

On the Complex Formation of Nickel with Dimethylglyoxime

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The distribution of $^{63}\text{Ni}^{2+}$ at 25°C between chloroform and 0.1 M perchlorate solution has been studied as a function of the concentration of H^+ and of dimethylglyoxime (HA) in the aqueous phase. The data may be completely explained with the equilibria; $\text{NiA}_2 \rightleftharpoons \text{NiA}_2$ (in CHCl_3), $\log \lambda_2 = 2.51 \pm 0.10$; $\text{Ni}^{2+} + 2\text{HA} \rightleftharpoons \text{NiA}_2$ (in CHCl_3) + 2H^+ , $\log K = -1.17 \pm 0.10$. Previous solubility¹ and emf² data have been recalculated.

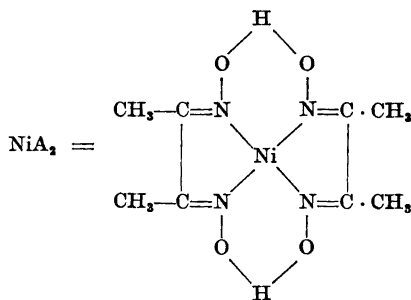
The present distribution data give no evidence for the presence of significant amounts of NiA^+ . By curve-fitting it is concluded that $\log K_1 \leq \log K_2 - 1.2$; the same conclusion is drawn from the solubility data¹. By using the value for $K_a(\text{HA})$ calculated from Ref¹, β_2 is obtained as 17.24 ± 0.07 (at $I = 0.10$) from the distribution data, and 17.23 ± 0.05 from the solubility data.

Charles and Freiser's emf data² would indicate $\log K_1 \sim 10.55$, $\log K_2 \sim 11.15$ in their medium, 50 % dioxane.

Dimethylglyoxime (HA) is a well-known reagent for nickel. The complex NiA_2 has a very low solubility in water but may be extracted, presumably as NiA_2 molecules, with organic solvents such as chloroform.

The crystal structure of NiA_2 (s) has been studied by Godycki and Rundle³ and its infrared spectrum by Rundle and Parasol⁴. The molecule is planar. There are two very strong, probably symmetrical, hydrogen bonds between the two A groups in each molecule, and metal-metal bonds between neighboring NiA_2 molecules. From a discussion of the properties of NiA_2 and a number of related compounds, Sharpe and Wakefield⁵ conclude, as was already suggested by Rundle^{3,4}, that the metal-metal bonds are the main factor in making NiA_2 insoluble.

It might be of interest to know to what extent the intermediate complex NiA^+ is formed in aqueous solution. Christopherson and Sandell¹ could explain their solubility data assuming only Ni^{2+} and NiA_2 in the aqueous phase; however, we shall see that their experiments were perhaps not ideally designed for a search for NiA^+ . On the other hand, Charles and Freiser²,



from pH measurements (presumably in 50 % dioxane-water), give complex formation constants K_1 and K_2 for $\text{A}^- - \text{Ni}^{2+}$, indicating $K_1 \sim 4K_2$. They point out, quite correctly, that a more accurate calculation of their data would give a lower K_1 and a higher K_2 .

To study the importance of NiA^+ , we have applied the distribution method (for surveys, see Rydberg ⁶, Dyrssen ⁷). In this case, we have measured how the distribution ratio, q , for Ni between chloroform and an aqueous solution varies with the concentrations $[\text{HA}]$ and $[\text{H}^+] = h$, in the aqueous solution.

GENERAL EQUATIONS

There is no evidence that the aqueous solutions with which we are concerned should contain Ni^{2+} and A^- in any species other than Ni^{2+} , NiA^+ , NiA_2 , A^- , and HA . With the usual definitions of the acidity constant, K_a , and the complex formation constants, $\beta_1 = K_1$ and $\beta_2 = K_1K_2$ we have:

$$[\text{A}^-] = K_a [\text{HA}] h^{-1}; [\text{NiA}^+] = \beta_1 [\text{Ni}^{2+}] [\text{A}^-]; [\text{NiA}_2] = \beta_2 [\text{Ni}^{2+}] [\text{A}^-]^2 \quad (1)$$

Our equations will be transformed to use h and $[\text{HA}]$ as variables; in general, $[\text{HA}]$ is more accurately known than $[\text{A}^-]$, since $[\text{HA}] \gg [\text{A}^-]$ in the solutions. We shall find it convenient to introduce an auxiliary variable, v , and a constant parameter, p :

$$v = [\text{A}^-]^{-1} \beta_2^{-\frac{1}{2}} = h [\text{HA}]^{-1} K_a^{-1} \beta_2^{-\frac{1}{2}}; p = \beta_1 \beta_2^{-\frac{1}{2}} = \sqrt{K_1/K_2} \quad (2)$$

The parameter, p , indicates the tendency towards formation of NiA^+ . In Dyrssen and Sillén's »two-parameter» notation ⁸, $\beta_1 = 10^{a+b}$, $\beta_2 = 10^{2a}$ and $p = 10^b$. If the distribution of A over the Ni atoms were statistical, one would have $p = 2$.

From (1) and (2) we may easily derive

$$\begin{aligned} [\text{Ni}^{2+}] &= [\text{NiA}_2] h^2 [\text{HA}]^{-2} \beta_2^{-1} K_a^{-2} = [\text{NiA}_2] v^2 \\ [\text{NiA}^+] &= [\text{NiA}_2] h [\text{HA}]^{-1} \beta_1 \beta_2^{-1} K_a^{-1} = [\text{NiA}_2] p v \end{aligned}$$

The total amount of Ni in the aqueous solution is thus

$$[\text{NiA}_2] + [\text{NiA}^+] + [\text{Ni}^{2+}] = [\text{NiA}_2] (1 + pv + v^2) \quad (3)$$

Solubility data. In Christopherson and Sandell's experiments¹, solutions of ionic strength 0.05 M were brought to equilibrium with NiA_2 (s) and HA (s) at 25°C. At equilibrium with these solids we have

$$[\text{HA}] = s_1 = \text{constant}; [\text{NiA}_2] = s_2 = \text{constant}$$

Thus the total solubility of NiA_2 in the solution is

$$S = [\text{NiA}_2] + [\text{NiA}^+] + [\text{Ni}^{2+}] = [\text{NiA}_2] (1 + pv + v^2) = s_2 (1 + pv + v^2) \quad (4a)$$

$$v = hs_1^{-1} K_a^{-1} \beta_2^{-\frac{1}{2}} = h \cdot \text{constant} \quad (4b)$$

To find the unknown constants we may plot the experimental data in a diagram $\log S$ ($\log h$) and move it along a family of standardized curves Y (X)

$$Y = \log (1 + pv + v^2); X = \log v \quad (5)$$

which may easily be constructed (Sillén⁹). From the curve that gives the best fit, one may obtain the parameter, p . From the positions of the coordinate axes at the best fit one obtains from (4) and (5).

$$\log S - Y = \log s_2; \log h - X = \log s_1 + \log K_a + \frac{1}{2} \log \beta_2 \quad (6)$$

Distribution data. When an aqueous solution with Ni^{2+} and HA is equilibrated with chloroform, the chloroform takes up NiA_2 and HA; the experiments have given no reason to assume any other species in the organic phase. Denoting by λ_2 the real equilibrium constant for the distribution of NiA_2 and by q the total distribution ratio for Ni, we have

$$[\text{NiA}_2]_{\text{org}} = \lambda_2 [\text{NiA}_2] = q([\text{NiA}_2] + [\text{NiA}^+] + [\text{Ni}^{2+}]) = q[\text{NiA}_2] (1 + pv + v^2) \quad (7)$$

This gives immediately

$$q^{-1} = \lambda_2^{-1} (1 + pv + v^2) \quad (8)$$

Since $v = h [\text{HA}]^{-1} \cdot \text{constant}$, (2), we may make a plot of $(-\log q)$ as a function of $\log (h [\text{HA}]^{-1})$ and compare it with the same family (5) of normalized curves as before, Y (X). From the position at the best fit we obtain

$$-\log q - Y = -\log \lambda_2; \log (h [\text{HA}]^{-1}) - X = \log K_a + \frac{1}{2} \log \beta_2 \quad (9)$$

Emf data. Charles and Freiser² made pH titrations in 50 % dioxane and calculated $\log [A^-]$ at the two points where \bar{n} , the average number of A bound per Ni, is 0.5 and 1.5. We have the equation

$$\bar{n} = \frac{2[\text{NiA}_2] + [\text{NiA}^+]}{[\text{NiA}_2] + [\text{NiA}^+] + [\text{Ni}^{2+}]} = \frac{2 + pv}{1 + pv + v^2} \quad (10)$$

From (10) we may derive the values for v where $\bar{n} = 0.5$ and 1.5:

$$v_{0.5} = (\sqrt{12 + p^2} + p)/2; v_{1.5} = (\sqrt{12 + p^2} - p)/6$$

$$v_{0.5}v_{1.5} = 1; v_{0.5}/v_{1.5} = (\sqrt{12 + p^2} + p)^2/4$$

Inserting the definition (2) of v we find

$$\log [A^-]_{0.5} + \log [A^-]_{1.5} = -\log \beta_2$$

$$\log [A^-]_{1.5} - \log [A^-]_{0.5} = 2 \log (\sqrt{12 + p^2} + p) - \log 4 \quad (11)$$

CHRISTOPHERSON AND SANDELL'S SOLUBILITY DATA

Christopherson and Sandell¹ determined the solubility at 25°C of HA(s) in dilute NaHCO₃-Na₂CO₃ buffers, or NaOH, of ionic strength 0.05(NaCl), and of NiA₂(s) in KCl-HCl mixtures of ionic strength 0.05, when saturated with HA(s), and also in some other solutions of pH between 5.6 and 8.9 and the same ionic strength, all saturated with HA(s). They gave the »pH» of the solution,

$$\text{»pH»} = -\log h - \log f$$

where f is the activity factor of the H⁺ ion. In the following we shall give the equilibrium constants as the concentration quotients at the corresponding ionic strength. As long as f remains constant (constant ionic strength), many of the conclusions are independent of any uncertainty that may exist in the f assumed.

For the solubility of HA, Christopherson and Sandell found a linear plot, solubility *versus* $(fh)^{-1}$, with the equation

$$\text{solubility} = 10^{-2.268} (1 + 10^{-10.585} (fh)^{-1})$$

Now it may easily be seen that the solubility is

$$[\text{HA}] + [\text{A}^-] = s_1 (1 + K_a h^{-1})$$

whence we deduce

$$s_1 = 10^{-2.268}; K_a = f^{-1} \cdot 10^{-10.585} (I = 0.05(\text{NaCl}))$$

The solubility, S , of NiA₂ is plotted in Fig. 1 as $\log S$ ($\log (fh)$). Over these experimental points is placed the family of curves, $Y(X)$, in the position of best fit. The full-drawn curve is the one calculated for $p = 0$, and the dotted one for $p = 1$. The broken lines are the asymptotes. It is readily seen that most of the experimental points are in parts where the curves differ very little on varying the value for p . Only one point is in the region with maximum influence of p , and thus of the intermediate complex NiA⁺, and this point

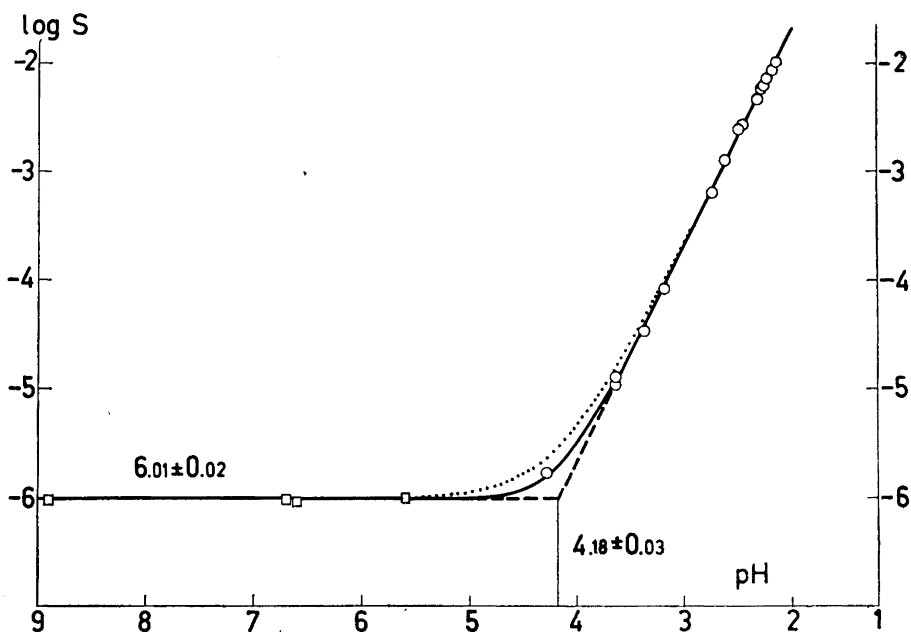


Fig. 1. Solubility of NiA_2 (25°C , $I = 0.05$, saturated with $\text{HA}(s)$) according to Christopherson and Sandell¹⁾. Experimental data: $\log S$ versus — "pH" = $\log h + \log f$. "Normalized curves" $Y(X)$, eqn. (5), in position of best fit, for $p = 0$ (full-drawn) and $p = 1$ (dotted). The broken lines are the asymptotes.

agrees well with $p \sim 0$. The data hence give no certain evidence for the existence of NiA^+ . Assuming $p = 0$, we obtain at the best fit (see eqn. 6):

$$\log S - Y = -6.01 \pm 0.02 = \log s_2$$

$$\log(fh) - X = -4.18 \pm 0.03 = \log s_1 + \log K_a + \frac{1}{2} \log \beta_2 + \log f$$

Combining this with the above values for s_1 and K_a we obtain

$$\log s_2 = -6.01 \pm 0.02; \log \beta_2 = 17.35 \pm 0.04 (I = 0.05)$$

It may be noted that the value for β_2 is independent of any uncertainty in f ; so is the conclusion that $p \sim 0$.

We might have obtained the same result and the following equation for S by using for the two constants average values from the data near to each of the asymptotes

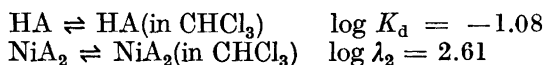
$$S = 10^{-6.013} + 10^{+2.340} (fh)^2 = [\text{NiA}_2] + [\text{Ni}^{2+}]$$

Applying the activity factors given by Kielland¹⁰ for the ions, and by Christopherson and Sandell¹ for the uncharged species, we may calculate, from their data, the following equilibrium constants for the ionic strengths 0, 0.05, and 0.10:

		$I = 0$	$I = 0.05$	$I = 0.10$
$\text{HA(s)} \rightleftharpoons \text{HA}$	$\log s_1 =$	- 2.26	- 2.27	- 2.28
$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$	$\log K_a =$	- 10.67	- 10.52	- 10.46
$\text{NiA}_2(\text{s}) \rightleftharpoons \text{NiA}_2$	$\log s_2 =$	- 6.00	- 6.01	- 6.03
$\text{Ni}^{2+} + 2\text{A}^- \rightleftharpoons \text{NiA}_2$	$\log \beta_2 =$	17.83	17.35	17.23

Reference¹ seems to have used the activity factors for 0.025 M instead of 0.05 M, which is easily done since Kielland's table gives f as a function of $2I$.

For distribution between chloroform and water, Christopherson and Sandell¹ moreover give



In water, saturated with CHCl_3 , the equilibrium constants may differ slightly from those in aqueous solution free from CHCl_3 . For instance, in the presence of CHCl_3 , $\log s_2 = -5.92$.

DISTRIBUTION EXPERIMENTS

Experimental. The experiments were made in a room thermostated at 25°C. All the reagents used were of analytical grade, and the chloroform was made alcohol-free by washing it with water. The ionic strength was kept constant at 0.1 M using HClO_4 , NaClO_4 , and NaOH . In some experiments, small amounts of acetate (≤ 0.01 M) were added to buffer the aqueous phase.

The distribution ratio, q , was measured using ^{63}Ni (half-life 80 years, 0.063 MeV β). The two phases had equal volumes, 15 ml. HA and Ni^{2+} were originally present in the aqueous phase, at concentrations $[\text{HA}]_{\text{total}} = 0.001$ to 0.0032, and $[\text{Ni}]_{\text{tot}} = 1.30 \times 10^{-4}$ M. After equilibration and separation of the phases, 1 ml of the chloroform phase was taken out, evaporated in a cup of stainless steel, and counted in a Tracerlab Flow Proportional Counter SC-16. The aqueous phase could not be evaporated directly, since it contained NaClO_4 ; to 5 ml aqueous phase, ammonia was added to $\text{pH} \sim 9$, and the nickel was extracted with 5 ml of chloroform, 1 ml of which was then evaporated, and the Ni counted as before.

In the aqueous phase, $[\text{H}^+] = h$ was measured with a glass electrode and a Radiometer pHM3i valve potentiometer, standardized against 0.01 M HClO_4 + 0.09 M NaClO_4 . To obtain the real $[\text{HA}]$ in the aqueous phase, from the $[\text{HA}]_{\text{tot}}$ added originally, it was necessary to introduce corrections for $[\text{HA}]_{\text{org}}$ and in some parts of the experimental range also for $[\text{A}^-]$ and $[\text{NiA}_2]_{\text{org}}$. The amounts of NiA_2 and NiA^+ in the aqueous phase were always negligible in comparison to $[\text{HA}]_{\text{tot}}$. We easily obtain

$$[\text{HA}] = ([\text{HA}]_{\text{tot}} - 2[\text{Ni}]_{\text{tot}} q(1 + q)^{-1}) (1 + K_d + K_a h^{-1})^{-1}.$$

The values for K_d and K_a were taken from Christopherson and Sandell's data¹. K_d is small, only 1/12, and any slight error in it will mean only a constant shift along the $\log(h[\text{HA}]^{-1})$ axis. The correction for K_a is negligible for most points, and the exceptions are not in the critical part of the curve.

The data ($[\text{HA}]_{\text{tot}}$, $\log h$, $\log q$) are given in Table 1; Fig 2 gives $(\log q)$ as a function of $(\log h - \log [\text{HA}])$. As in Fig 1, the calculated curves for $Y(X)$ with $p = 0$ (full-drawn) and $p = 1$ (dotted), and the asymptotes (broken) are given in the position of best fit. The spread is seen to be greater than for the solubility measurements, which is due to the difficulty of measuring dry samples with the very weak α -emitter ^{63}Ni (0.063 MeV). On the other hand, a much larger number of experimental points has been placed in the critical region from which the value of p can be deduced. As seen from Fig. 2, the data agree, within the experimental error, with the curve for $p = 0$, and thus give no evidence for the existence of NiA^+ in appreciable amounts.

From the position at the best fit we find, using points close to the asymptotes

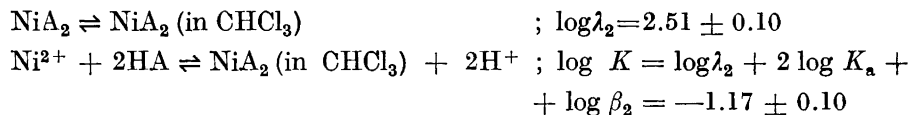
$$q^{-1} = 10^{-2.51} + 10^{1.17} (h/[\text{HA}])^2$$

We may also read directly (see eqn. 9)

$$-\log q - Y = -\log \lambda_2 = -2.51 \pm 0.10$$

$$(\log h - \log [\text{HA}]) - X = \log (h/[\text{HA}]v) = \log K_a + \frac{1}{2} \log \beta_2 = -1.84 \pm 0.07$$

which gives, for 25°C and $I = 0.1$, the following equilibrium constants:



Inserting the value $\log K_a = -10.46$, calculated from the solubility data¹, we obtain

$$\text{Ni}^{2+} + 2\text{A}^- \rightleftharpoons \text{NiA}_2 ; \log \beta_2 = 17.24 \pm 0.07$$

which is seen to agree very well with the estimate from the solubility data¹, 17.23.

The crossed and solid symbols in Fig. 2 denote experiments where up to 0.01 M acetate was added for buffering. A comparison with the open symbols indicates that the acetate had no perceptible influence, which is reasonable in view of the equilibrium constants given by Fronaus¹¹ ($\log K_1 \sim 0.7$, $\log \beta_2 \sim 1.25$ for $\text{Ac}^- \text{-Ni}^{2+}$ in 1 M NaClO_4 at 20°C).

Estimates of p and K_1

We have seen from Figs. 1 and 2 that both the solubility and the distribution data, when plotted and compared with «normalized curves», $Y(X)$, give good agreement with the curve for $p = 0$. A deviation of p from the value 0

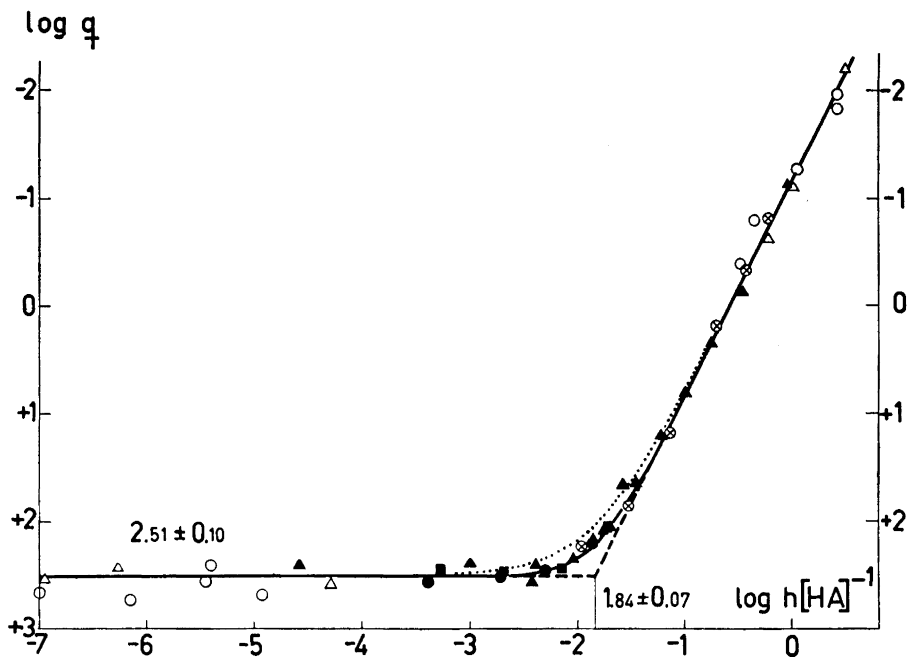


Fig. 2. Distribution data (present work). Experimental points: $(-\log q)$, distribution ratio, versus $(\log h - \log [\text{HA}])$. "Normalized curves" $Y(X)$ in position of best fit, for $p = 0$ (full-drawn) and $p = 1$ (dotted). The broken lines are the asymptotes.

Table 1. Distribution of Ni^{2+} between chloroform and 0.1 M perchlorate solutions at 25°C. Initial concentrations in the aqueous phase $[\text{Ni}]_{\text{tot}} = 1.30 \times 10^{-4}$ M, $[\text{HA}]_{\text{tot}} = 0.0032$ (\circ \otimes \bullet), 0.002 (\blacksquare) or 0.001 (\triangle \blacktriangle) M. Acetate concentrations: 0 (\circ , \triangle), 0.004 (\otimes), or 0.010 (\bullet , \blacksquare , \blacktriangle) M.

$\log q$	$-\log h$	$\log q$	$-\log h$	$\log q$	$-\log h$
0.0032 M HA, \circ		0.0032 M HA, \bullet		0.001 M HA, \blacktriangle	
- 1.962	2.12	+ 2.214	4.44	- 1.066	3.09
- 1.830	2.12	+ 2.464	4.88	- 0.130	3.55
- 1.255	2.49	+ 2.521	5.30	+ 0.339	3.88
- 0.793	2.89	+ 2.560	5.96	+ 0.812	4.15
- 0.388	3.03	0.002 M HA, \blacksquare		+ 1.200	4.38
+ 2.675	7.50	+ 2.049	4.52	+ 1.636	4.62
+ 2.409	7.97	+ 2.438	4.95	+ 1.660	4.75
+ 2.555	8.02	+ 2.467	5.48	+ 2.042	4.87
+ 2.727	8.74	+ 2.447	6.07	+ 2.078	4.92
+ 2.658	9.81	0.001 M HA, \triangle		+ 2.162	5.03
0.0032 M HA, \otimes		- 2.206	2.45	+ 2.358	5.23
- 0.806	2.75	- 1.095	3.03	+ 2.397	5.56
- 0.328	2.97	- 0.626	3.29	+ 2.564	5.59
+ 0.194	3.24	+ 2.566	7.46	+ 2.383	6.17
+ 1.182	3.70	+ 2.432	9.47	+ 2.391	7.75
+ 1.864	4.10	+ 2.531	10.32		
+ 2.244	4.54				

would cause the largest deviation in the curve at the abscissa corresponding to $X = 0$ (intersection point of the asymptotes). Here, $Y = \log(2 + p)$, as seen from eqn. (5). From the data it may be estimated that the deviation from the curve with $p = 0$, denoted by Δ by Dyrssen and Sillén⁸, is probably less than 0.05:

$$\Delta = \log(2 + p) - \log 2 \leq 0.05$$

thus $p \leq 0.25$, or $\log K_1 \leq \log K_2 - 1.2$

From Charles and Freiser's data² for 50 % dioxane (25° to 39.6°C) we obtain, using eqns. (11)

$$\log \beta_2 = -\log([A^-]_{0.5}[A^-]_{1.5}) = 21.7 \pm 0.1$$

$$\log([A^-]_{1.5}/[A^-]_{0.5}) = 2 \log(\sqrt{12 + p^2} + p) - \log 4 = 0.60 \pm 0.02$$

thus $p = 0.5 \pm 0.1$, $\log K_1 \sim 10.55$, $\log K_2 \sim 11.15$ (in 50 % dioxane)

Charles and Freiser have also measured the complex formation between Ni^{2+} and the O-monomethyl ether of dimethylglyoxime, HA_{Mc} in 50 % dioxane at 25°C. Applying the same eqns. (11) to their single set of $[A_{Mc}^-]$ values, we obtain

$$\text{for } A_{Mc}^- - Ni^{2+}: \beta_2 = 12.07; 2 \log(\sqrt{12 + p^2} + p) - \log 4 = 0.69$$

thus $p \sim 0.85$, $\log K_1 = 5.97$, $\log K_2 = 6.10$

Accordingly we would have for $A_{Mc}^- - Ni^{2+}$, $K_1 \sim 10^{6.0}$ and $K_2 \sim 10^{6.1}$. Even in this case, the second complex would be favored since p is less than the »statistical» value, 2. This is remarkable, since with A_{Mc}^- the formation of the second complex cannot be favored by hydrogen bonds as with A^- . The great difference makes one suspect for a moment that there might be in the aqueous phase a complex where Ni is bound to the doubly charged ion of HA; we might formally write this complex as $NiH_{-1}A$, and it could have no counterpart with HA_{Mc} . For such a complex we would have



In the solubility experiments, with $[HA] = \text{constant}$, considerable amounts of such a complex might have passed as » NiA_2 ». In the distribution experiments, however, it would make q shift with $[HA]$, whereas really q is found to be a function of $h/[HA]$ only, so this complex does not seem to be important.

On the other hand, one might disbelieve completely the p obtained from Charles and Freiser's data but still put some confidence in their β_2 . Estimating that K_1 for A_{Mc}^- is $\sim 10^6$ and that K_1 for A^- has the same order of magnitude, we would have K_2 for A^- about 10^{16} , and $p \sim 10^{-5}$, in 50 % dioxane. This is, however, a very uncertain estimate.

Returning to our first treatment: if Charles and Freiser's data² are taken at their face value, the first complex of the methyl ether, A_{Mc}^- , would be much

less stable than that of A^- . One possible reason is a steric hindrance, or strain in the chelate ring caused by the CH_3 group. It would be interesting to know the crystal structure of $Ni(A_{Mc})_2$, and also to have more accurate equilibrium data on the $A_{Mc}^-Ni^{2+}$ complexes.

The only conclusion that the present data allow us to draw about p for A^-Ni^{2+} in aqueous solution is that it is certainly less than 1, and probably less than 0.25. At any rate, p is thus less than would be expected from a statistical distribution of A^- over Ni^{2+} ions: 2.0 at $I = 0$, 1.65 at $I = 0.05$, and 1.55 at $I = 0.10$, corrected with Kielland's activity coefficients¹⁰.

Finally, we should like to remark that the quite good agreement of the experimental data with the calculated curve over a wide range of concentrations has added to our confidence in the distribution method as a way of studying equilibria. If there had been any serious systematic errors, they would have been likely to show up in this very simple system which contains only two adjustable parameters, λ_2 and the product $K_a^2\beta_2$.

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