Studies on Cobalt(II) Halide Complex Formation. I.
A Spectrophotometric Study of the Chloro Cobalt(II) Complexes
in Strong Aqueous Chloride Solutions

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In this paper the stability constants for the chloro cobalt(II) complexes are estimated from
spectrophotometric measurements on solutions of HCl, LiCl and CaCl₂. It was shown that in a
certain wavelength range (610–690 nm), and for chloride concentrations higher than ≈ 5 M,
the fraction of tetrachloro complex \( a_4 \) could be calculated from the relation \( a_4 = \varepsilon / \varepsilon_0 \), where \( \varepsilon_0 \) is the limiting molar absorbivity for the most
concentrated solutions of LiCl and HCl. Activity corrections were included semiquantita-
tively by introducing a one parameter activity function: \( \alpha_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{\beta_{\text{Cl}^-} \cdot [\text{Cl}^-]} \) adjusted to
the measurements and assumed to be valid for
[\text{Cl}^-] \geq 5 M. On this basis the following values were obtained for the stability constants at
25 °C: \( K_1 (1 \text{ mol}^{-1}) = 10^{-3.05 \pm 0.38} \), \( K_2 = 10^{-3.39 \pm 0.30} \), \( K_3 = 10^{-1.34 \pm 0.28} \), \( K_4 = 10^{-2.48 \pm 0.25} \), \( K_5 = 10^{-1.34 \pm 0.12} \) and \( \beta_{1} (1^4 \text{ mol}^{-1}) = 10^{-4.48 \pm 0.14} \) from measurements of LiCl
solutions with the activity parameter \( B = 0.170 \pm 0.005 \). The same stability constants could
also be used for HCl, with \( B = 0.185 \), and for CaCl₂ solutions, with \( B = 0.132 \). The distribution
of the complexes is shown graphically in Fig. 3.

The change in colour of cobalt(II) chloride solutions from red to blue with increasing
temperature and chloride concentration has been the subject of numerous studies since the
last century. Some of the early authors\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} assume that the colour change is caused by
dehydration of the solvated cobalt(II) ion, others\footnote{Present address: Chemistry Department,
Royal Veterinary and Agricultural University, DK-1871 Copenhagen V, Denmark.} that the colour change is caused by

complex formation. It is now generally recog-
nized that the octahedral hexaquo cobalt(II)
ion at high chloride concentrations is more or
less converted into a tetrahedral tetrachloro complex.\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} Some authors\footnote{Present address: Chemistry Department,
Royal Veterinary and Agricultural University, DK-1871 Copenhagen V, Denmark.} do not find
evidence for other chloro complexes than the
tetra complex. Others\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} have estimated
values for \( K_1 \) varying from 0.004 to 0.67 l mol⁻¹.
The lowest of these values, \( K_1 = 10^{-2.69} \), is
estimated by Job,\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} who also estimates a value for \( \beta_4 \) of \( 10^{-4.81} \) l mol⁻¹ but wrongly assumes, as later do Cotton et al.,\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} that CoCl₄(H₂O)⁻
is the dominating complex in concentrated aqueous
hydrochloric acid solutions. Stability constants
for all the chloro complexes have only been estimated by Zeitzmann et al.,\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} and Belousov
et al.\footnote{On leave from Metallurgical Faculty, Kalinin's
Polytechnical Institute, Leningrad, USSR.} Zeitzmann et al. identify the species
present in hydrochloric acid solutions by means of
NMR methods and they correct for activity
semiquantitatively simply by equating the
chloride ion activity with the hydrochloric acid
activity. Belousov et al., on the other hand, estimate concentration constants in mixtures
of HCl and HClO₄ at different high, but constant
ionic strengths from spectrophotometric meas-
urements. The findings of these authors are
discussed in connection with the results ob-
tained in this paper, in which the stability
constants are computed from a spectrophoto-
metric determination of the fraction of cobalt
present as tetrachloro complex in dilute Co(II)
solutions with chloride concentration higher than \( \approx 5 \) M.

EXPERIMENTAL

Measurements of absorption spectra were performed with a Cary 14 recording spectrophotometer and in the case of measurements at selected wavelengths with a Beckman DU spectrophotometer. Both instruments were thermostatted to 25.0 ± 0.1 °C. Cobalt concentrations and cell lengths were chosen so that the absorbance was always in the well defined measuring range of the instrument. Solutions of known molar concentration at 25 °C were made up from analyzed stock solutions of CoCl₂, HCl, LiCl, CaCl₂, and HClO₄ by weighing or pipetting the components into calibrated measuring flasks. Analytical reagents and redistilled water were used.

TREATMENT OF DATA

The characteristic absorption band between 600 and 700 nm which causes the blue colour of Co(II) in strong solutions of HCl, LiCl, and CaCl₂ is shown in Fig. 1. This band is due to the tetrachloro complex and it can be seen from Fig. 2 that the formation of this complex is nearly complete in concentrated HCl and LiCl solution. This figure (in which log ε for the two wavelengths 624 and 690 nm is plotted versus the total chloride concentrations) shows that the same limiting molar absorptivity is reached for HCl concentrations higher than ≈11 M and LiCl concentrations higher than ≈13 M. Furthermore, it can be seen that the limiting absorptivity is not yet reached in saturated CaCl₂ solutions having $C_{Cl^{-}}$ ≈ 12 M. That the absorption between 600 and 700 nm is nearly exclusively due to the tetrachloro complex, even in solutions with a relatively small degree of formation of this complex, is demonstrated in Fig. 1, in which the low absorption band for a solution of the composition 0.125 M CoCl₂, 8.05 M HClO₄ is also given enlarged by a factor of 12. It is remarkable how closely the enlarged spectrum agrees, in details of maxima, minima, and shoulders, with that measured for the tetrachloro complex in concentrated HCl and LiCl solutions. Therefore, denoting the limiting molar absorptivity in these solutions by $\varepsilon_4$ it should be possible, down to a certain limit of chloride concentration, to calculate the degree of formation of the tetrachloro species from the relationship $\varepsilon_4 = \varepsilon / \varepsilon_4$. The result of such a calculation for 5 wavelengths between 610 and 690 nm (one for each maximum or shoulder) is given in Table 1. In the case of CaCl₂ solutions the value of $\varepsilon_4$ is taken to be the same as in the HCl and LiCl solutions. It is notable that the same degree of formation is found at all the wavelengths for values of $\varepsilon / \varepsilon_4$ higher than ≈0.05. In the range $\varepsilon_4$ ≈ 0.01–0.05 there is a trend towards lower values for $\varepsilon / \varepsilon_4$ with increasing wavelength, but not more than that the smallest of the values may be assumed to be a

Table I. Estimation of the degree of formation of the tetrachloro complex as $\alpha_4 = \epsilon / \epsilon_4$.

<table>
<thead>
<tr>
<th>$\epsilon_4$</th>
<th>279</th>
<th>380</th>
<th>372</th>
<th>550</th>
<th>600</th>
<th>$\alpha_4$ (exp)</th>
<th>$\alpha_4$ (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{CoCl_3}$</td>
<td>$C_{LiCl}$</td>
<td>610</td>
<td>624</td>
<td>641</td>
<td>662</td>
<td>690 nm</td>
<td>0.0033</td>
</tr>
<tr>
<td>0.1000</td>
<td>4.98</td>
<td>0.0053</td>
<td>0.0045</td>
<td>0.00435</td>
<td>0.0038</td>
<td>0.0033</td>
<td>0.0033 ± 0.0005</td>
</tr>
<tr>
<td>0.1016</td>
<td>5.24</td>
<td>0.0065</td>
<td>0.0059</td>
<td>0.0057</td>
<td>0.00434</td>
<td>0.0033</td>
<td>0.0033 ± 0.0005</td>
</tr>
<tr>
<td>0.0503</td>
<td>5.60</td>
<td>0.0099</td>
<td>0.0094</td>
<td>0.00925</td>
<td>0.0087</td>
<td>0.0082</td>
<td>0.0077 ± 0.0005</td>
</tr>
<tr>
<td>0.0504</td>
<td>5.75</td>
<td>0.0124</td>
<td>0.0119</td>
<td>0.0123</td>
<td>0.0112</td>
<td>0.0105</td>
<td>0.0105 ± 0.0005</td>
</tr>
<tr>
<td>0.0402</td>
<td>6.05</td>
<td>0.0212</td>
<td>0.0207</td>
<td>0.0204</td>
<td>0.0194</td>
<td>0.0183</td>
<td>0.0176 ± 0.0007</td>
</tr>
<tr>
<td>0.0261</td>
<td>6.25</td>
<td>0.0254</td>
<td>0.0256</td>
<td>0.0254</td>
<td>0.0253</td>
<td>0.0234</td>
<td>0.0225 ± 0.001</td>
</tr>
<tr>
<td>0.0251</td>
<td>6.50</td>
<td>0.0372</td>
<td>0.0378</td>
<td>0.0374</td>
<td>0.0365</td>
<td>0.0350</td>
<td>0.034 ± 0.001</td>
</tr>
<tr>
<td>0.00905</td>
<td>7.00</td>
<td>0.0742</td>
<td>0.0765</td>
<td>0.0750</td>
<td>0.0750</td>
<td>0.0750</td>
<td>0.072 ± 0.002</td>
</tr>
<tr>
<td>0.0217</td>
<td>7.09</td>
<td>0.0858</td>
<td>0.0870</td>
<td>0.0850</td>
<td>0.0848</td>
<td>0.0818</td>
<td>0.081 ± 0.002</td>
</tr>
<tr>
<td>0.01005</td>
<td>7.49</td>
<td>0.149</td>
<td>0.1485</td>
<td>0.149</td>
<td>0.148</td>
<td>0.147</td>
<td>0.147 ± 0.002</td>
</tr>
<tr>
<td>0.00303</td>
<td>7.73</td>
<td>0.192</td>
<td>0.192</td>
<td>0.188</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190 ± 0.002</td>
</tr>
<tr>
<td>0.00300</td>
<td>8.12</td>
<td>0.317</td>
<td>0.318</td>
<td>0.317</td>
<td>0.311</td>
<td>0.315</td>
<td>0.315 ± 0.002</td>
</tr>
<tr>
<td>0.00203</td>
<td>8.23</td>
<td>0.328</td>
<td>0.328</td>
<td>0.328</td>
<td>0.322</td>
<td>0.325</td>
<td>0.325 ± 0.002</td>
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<tr>
<td>0.00201</td>
<td>8.74</td>
<td>0.485</td>
<td>(0.419)</td>
<td>0.484</td>
<td>0.480</td>
<td>0.483</td>
<td>0.483 ± 0.002</td>
</tr>
<tr>
<td>0.00155</td>
<td>9.09</td>
<td>0.609</td>
<td>0.610</td>
<td>0.610</td>
<td>0.602</td>
<td>0.610</td>
<td>0.610 ± 0.003</td>
</tr>
<tr>
<td>0.00101</td>
<td>10.11</td>
<td>0.799</td>
<td>0.798</td>
<td>0.791</td>
<td>0.797</td>
<td>0.797</td>
<td>0.797 ± 0.003</td>
</tr>
<tr>
<td>0.00102</td>
<td>11.17</td>
<td>0.990</td>
<td>0.992</td>
<td>0.985</td>
<td>0.989</td>
<td>0.989</td>
<td>0.989 ± 0.004</td>
</tr>
<tr>
<td>0.00102</td>
<td>12.20</td>
<td>0.955</td>
<td>0.955</td>
<td>0.952</td>
<td>0.951</td>
<td>0.954</td>
<td>0.954 ± 0.004</td>
</tr>
<tr>
<td>0.00101</td>
<td>13.36</td>
<td>0.958</td>
<td>0.958</td>
<td>0.958</td>
<td>0.953</td>
<td>0.955</td>
<td>0.955 ± 0.005</td>
</tr>
</tbody>
</table>

$\alpha_4$ (calc) calculated with the stability constants obtained for LiCl solutions, but with different values for the activity parameter $B$, 0.185 for HCl, and 0.132 for CaCl$_2$ compared to 0.170 for LiCl.

relatively good measure of the degree of formation of the tetrachloro complex. It can be seen directly from the lower part of the absorption curves for CaCl$_2$ solutions in Fig. 2 that there is some disturbance from other complexes for $C_{Cl^-} \leq 5$ M.

In order to calculate the stability constants in solutions of strongly varying concentrations of a single electrolyte, such as, e.g., HCl, it is necessary to make some rough assumptions about the activity coefficients of the species involved. Zeltmann et al. In order to calculate the stability constants in solutions of strongly varying concentrations of a single electrolyte, such as, e.g., HCl, it is necessary to make some rough assumptions about the activity coefficients of the species involved. Zeltmann et al. assume that the

ratio of activity coefficients for the chlorocobalt complexes is constant and introduce for the chloride ion activity the hydrochloric activity. As the uptake of a chloride ion is accompanied by a splitting-off of water molecules, these authors also correct for the change in the water activity. In the present paper, as in an earlier paper of one of the authors, it has also been found necessary to assume that the ratio of the activity coefficients for the chloro complexes, f(CoCl₄₋₋₋₋+)/f(CoCl₄₋₋₋₋), is independent of [Cl⁻]. Such an assumption is reasonable for concentrated electrolyte solutions in which the Coulombic attraction is of relatively little importance. However, instead of applying arbitrarily the mean activity of the complex-forming chloride electrolyte, a one parameter activity function adjusted to the measurements has been introduced. It is an empirical fact that log γ⁺ for solvated strong electrolytes increases linearly with the molar concentration for high concentrations of the salt. Thus the following relationships are approximately valid for chloride concentrations higher than 3 to 5 M:

\[
\begin{align*}
\log γ(\text{HCl})^{(C)} &= -0.42 + 0.18 \, C_{\text{Cl}^-} \\
\log γ(\text{CoCl₄})^{(C)} &= -0.55 + 0.20 \, C_{\text{Cl}^-}
\end{align*}
\]

(γ(C) indicates molar concentration scale). The negative term in these expressions is of little importance for concentrated electrolyte solutions and the following one parameter activity expression:

\[
a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{0.8[\text{Cl}^-] - 0.5}
\]

has therefore been assumed to be sufficiently accurate. This function for the chloride ion activity, with a value for B adjusted to suit the measurements, is furthermore assumed to include a correction for the change in the water activity. Expressed more precisely, the consecutive stability constants given by the expression:

\[
K_n = \frac{[\text{CoCl}_{n-1} \text{Cl}^-]}{[\text{CoCl}_n \text{Cl}^-]^n a_{\text{Cl}^-}}, \quad n = 1, 2, 3, 4
\]

are assumed to be valid in the limited concentration range (5–12 M) in which it has been possible to obtain reliable values for the degree of formation of the tetracloro complex. In the terminology of Marcus, a Cl^- is the effective ligand activity, and the \(K_n\)'s (denoted by an asterisk) are the effective stepwise formation constants. The latter are to be distinguished from, but are assumed to approximate to, the true activity formation constants.

**CALCULATION OF STABILITY CONSTANTS**

The stability constants were calculated by use of the values for the degree of formation of the fourth complex:

\[
a_4 = \beta_4 \frac{a_{Cl}^{-4}}{K_4}, \quad \beta_n = K_1 K_2 \cdots K_n
\]

Since most of the determinations of \(a_4\) were made for LiCl solutions these measurements were used in the calculation. A preliminary calculation was made by making the reasonable assumption that apart from the small fractions of tetrachloro complex mainly the aqua and monochloro complexes were present in the range of chloride concentrations from \(\approx 5\) to \(8\) M. \(K_1\) was tentatively taken to be 0.1 l mol⁻¹, and values of \(\beta_4\) calculated by means of the expression

\[
\beta_4 = a_4/(1 - a_4) a_{Cl}^{-4}
\]

with \(1 - a_4\) inserted for \(a_5\). In this way it was found by trial and error that the parameter \(B\) must be close to 0.17 in order to obtain constant values for \(\beta_4\). \(\beta_4\) itself was found to be \(\approx 10^{-4.8}\) l mol⁻⁴, and \(K_1\) was estimated to be \(10^{-1.3}\) l mol⁻¹ from the values of \(a_4\) for chloride concentrations \(> 11\) M, where \(a_4 \rightarrow 1\). The final calculation of the four stability constants was made by the method of least squares. With the preliminary estimated stability constants as starting values, the expression was minimized as a function of the four stability constants.

\[
\sum_{i=1}^{n} \left( \frac{[a_4\text{calc}] - [a_4\text{obs}]}{\sigma_i} \right)^2
\]

The \(\sigma_i\) are the tentatively assumed uncertainties in the values of \(a_4\) shown in Table 1. No distinction was made between total and free chloride ion concentration and the activity parameter \(B\) was taken to be \(0.170 \pm 0.005\). Minimization under these conditions gave the results shown in Table 3. A calculation in which the parameter \(B\) was taken to be \(0.17 \pm 0.02\) gave unchanged values for the constants with nearly unchanged uncertainties in \(K_1\) and \(K_4\) but with somewhat higher uncertainties (about 60%) in \(K_3\) and \(K_2\).
Table 2. Results of calculations of the stability constants with different fixed values for the parameter B.

<table>
<thead>
<tr>
<th>B</th>
<th>log $K_1$</th>
<th>log $K_2$</th>
<th>log $K_3$</th>
<th>log $K_4$</th>
<th>log $\beta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>$-1.33 \pm 0.28$</td>
<td>$-2.40 \pm 0.81$</td>
<td>$-1.64 \pm 0.78$</td>
<td>$-1.17 \pm 0.14$</td>
<td>$-6.54 \pm 0.16$</td>
</tr>
<tr>
<td>0.17</td>
<td>$-1.05 \pm 0.31$</td>
<td>$-2.73 \pm 0.97$</td>
<td>$-1.49 \pm 0.97$</td>
<td>$-1.33 \pm 0.11$</td>
<td>$-6.80 \pm 0.23$</td>
</tr>
<tr>
<td>0.18</td>
<td>$-0.82 \pm 0.42$</td>
<td>$-2.71 \pm 0.68$</td>
<td>$-1.65 \pm 0.68$</td>
<td>$-1.46 \pm 0.10$</td>
<td>$-6.63 \pm 0.37$</td>
</tr>
</tbody>
</table>

Table 3. Comparison of stability constants for the cobalt(II) chloride system.

<table>
<thead>
<tr>
<th>Reference</th>
<th>log $K_1$</th>
<th>log $K_2$</th>
<th>log $K_3$</th>
<th>log $K_4$</th>
<th>log $\beta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This paper $^a$</td>
<td>$-1.05 \pm 0.38$</td>
<td>$-2.69 \pm 0.90$</td>
<td>$-1.54 \pm 0.89$</td>
<td>$-1.34 \pm 0.13$</td>
<td>$-6.62 \pm 0.24$</td>
</tr>
<tr>
<td>Zeltmann et al. $^{12}$ $^b$</td>
<td>$-0.77 \pm 0.19$</td>
<td>$-2.77 \pm 0.12$</td>
<td>$-2.51 \pm 0.15$</td>
<td>$-2.06 \pm 0.09$</td>
<td>$-8.11$</td>
</tr>
<tr>
<td>Belousov et al. $^{18}$ $^c$</td>
<td>$+0.64 \pm 0.03$</td>
<td>$0.13$</td>
<td>$-0.01$</td>
<td>$-0.57$</td>
<td>$0.20 \pm 0.12$</td>
</tr>
</tbody>
</table>

$^a$ $C_{\text{LiCl}}$ var., calc. with $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{0.170 \pm 0.005}[\text{Cl}^-]^{-0.8}$. $^b$ $m_{\text{HCl}}$ var., calc. with $a_{\text{Cl}^-} = m_{\text{HCl}}/\text{[HCl]/a_{\text{H2O}}}$.

$^c$ $9 \text{ M HClO}_4$, calc. with $a_{\text{Cl}^-} = [\text{Cl}^-]$.

and $\beta_4$. Calculations with different fixed values for $B$ of 0.16, 0.17, and 0.18, respectively, were also made (see Table 2).

Calculated values for $\alpha_4$ corresponding to the constants, with $B$ taken as $0.170 \pm 0.005$, are shown in Table 1 and it can be seen that the agreement with the experimental values is satisfactory. The values of $\alpha_4$(calc) for HCl and CaCl$_2$, given in the same table, are calculated using the same constants but with $B$ chosen to be 0.185 and 0.132, respectively.

**DISCUSSION**

A graphical picture of the distribution of the cobalt complexes, which shows the very small range of existence of the dichloro and trichloro complexes, is presented in Fig. 3. In this figure the fractions $\alpha_n$ of the various complexes are plotted versus the logarithm of the chosen chloride ion activity function. The full curves are calculated by the use of the stability constants obtained for the LiCl solutions. The experimental values of $\alpha_n$ obtained for HCl and CaCl$_2$ solutions are also plotted in the figure. The latter are plotted versus the activity function based on the values for $B$ used to compute $\alpha_n$(calc) in Table 1. The points plotted (+ for HCl and $\times$ for CaCl$_2$) are seen to lie close to the full curve valid for LiCl solutions. This agreement (excellent for the HCl, and satisfactory for the CaCl$_2$)

![Fig. 3. Plots of the fractions $\alpha_n$ for various complexes CoCl$_{n-3}$ versus the logarithm of the chloride ion activity function: $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{0.170\pm0.005}[\text{Cl}^-]^{-0.8}$. The full curves show graphically the distribution of the complexes, calculated using the stability constants valid for LiCl solutions with the parameter $B = 0.170$. The experimental values for $\alpha_n$ (HCl, $+$; CaCl$_2$, $\times$) shown are plotted versus $\log a_{\text{Cl}^-}$ calculated using the values for $B$ (HCl, 0.185; CaCl$_2$, 0.132), which give the best fit to the full curve for LiCl. Below the activity scale are given scales for the molar chloride concentrations which correspond to the stated values of the $B$ parameter. For comparison purposes, connected values of $\alpha_n$ and $C_{\text{HCl}}$ from the paper of Zeltmann et al. $^{18}$ (converted from moles to molar concentrations) are indicated by O points in the figure.](image-url)
solutions) shows directly that it is possible with some approximation, and by simply changing the value for the parameter $B$, to use the same set of stability constants for all three of the chloride electrolytes studied.

The composition of a given cobalt(II) chloride solution can be estimated from Fig. 3, which gives scales for the molar chloride concentrations corresponding to the activity function for the different chloride electrolytes. The scale for HCl makes possible a direct comparison with the values of $x_4$ obtained by Zeltmann et al. These authors use molal HCl concentrations but their values converted for molar concentrations are plotted as O points. The figure shows how closely these values, obtained in a completely different way by means of NMR measurements with oxygen-17 and chlorine-35, follow our curve, and this agreement gives support to our assumption that the tetrachloro complex is nearly exclusively producing the absorbance in the wavelength range 600–700 nm in strong aqueous chloride solutions. On the other hand, measurements in non-aqueous solutions as well as the measurements of Zeltmann et al. provide evidence that the molar absorptivity of the tetrachloro complex may amount to as much as one third to more than one half of that of the tetrachloro complex in the stated wavelength range. It must, therefore, be the small range of existence of the tetrachloro complex in aqueous medium that is mainly responsible for the justification of the calculations made.

The stability constants obtained in this paper with $B = 0.170 \pm 0.005$ are compared Table 3 with the activity-corrected constants obtained by Zeltmann et al. and with the concentration constants estimated by Belousov et al. for a 9 M perchloric acid medium. The constants obtained by Zeltmann et al. agree fairly well with ours but their values for $K_4$ and $\beta_4$ are most probably too high, considering the fine agreement between their values of $x_4$ and ours for HCl solutions of given molarity. The discrepancy can only be due to the fact that Zeltmann et al. arbitrarily introduce too strong an activity correction, and an activity correction derived from the measurements themselves, as in the present paper, is probably more realistic.

The concentration stability constants estimated by Belousov et al. for 9 M and other strong perchloric acid solutions are, as should be expected (considering the high activity of hydrochloric acid in these solutions), much higher than our activity-corrected values but the relative magnitude of their constants is suspect. According to the ratio between the consecutive constants the dichloro and trichloro complexes have a rather large range of existence, in contradiction with our results. We find, in disagreement with Belousov et al., that the tetrachloro complex also in strong perchloric acid solutions is almost solely responsible for the absorption in the wavelength range 600–700 nm, even when it is present in only a few percent. The spectrum of such a solution (0.125 M CoCl$_3$ in 8.05 M HClO$_4$) with $x_4 = 0.078$ is, as already mentioned, shown in Fig. 1. Assuming that the distribution of the complexes for a given value of $x_4$ is the same as in Fig. 3, this solution is estimated to have $x_4 = 0.2$, [Cl$^-$] = 0.10 M and $\beta_4 = [x_4]/(x_4[Cl^-]^4)$ = 10$^4$. Another solution (0.05 M CoCl$_3$ in 8.99 M HClO$_4$) with $x_4 = 0.027$ was estimated to have $x_4 \approx 0.28$, [Cl$^-$] = 0.057 M and $\beta_4 \approx 10^4$. Using the constants given by Belousov et al. one calculated $x_4 \approx 0.0006$ for the same solution. Such a value for $x_4$ is not even of the right order of magnitude and the constants given by these authors cannot therefore stand closer criticism.

According to our estimate, the concentration constant $\beta_4 = [CoCl_4^{2-}]/([Co^{2+}][Cl^-]^4)$ increases from 10$^{-4}$ to 10$^4$ on going from water at ionic strength zero to 9 M HClO$_4$. This is perhaps too great an increase but not unreasonable considering that $\beta_4$ is a function of the fourth power of the chloride ion activity. The activity coefficient of hydrochloric acid in 9 M HClO$_4$ is not known but that of perchloric acid is estimated to be $\approx 350$. The fourth power of this figure for $\gamma_\pm(C)$ is as high as $1.5 \times 10^{10}$, which supports our estimate of the value of $\beta_4$ in 9 M HClO$_4$.

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