On the Complex Formation of Nickel with Dimethylglyoxime

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The distribution of $^{65}\text{Ni}^{2+}$ at 25°C between chloroform and 0.1 M perchlorate solution has been studied as a function of the concentration of $\text{H}^+$ and of dimethylglyoxime (HA) in the aqueous phase. The data may be completely explained with the equilibria; $\text{NiA}_2 \rightleftharpoons \text{NiA}_4$ (in CHCl$_3$), log $\lambda_1 = 2.51 \pm 0.10$; $\text{Ni}^{2+} + 2\text{HA} \rightleftharpoons \text{NiA}_4$ (in CHCl$_3$) + 2H$^+$, log $K = -1.17 \pm 0.10$. Previous solubility$^1$ and emf$^2$ 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 $\log K_1 \leq \log K_4 - 1.2$; the same conclusion is drawn from the solubility data$^1$. By using the value for $K_9$(HA) calculated from Ref$^1$, $\beta_9$ is obtained as $17.24 \pm 0.07$ (at $I = 0.10$) from the distribution data, and $17.23 \pm 0.05$ from the solubility data.

Charles and Freiser’s emf data$^4$ would indicate $\log K_1 \sim 10.55$, $\log K_4 \sim 11.15$ 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 Rundle$^9$ and its infrared spectrum by Rundle and Parasol$^4$. 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 Wakefield$^5$ 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 Sandell$^1$ 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 Freiser$^2$. 

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from pH measurements (presumably in 50% dioxane-water), give complex formation constants $K_1$ and $K_2$ for $\Lambda^-\text{Ni}^{2+}$, indicating $K_1 \approx 4K_2$. 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 8, Dyrrsen 7). In this case, we have measured how the distribution ratio, $q$, for Ni between chloroform and an aqueous solution varies with the concentrations [HA] and [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 $\Lambda^-$ in any species other than Ni$^{2+}$, NiA$^+$, NiA$_2$, $\Lambda^-$, 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:

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

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

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

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

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

$$[\text{Ni}^{2+}] = [\text{NiA}_2]h^2[HA]^{-2}\beta_2^{-1}K_a^{-2} = [\text{NiA}_2]v^2$$

$$[\text{NiA}^+] = [\text{NiA}_2]h[HA]^{-1}\beta_1\beta_2^{-1}K_a^{-1} = [\text{NiA}_2]pv$$

*Acta Chem. Scand.* 13 (1959) No. 1
The total amount of Ni in the aqueous solution is thus

\[ [\text{NiA}_2] + [\text{Ni}^\cdot] + [\text{Ni}^{2+}] = [\text{NiA}_2] (1 + pv + v^2) \]  \hspace{1cm} (3)

**Solubility data.** In Christopherson and Sandell's experiments\(^1\), 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

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

Thus the total solubility of NiA\(_2\) in the solution is

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

\[ v = h s_1^{-1} K_a^{-1} \beta_2^{-\frac{1}{2}} = h \cdot \text{constant} \]  \hspace{1cm} (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 \( Y (X) \)

\[ Y = \log (1 + pv + v^2); \quad X = \log v \]

which may easily be constructed (Sillén\(^9\)). 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).

\[ \log S = \log s_2; \quad \log h = X = \log s_1 + \log K_a + \frac{1}{2} \log \beta_2 \]  \hspace{1cm} (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 \( \lambda_2 \) the real equilibrium constant for the distribution of NiA\(_2\) and by \( q \) the total distribution ratio for Ni, we have

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

This gives immediately

\[ q^{-1} = \lambda_2^{-1} (1 + pv + v^2) \]  \hspace{1cm} (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

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

**Emf data.** Charles and Freiser\(^2\) made pH titrations in 50% dioxane and calculated \( \log [\text{A}^-] \) 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

\[ \bar{n} = \frac{2 [\text{NiA}_2] + [\text{Ni}^\cdot]}{[\text{NiA}_2] + [\text{Ni}^\cdot] + [\text{Ni}^{2+}]} = \frac{2 + pv}{1 + pv + v^2} \]  \hspace{1cm} (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

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

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

(11)

**CHRISTOPHERSON AND SANDELL'S SOLUBILITY DATA**

Christopherson and Sandell\(^1\) determined the solubility at 25°C of HA(s) in dilute NaHCO\(_3\)-Na\(_2\)CO\(_3\) buffers, or NaOH, of ionic strength 0.05(NaCl), and of NiA\(_2\)(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 \(\nu\text{pH}\) of the solution,

\[
\nu\text{pH} = -\log h - \log f
\]

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 \((1/h)^{-1}\), with the equation

\[
\text{solubility} = 10^{-2.268} (1 + 10^{-10.585} (1/h)^{-1})
\]

Now it may easily be seen that the solubility is

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

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 NiA\(_2\) is plotted in Fig. 1 as log $S$ (log $(1/h)$). 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

*Acta Chem. Scand.* 13 (1959) No. 1
Fig. 1. Solubility of NiA₄ (25°C, I = 0.05, saturated with HA(s)) according to Christopherson and Sandell 1). Experimental data: log S versus -"pH" = log k + 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 ~ 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):

\[ \log S - Y = -6.01 \pm 0.02 = \log s_2 \]
\[ \log (f'h) - X = -4.18 \pm 0.03 = \log s_1 + \log K_a + \frac{1}{2} \log \beta_2 + \log f \]

Combining this with the above values for s₁ and Kₐ 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 \( \beta_2 \) 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

\[ S = 10^{-6.013} + 10^{+2.340} (f'h)^2 = [\text{NiA}_2] + [\text{Ni}^{2+}] \]
Applying the activity factors given by Kielland for the ions, and by Christopherson and Sandell for the uncharged species, we may calculate, from their data, the following equilibrium constants for the ionic strengths 0, 0.05, and 0.10:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activity Factor</th>
<th>$I = 0$</th>
<th>$I = 0.05$</th>
<th>$I = 0.10$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA(s) $\rightleftharpoons$ HA</td>
<td>$s_1 = 0$</td>
<td>-2.26</td>
<td>-2.27</td>
<td>-2.28</td>
</tr>
<tr>
<td>HA $\rightleftharpoons$ H$^+$ + A$^-$</td>
<td>$K_a = 10^{-10.57}$</td>
<td>-10.57</td>
<td>-10.52</td>
<td>-10.46</td>
</tr>
<tr>
<td>NiA$_2$(s) $\rightleftharpoons$ NiA$_2$</td>
<td>$s_2 = 0$</td>
<td>-6.00</td>
<td>-6.01</td>
<td>-6.03</td>
</tr>
<tr>
<td>Ni$^{2+}$ + 2A$^-$ $\rightleftharpoons$ NiA$_2$</td>
<td>$\beta_2 = 17.83$</td>
<td>17.83</td>
<td>17.35</td>
<td>17.23</td>
</tr>
</tbody>
</table>

Reference 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 Sandell moreover give

$$ HA \rightleftharpoons HA$(in CHCl$_3$) \qquad log $K_A = -1.08$

$$ NiA$_2$ $\rightleftharpoons$ NiA$_2$(in CHCl$_3$) \qquad log $\lambda_2 = 2.61$

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$_3$, $s_2 = -5.92$.

**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 ($\leq 0.01$ M) were added to buffer the aqueous phase.

The distribution ratio, $q$, was measured using $^{63}$Ni (half-life 80 years, 0.063 MeV $\beta$). The two phases had equal volumes, 15 ml. HA and Ni$^{2+}$ were originally present in the aqueous phase, at concentrations $[HA]_{\text{total}} = 0.001$ to 0.0032, and $[Ni]_{\text{tot}} = 1.30 \times 10^{-4}$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 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, $[H^+] = h$ 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 $[HA]$ in the aqueous phase, from the $[HA]_{\text{tot}}$ added originally, it was necessary to introduce corrections for $[HA]_{\text{org}}$ and in some parts of the experimental range also for $[A^-]$ and $[NiA_2]_{\text{org}}$. The amounts of NiA$_2$ and NiA$_2^+$ in the aqueous phase were always negligible in comparison to $[HA]_{\text{tot}}$. We easily obtain

$$ [HA] = ([HA]_{\text{tot}} - 2 [Ni]_{\text{tot}} q(1 + q)^{-1}) (1 + K_d + K_a h^{-1})^{-1}.$$
The values for $K_d$ and $K_a$ were taken from Christopherson and Sandell's data. $K_d$ is small, only $1/12$, and any slight error in it will mean only a constant shift along the log $(h/[HA])^{-1}$ 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 ([HA]$_{tot}$, log $h$, log $q$) are given in Table 1; Fig 2 gives (log $q$) as a function of (log $h$ — log [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 a-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

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

We may also read directly (see eqn. 9)

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

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

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

$\text{NiA}_2 \rightleftharpoons \text{NiA}_2 \text{ (in CHCl}_3) ; \log \lambda_2 = 2.51 \pm 0.10$

$\text{Ni}^{2+} + 2\text{HA} \rightleftharpoons \text{NiA}_2 \text{ (in CHCl}_3) + 2\text{H}^+ ; \log K = \log \lambda_2 + 2 \log K_a + \log \beta_2 = -1.17 \pm 0.10$

Inserting the value $\log K_a = -10.46$, calculated from the solubility data, 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 data, 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 Fromansus $^{11}$ (log $K_1 \sim 0.7$, log $\beta_2 \sim 1.25$ for Ac$^-\text{-Ni}^{2+}$ in 1 M NaClO$_4$ at $20^\circ$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

*Acta Chem. Scand.* 13 (1959) No. 1
**Complex Formation of Nickel**

Fig. 2. Distribution data (present work). Experimental points: \((−\log q)\) distribution ratio, versus \((\log h − \log [HA])\). "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 \(\text{Ni}^{2+}\) between chloroform and 0.1 M perchlorate solutions at 25\(^\circ\)C. Initial concentrations in the aqueous phase \([\text{Ni}]_{\text{tot}} = 1.30 \times 10^{-4} \text{ M}, [\text{HA}]_{\text{tot}} = 0.0032 \text{ (O } \otimes \text{ ●), 0.002 (□) or 0.001 (△ ▲) M. Acetate concentrations: 0 \text{ (O, △), 0.004 (□), or 0.010 (●, ▲) M.}\)

<table>
<thead>
<tr>
<th>(\log q)</th>
<th>(- \log h)</th>
<th>(\log q)</th>
<th>(- \log h)</th>
<th>(\log q)</th>
<th>(- \log h)</th>
</tr>
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<tbody>
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<td>0.0032 M HA, O</td>
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<td>5.96</td>
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<td>10.32</td>
<td>+2.391</td>
<td>7.75</td>
</tr>
</tbody>
</table>

*Acta Chem. Scand. 13 (1959) No. 1*
would cause the largest deviation in the curve at the abcissa 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 \( \Delta \) by Dyrrsen and Sillén \( ^8 \), 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 data \( ^2 \) for 50 \% dioxane (25° to 39.6°C) we obtain, using eqns. (11)

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

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

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 \( \text{Ni}^{2+} \) and the O-monomethyl ether of dimethylglyoxime, \( \text{HA}\text{Me} \), in 50 \% dioxane at 25°C. Applying the same eqns. (11) to their single set of \( [\text{A}\text{Me}] \) values, we obtain

for \( \text{A}\text{Me}^- - \text{Ni}^{2+} \): \( \beta_2 = 12.07 \); \( 2 \log (\sqrt[12]{12} + p^2 + p) - \log 4 = 0.69 \)

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

Accordingly we would have for \( \text{A}\text{Me}^- - \text{Ni}^{2+} \), \( K_1 \sim 10^{6.0} \) and \( K_2 \sim 10^{6.1} \). Even in this case, the second complex would be favored since \( p \) is less than the \( \approx \text{statistical} \) value, 2. This is remarkable, since with \( \text{A}\text{Me}^- \), the formation of the second complex cannot be favored by hydrogen bonds as with \( \text{A}^- \). 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 \( \text{NiH}_2\text{A} \), and it could have no counterpart with \( \text{HA}\text{Me} \). For such a complex we would have

\[
[\text{NiH}_2\text{A}] = K [\text{NiA}_2] [\text{HA}]^{-1}
\]

In the solubility experiments, with \( [\text{HA}] = \text{constant} \), considerable amounts of such a complex might have passed as \( \text{NiA}_2 \). In the distribution experiments, however, it would make \( q \) shift with \( [\text{HA}] \), whereas really \( q \) is found to be a function of \( k/[\text{HA}] \) 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 \( \beta_2 \). Estimating that \( K_1 \) for \( \text{A}\text{Me}^- \) is \( \sim 10^6 \) and that \( K_1 \) for \( \text{A}^- \) has the same order of magnitude, we would have \( K_2 \) for \( \text{A}^- \) 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 data \( ^2 \) are taken at their face value, the first complex of the methyl ether, \( \text{A}\text{Me}^- \), 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(AM\(_{14}\))\(_2\), and also to have more accurate equilibrium data on the AM\(_{14}\)—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 coefficients\(^\text{10}\).

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, \(\lambda_2\) and the product \(K_2^2\beta_2\).

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