

# Metal Complexes with Mixed Ligands. 16. A Potentiometric Study of $\text{Ni}^{2+}$ – Imidazole and $\text{Ni}^{2+}$ – $\text{OH}^-$ – Imidazole in 1.0 M (Na)Cl Medium

WILLIS FORSLING

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Three component equilibria between nickel(II) imidazole ( $\text{C}_3\text{H}_4\text{N}_2$ ) and  $\text{OH}^-$  were studied by means of emf titrations at 25 °C in 1.0 M (Na)Cl with a glass electrode. The total nickel,  $B$ , and the total imidazole,  $C$ , were varied within the limits  $0.0017 \leq B \leq 0.050$  M and  $0.033 \leq C \leq 0.240$  M and the ratios  $C/B$  between  $0.20 \leq C/B \leq 20$ . At high  $C/B$  ratios, data can be explained with stepwise metal complexes  $\text{NiL}_n^{2+}$ , ( $L = \text{C}_3\text{H}_4\text{N}_2$ ),  $n = 1, 2, 3, 4$  and the following  $\log(\beta_n \pm 3\sigma)$  values could be determined:  $\log \beta_1 = 3.106 \pm 0.003$ ,  $\log \beta_2 = 5.541 \pm 0.009$ ,  $\log \beta_3 = 7.44 \pm 0.01$  and  $\log \beta_4 = 8.81 \pm 0.03$ . At lower  $C/B$  ratios, ternary complexes of the type  $\text{Ni}(\text{OH})\text{L}_n^+$  seem to be formed.

In separate titrations the  $\log K_a$ -value according to the reaction  $\text{HL}^+ \rightleftharpoons \text{H}^+ + \text{L}$  was found to be  $-7.215 \pm 0.001$ .

Data were analyzed with the least squares computer program LETAGROPVRID.

In part 10 of this series<sup>1</sup> the system nickel(II)–imidazole ( $\text{C}_3\text{H}_4\text{N}_2$ )– $\text{OH}^-$  was investigated in the two media 3.0 M (Na)ClO<sub>4</sub> and 3.0 M (Na)Cl. It was then found that besides the stepwise metal complexes  $\text{NiL}_n^{2+}$ ,  $n = 1, 2, 3, 4$ , data from both media can be explained by the ternary complex  $\text{Ni}(\text{OH})\text{L}^+$ . In a lower ionic medium, where the solubilities of the complexes are probably higher, greater amounts of the ternary species  $\text{Ni}_q(\text{OH})_p\text{L}_r^{(2q-p)+}$  should be obtained. The purpose of this investigation was to make use of this higher solubility to obtain a more accurate determination of the ternary hydrolytic species.

## EXPERIMENTAL

*Chemicals and analysis.* All solutions used were prepared and analyzed as described earlier.

*Apparatus.* The cell arrangement and experimental details of the emf measurements are fully described earlier.

*Method.* The titrations were performed as potentiometric titrations at 25 °C similar to those described in earlier papers.<sup>1</sup> The free hydrogen ion concentration,  $h$ , was varied by addition of hydroxide ions or hydrogen ions and measured with a glass electrode. A constant ionic medium of 1.0 M (Na)Cl was used to avoid activity coefficient variations. Both forward and backward titrations were performed to test reproducibility and reversibility of equilibria. Dilution experiments at constant  $Z$ -values were also carried out to obtain more data at the most interesting  $C/B$  ratios. Due to the formation of precipitates, the available  $-\log h$  range was restricted to an upper limit of 7–9. The mathematical analysis of data was performed with the least squares computer program LETAGROPVRID<sup>2</sup> (version ETITR).<sup>3</sup> On treating the emf data, the error squares sums  $U = \sum (Z_{\text{calc}} - Z_{\text{exp}})^2$  were minimized, where  $Z = (h - H)/C$ . The standard deviations were defined and calculated according to Sillén.<sup>4</sup> The computation was performed on a CYBER 172 computer.

## DATA, CALCULATIONS AND RESULTS

The acidity constant of  $\text{HL}^+$  in 1.0 M (Na)Cl,  $K_a$ , was determined by separate titrations comprising 6 different total imidazole concentrations within the range  $0.020 \leq C \leq 0.200$  M. Titrations were performed in both directions (decreasing and

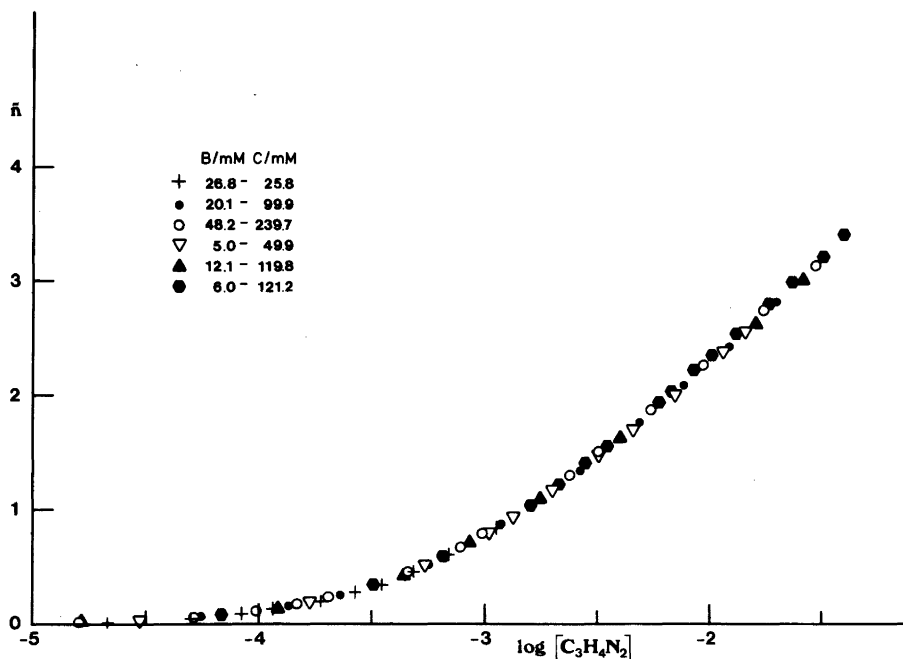


Fig. 1. Experimental data plotted as curves  $\bar{n}(\log[C_3H_4N_2])$  for mainly high  $C/B$  ratios and high  $C$  concentrations. In order to make the figure clear, only a few titrations have been plotted. The concentrations given are start concentrations.

increasing  $-\log h$ ) and the actual  $\log K_a$ -value according to the reaction



was found to be  $-7.215 \pm 0.001$ .

The analysis of experimental data was started by making a Bjerrum plot,  $\bar{n}(\log[L])$ . The plot including a part of the titration set is shown in Fig. 1. It is seen that at high quotients  $C/B$  the function  $\bar{n}(\log[L])$  seems to be independent of  $B$  and  $C$  thus indicating the formation of a series of stepwise metal complexes  $NiL_n^{2+}$ . However, at low  $\log [L]$  values even data with low  $C/B$  ratios fulfil these conditions, i.e. all titrations start with a mononuclear part. At quotients  $C/B < 10$  and at low total nickel(II) concentrations,  $B < 0.010$  M, the function  $\bar{n}(\log[L])$  is not independent of  $B$  and  $C$  (Fig. 2). This behaviour indicates that ternary hydrolytic species of the type  $Ni_q(OH)_p L_r^{(2q-p)+}$  are probably formed.

In the search for the ternary hydrolytic species it was assumed that the species  $NiL_n^{2+}$ ,  $n = 1, 2, 3, 4$ ,

were known and that the equilibrium constants had the values given in Table 1. The search was started with a  $pqr$ -analysis (systematic testing of different  $pqr$  complexes) on a representative part of data including 10 different  $C/B$  ratios with 140 experimental points. The result of the analysis is given in Fig. 3 and Table 1. It is seen from these calculations that the lowest error squares sum is obtained for the complex  $Ni(OH)L^+$ . Thus the calculation in this medium confirms the result from the earlier investigations in the 3.0 M  $(Na)ClO_4$  and 3.0 M  $(Na)Cl$  media.

However, remaining effects at high  $C/B$  quotients indicated the formation of another ternary hydrolytic species with a higher  $\bar{n}$ -value (more imidazole bound per nickel). Assuming two complexes, the best combination appeared to be  $Ni(OH)L^+$  and  $Ni(OH)L_3^+$ . The constants were later adjusted by a LETAGROP calculation on the whole data material, giving the final formation constants with standard deviations (Table 1). In order to visualize the amounts of the ternary complexes at some typical concentrations and  $C/B$  ratios, we have

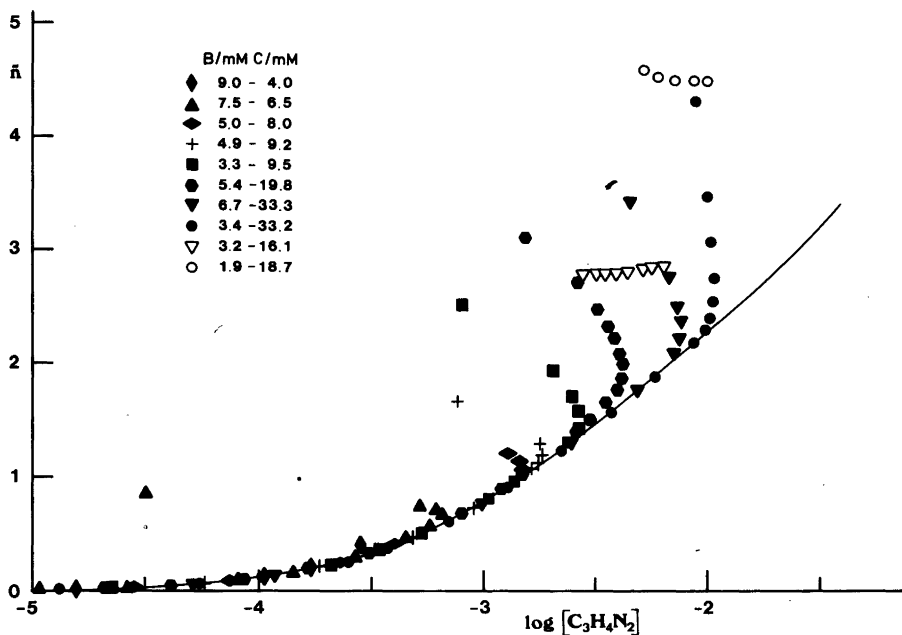


Fig. 2. Experimental data plotted as curves  $\bar{n}(\log[C_3H_4N_2])$  for mainly low  $C/B$  ratios and low  $B, C$  concentrations. Open symbols mark back titrations with pure ionic medium. The concentrations given are start concentrations. Only a few titrations have been plotted. The full curve represents the mononuclear curve with constants given in Table 1.

Table 1. Results of some final covariations of binary and ternary constants in the medium investigated. When no  $3\sigma(\log \beta_{pqr})$  is given, the formation constant has not been varied. The constants  $\beta_{pqr}$  are defined according to  $pH^+ + qNi^{2+} + rHL^+ \rightleftharpoons (H^+)_p(Ni^{2+})_q(HL^+)_r$ ;  $\beta_{pqr}$ . The results under the line refer to the data used in the calculation of the ternary hydrolytic species.

Number of titr./ Number of points	$\log \beta_{-101}$	$\log \beta_{-111}$	$\log \beta_{-212}$	$\log \beta_{-313}$	$\log \beta_{-414}$	$\log \beta_{-211}$	$\log \beta_{-413}$	$\sigma(Z)$	$U \times 10^{-2}$
	$\pm 3\sigma$	$\pm 3\sigma$	$\pm 3\sigma$	$\pm 3\sigma$	$\pm 3\sigma$	$\pm 3\sigma$	$\pm 3\sigma$	$\times 1000$	
6/191	-7.215 $\pm 0.001$							2.2	9.3
14/287	-7.215	-4.109 $\pm 0.003$	-8.889 $\pm 0.009$	-14.21 $\pm 0.02$	-20.05 $\pm 0.03$			1.8	8.7
10/140	-7.215	-4.109	-9.889	-14.21	-20.05	-13.33 $\pm 0.06$		4.2	23.9
10/140	-7.215	-4.109	-8.889	-14.21	-20.05	-13.40 $\pm 0.06$	-23.54 $\pm 0.16$	3.4	15.9
24/355	-7.215	-4.109	-8.889	-14.21	-20.05	-13.37 $\pm 0.04$	-23.68 $\pm 0.10$	3.4	39.9

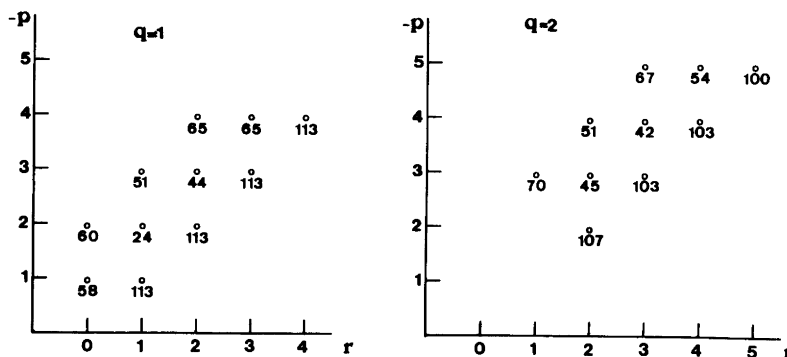


Fig. 3. LETAGROP-search for ternary  $H_pNi_q(C_3H_5N_2)_r^{(2q+p+n)+}$ -species. The diagrams give error square sums  $U(pr)_q \times 10^{-2}$  assuming only one complex. In the calculations  $Ni(C_3H_4N_2)_n^{2+}$ ,  $n=1 \dots 4$ , have been assumed to be known.

calculated a set of distribution diagrams, which are shown in Fig. 4. It can be seen from the diagrams that the amounts of  $Ni(OH)L^+$  and  $Ni(OH)L_3^+$  are rather low and about 10–15% of the total nickel is present as ternary species. No effects due to complexes other than those given in Table 1 were found.

## DISCUSSION

The present emf investigation has confirmed the existence of the hydrolyzed nickel imidazole complex,  $Ni(OH)L^+$ , together with a series of stepwise metal complexes  $NiL_n^{2+}$ ,  $n=1, 2, 3, 4$ . Data also indicated the formation of another ternary hydrolytic species  $Ni(OH)L_3^+$  at higher  $C/B$  quotients, but no evidence for the existence of any polynuclear ternary complexes  $Ni_q(OH)_pL_r^{(2q-p)+}$  was found.

Thus the higher solubility in this medium compared to 3.0 M (Na)Cl and 3.0 M (Na)ClO<sub>4</sub> media caused the appearance of greater amounts of the mononuclear ternary hydrolytic species, but the available  $-\log h$  and solubility range is still too limited to permit formation of polynuclear ternary hydrolytic species. To obtain these complexes in measurable amounts it seems necessary to exchange the imidazole ligand for another one, which fulfills the demands for the solubility and acidity strength.<sup>5</sup>

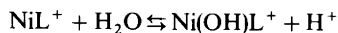
With regard to the stepwise metal complexes  $NiL_n^{2+}$ , it was found that they could be well explained with a two-parameter approximation of the following type:



equilibria of which, could be approximated with the two parameters  $K_0$  and  $K$ ,  $K_{n+1} = K_0 K^n$ , i.e.  $K_{n+1}/K_n = K$ .

In 3.0 M (Na)ClO<sub>4</sub> the actual values were  $\log(K_0 \pm 3\sigma) = -4.58 \pm 0.01$  and  $\log(K \pm 3\sigma) = -0.577 \pm 0.004$  and in 3.0 M (Na)Cl the parameters appeared to be  $\log(K_0 \pm 3\sigma) = -4.38 \pm 0.01$  and  $\log(K \pm 3\sigma) = -0.647 \pm 0.007$ . In this medium (1.0 M (Na)Cl) the corresponding constants are  $\log(K_0 \pm 3\sigma) = -4.13 \pm 0.003$  and  $\log(K \pm 3\sigma) = -0.605 \pm 0.004$ . The standard deviations of  $K_0$  and  $K$  are very low and the fit to experimental data is good. Furthermore, the agreement between stepwise constants determined with this method and with those obtained in ETITR calculations is remarkable (see Table 2).

Comparing the acidities (tendency to hydrolyze) of the species  $NiL(H_2O)_x^{2+}$  in the three media, it is found that  $\log K_a(NiL^+)$  related to the equilibrium



is of the same order.

(cf.  $-\log K_a = -9.19$  (3 M (Na)ClO<sub>4</sub>),  $-9.30$  (3 M (Na)Cl) and  $-9.26$  (1.0 M (Na)Cl)).

Unlike the investigations in 3.0 M (Na)ClO<sub>4</sub> and 3.0 M (Na)Cl, indications of two ternary species are obtained in this medium. This statement is clearly illustrated in Fig. 2, where the deviations from the mononuclear curve are great even at high quotients  $C/B$ . This behaviour was not found in the higher media, probably due to solubility reasons. As earlier mentioned, the calculations on the data

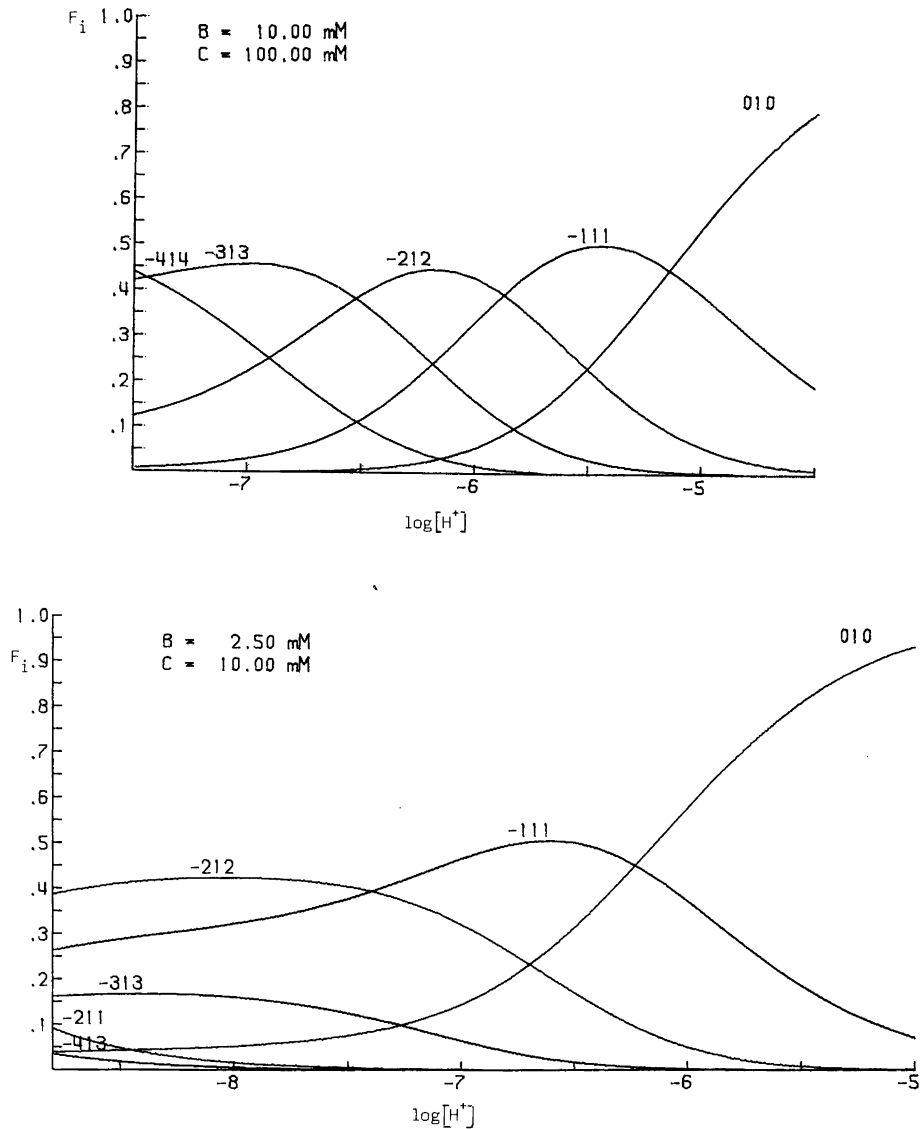


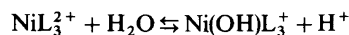
Fig. 4. Distribution diagrams  $F_i(\log[H^+])_{B,C}$ .  $F_i$  is defined as the ratio between nickel(II) in a species and total nickel(II). The calculations have been performed using a version of the computer program SOLGASWATER valid for equilibria in solution and equipped with a plotting procedure (Gunnar Eriksson: To be published).

material used in the *pqr*-analysis indicated that the species  $\text{Ni}(\text{OH})\text{L}_3^+$  together with  $\text{Ni}(\text{OH})\text{L}^+$  were obtained with the lowest error squares sum. However, when the whole data material was used to adjust the equilibrium constants, even the species  $\text{Ni}(\text{OH})\text{L}_2^+$  together with  $\text{Ni}(\text{OH})\text{L}^+$  "fitted" com-

paratively well, but as the equilibrium constant for  $\text{Ni}(\text{OH})\text{L}^+$  was considerably affected in the latter case and even obtained with larger standard deviations ( $\log \beta_{-211} = -13.47 \pm 0.07$ ), the species  $\text{Ni}(\text{OH})\text{L}_3^+$  is preferable. It is possible to establish the equilibrium

Table 2. LETAGROP calculations concerning the equilibria  $\text{Ni}^{2+} + n\text{HL}^+ \rightleftharpoons \text{NiL}_n^{2+} + n\text{H}^+$ ;  $\beta_{-n1n} = K_0^n \times K^{n(n-1)/2}$  with  $n=1, 2, 3, 4$  and  $\beta_{-n1n}$ -values obtained from the ETITR calculations.

Medium	$\log(\beta_{pqr} \pm 3\sigma)$				Ref.
	- 111	- 212	- 313	- 414	
3.0 M	-4.58	-9.74	-15.48	-21.80	
(Na)ClO <sub>4</sub>	-4.57 ± 0.01	-9.74 ± 0.01	-15.43 ± 0.01	-21.73 ± 0.03	1
3.0 M	-4.38	-9.41	-15.08	-21.41	
(Na)Cl	-4.39 ± 0.01	-9.42 ± 0.01	-15.05 ± 0.02	-21.47 ± 0.06	1
1.0 M	-4.13	-8.87	-14.21	-20.15	
(Na)Cl	-4.11 ± 0.01	-8.89 ± 0.01	-14.21 ± 0.02	-20.05 ± 0.03	



with  $\log K_a = -9.47$ . Evidently the species  $\text{NiL}_3^{2+}$  is an acid of the same order as  $\text{NiL}^{2+}$  (cf.  $\log K_a(\text{NiL}^{2+}) = -9.26$ ).

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