^{(2q-p)+}$ was found.

The logarithms of the formation constants could be determined with an accuracy ($3\sigma$) greater than 0.02 for the stepwise complexes and greater than 0.05 for the hydrolyzed complex.

The behaviour of the nickel system differs a little from the corresponding copper system due to the fact that in the copper system polynuclear complexes are formed whereas in the nickel system no such complexes could be detected. However, in both systems a ternary hydrolyzed complex of the type
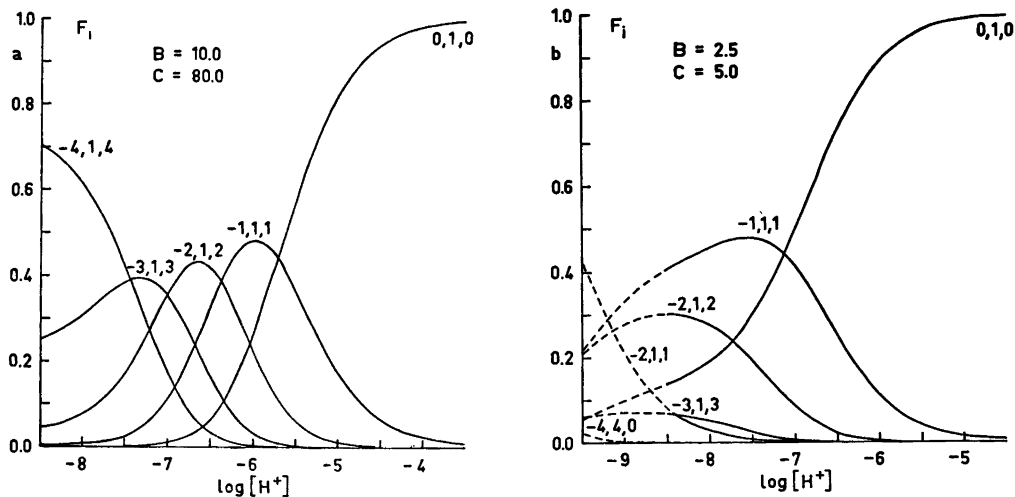


*Fig. 4.* Distribution diagrams $F_i$ (log [H$^+$])$_{B,C}$. $F_i$ is defined as the ratio between nickel(II) in a species and total nickel(II). The calculations have been performed using a version of the computer program SOLGAS [20] valid for equilibria in solution and equipped with a plotting procedure (Gunnar Eriksson, to be published). Broken lines denote ranges where no measurements have been performed due to precipitation (extrapolated range).

Me(OH)$C_3H_4N_2^+$ seems to be formed in a not negligible amount.

The logarithms of the formation constants are in 3 M (Na)$ClO_4$ log $\beta_{-211}$ (Ni(OH)$C_3H_4N_2^+$) = $-13.76$ and log $\beta_{-211}$ (Cu(OH)$C_3H_4N_2^+$) = $-10.44$. Thus the ternary complex in the copper system is more easily formed than the corresponding complex in the nickel system. Furthermore the chloride media seem to increase the stability in both systems.

The reason that no polynuclear complexes can be detected in the nickel system is probably due to the fact that at high $B$ concentrations, the available $-\log h$ range is too restricted to permit polynuclear complexes to be formed. The precipitated nickel hydroxoperchlorate and nickel hydroxochloride seem to be less soluble than the corresponding copper compounds.

By means of the present investigation it has also become possible to compare the acidities (tendency to hydrolyze) of the species Ni($H_2O)_x^{2+}$ and Ni($H_2O)_y(C_3H_4N_2)^{2+}$. For both the perchlorate and chloride media it was found that log $K_a$(Ni$C_3H_4N_2^{2+}$) $>$ log$K_a$(Ni$^{2+}$). The actual values of log $K_a$ are $-9.19$ [3 M (Na)$ClO_4$] and $-9.30$ [3 M (Na)Cl]. (*Cf.* log $K_a$(Ni$^{2+}$) $\leq -10.5$.) It seems that the introduction of an imidazole ligand increases the acidity of the nickel ion. The same effect is observed by Sjöberg in the copper(II) imidazole system.

With regard to the complexes in the Ni($C_3H_4N_2)_n^{2+}$ series we found that they could be well explained with a two-parameter approximation of the following type:

$$Ni(C_3H_4N_2)_n^{2+} + C_3H_4N_2 \rightleftharpoons Ni(C_3H_4N_2)_{n+1}^{2+},$$
$$n = 0, \cdots 3 \tag{12}$$
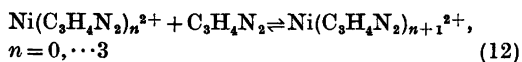
$$K_{n+1} = \frac{[Ni(C_3H_4N_2)_{n+1}^{2+}]}{[Ni(C_3H_4N_2)_n^{2+}][C_3H_4N_2]} \tag{13}$$

$K_{n+1} = K_0K^n$ where $K_0 = 10$ exp (3.34) M and $K = 10$ exp $(-0.55)$ in 3 M (Na)$ClO_4$ and $K_0 = 10$ exp (3.25) M and $K = 10$ exp $(-0.59)$ in 3 M (Na)Cl, respectively.

This two-parameter behaviour was also found in the copper imidazole system by Sjöberg and in 3 M (Na)$ClO_4$ he found $K_0 = 10$ exp (4.66) M and $K = 10$ exp $(-0.67)$.

By comparing the two systems we can see that the higher tendency for complex formation

in the copper system is reflected in a greater value of $K_0$ whereas the value of $K$ is greater in the nickel system, but, however, of the same order of magnitude.

In 3 M (Na)$ClO_4$, as well as in 3 M (Na)Cl medium, the following equilibrium could be established:

$$NiOH^+ + C_3H_4N_2 \rightleftharpoons NiOH(C_3H_4N_2)^+ \tag{14}$$

with log $K = 4.65$ in 3 M (Na)$ClO_4$ and log $K = 4.56$ in 3 M (Na)Cl.

Comparing these values with log $k$ for the following equilibrium

$$Ni^{2+} + C_3H_4N_2 \rightleftharpoons NiC_3H_4N_2^{2+} \tag{15}$$

with log $K_1 = 3.34$ in 3 M (Na)$ClO_4$ and log $K_1 = 3.25$ in 3 M (Na)Cl, we find that the hydrolyzed nickel ion is a stronger complexing agent than the corresponding hydrated nickel ion.

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Received January 14, 1975.