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 CaCl$_2$. 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 α_4 could be calculated from the relation $\alpha_4 = \varepsilon/\varepsilon_4$, where ε_4 is the limiting molar absorptivity for the most concentrated solutions of LiCl and HCl. Activity corrections were included semiquantitatively by introducing a one parameter activity function: $a_{Cl^-} = [Cl^-] \times 10^{B[Cl^-]-0.5}$ adjusted to the measurements and assumed to be valid for $[Cl^-] \geq 5$ M. On this basis the following values were obtained for the stability constants at 25 °C: $K_1(l\ mol^{-1}) = 10^{-1.05 \pm 0.38}$, $K_2 = 10^{-2.69 \pm 0.90}$, $K_3 = 10^{-1.54 \pm 0.89}$ $K_4 = 10^{-1.34 \pm 0.13}$ and β_4, (l^4 $mol^{-4}) = 10^{-6.62 \pm 0.34}$ 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 CaCl$_2$ 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 [1,2] assume that the colour change is caused by dehydration of the solvated cobalt(II) ion, others [3,4] that the colour change is caused by

complex formation. It is now generally recognized that the octahedral hexaquo cobalt(II) ion at high chloride concentrations is more or less converted into a tetrahedral tetrachloro complex.[5-15] Some authors [6,10,13] do not find evidence for other chloro complexes than the tetra complex. Others [8,11,16-18] have estimated values for K_1 varying from 0.004 to 0.67 l mol^{-1}. The lowest of these values, $K_1 = 10^{-2.40}$, is estimated by Job,[16] who also estimates a value for β_3 of $10^{-5.92}$ l^3 mol^{-3} but wrongly assumes, as later do Cotton et al.,[19] that CoCl$_3$(H$_2$O)$^-$ is the dominating complex in concentrated aqueous hydrochloric acid solutions. Stability constants for all the chloro complexes have only been estimated by Zeltmann et al.[12] and Belousov et al.[15] Zeltmann 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 HClO$_4$ at different high, but constant ionic strengths from spectrophotometric measurements. The findings of these authors are discussed in connection with the results obtained in this paper, in which the stability constants are computed from a spectrophotometric determination of the fraction of cobalt present as tetrachloro complex in dilute Co(II) solutions with chloride concentration higher than ≈ 5 M.

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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 $CoCl_2$, HCl, LiCl, $CaCl_2$, and $HClO_4$ 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 $CaCl_2$ 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 figures (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
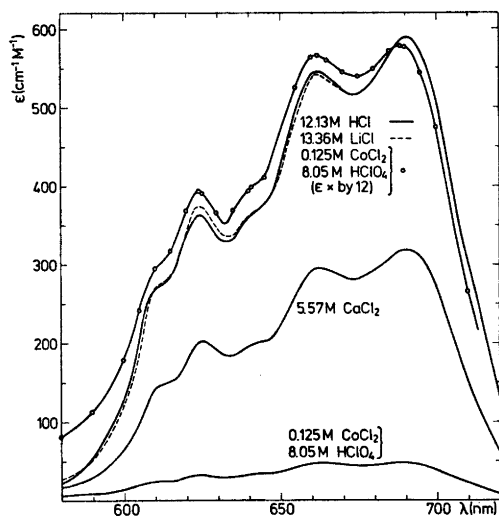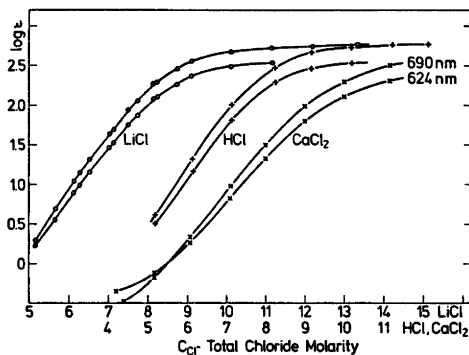
Fig. 2. Logarithm of molar absorptivity, at 624 and 690 nm, of Co(II) in solutions of HCl, LiCl, and $CaCl_2$ as a function of the total chloride concentration. Note the different scale division of the abscissa for HCl and $CaCl_2$ relative to that for LiCl.

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 $CaCl_2$ solutions having $C_{Cl^-} \approx 12$ 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 $CoCl_2$, 8.05 M $HClO_4$ 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 ε_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 $\alpha_4 = \varepsilon/\varepsilon_4$. 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 $CaCl_2$ solutions the value of ε_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 $\alpha_4 \approx 0.01 - 0.05$ 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

Fig. 1. Absorption spectra of 10^{-3} M $CoCl_2$ in aqueous 12.13 M HCl, 13.36 M LiCl, and 5.57 M $CaCl_2$, and of 0.125 M $CoCl_2$ in 8.05 M $HClO_4$. The spectrum of the $CoCl_2, HClO_4$ solution with the molar absorptivities multiplied by 12 is also shown.

Table 1. Estimation of the degree of formation of the tetrachloro complex as $\alpha_4 = \varepsilon/\varepsilon_4$.

$CoCl_2 - LiCl - H_2O$

	ε_4	279	380	372	550	600		
C_{CoCl_2}	C_{LiCl}	610	624	641	662	690 nm	α_4 (exp)	α_4 calc)
0.1000	4.98	0.0053	0.0045	0.00435	0.0038	0.0033	0.003 ± 0.0005	0.0027
0.1016	5.24	0.0065	0.0059	0.0057	0.0034	0.0031	0.0028 ± 0.0005	0.0037
0.0503	5.60	0.0099	0.0094	0.00925	0.0087	0.0082	0.0077 ± 0.0005	0.0068
0.0504	5.75	0.0124	0.0119	0.0123	0.0112	0.0105	0.0105 ± 0.0005	0.0090
0.0402	6.05	0.0212	0.0207	0.0204	0.0194	0.0183	0.0176 ± 0.0007	0.0164
0.0251	6.25	0.0254	0.0256	0.0254	0.0253	0.0234	0.0225 ± 0.001	0.0213
0.0251	6.50	0.0372	0.0376	0.0374	0.0363	0.0350	0.034 ± 0.001	0.0327
0.00995	7.00	0.0742	0.0765	0.0750	0.0750	0.0730	0.072 ± 0.002	0.0718
0.0217	7.09	0.0855	0.0870	0.0868	0.0848	0.0818	0.081 ± 0.002	0.0860
0.01005	7.49	0.149	0.1485	0.149	0.146	0.147	0.147 ± 0.002	0.145
0.00303	7.73	0.192	0.192	0.192	0.188	0.190	0.190 ± 0.002	0.193
0.00300	8.12	0.317	0.318	0.317	0.311	0.315	0.315 ± 0.002	0.297
0.00203	8.23	0.328	0.324	0.328	0.322	0.325	0.325 ± 0.002	0.330
0.00201	8.74	0.485	(0.419)	0.484	0.480	0.483	0.483 ± 0.002	0.488
0.00155	9.09	0.609	0.610	0.610	0.602	0.610	0.610 ± 0.003	0.596
0.00101	10.11	0.800	0.799	0.798	0.791	0.797	0.797 ± 0.003	0.807
0.00102	11.17	0.899	0.902	0.900	0.895	0.899	0.899 ± 0.004	0.905
0.00102	12.20	0.955	0.955	0.952	0.951	0.954	0.954 ± 0.004	0.948
0.00101	13.36	0.985	0.986	0.985	0.983	0.985	0.985 ± 0.005	0.971

$CoCl_2 - HCl - H_2O$

	ε_4	279	380	380	560	610		
C_{CoCl_2}	C_{HCl}	610	624	641	662	690 nm	α_4 (exp)	α_4 (calc)[a]
0.0401	5.13	0.0087	0.0082	0.0078	0.0073	0.0067	0.006	0.0053
0.0201	6.10	0.038	0.038	0.037	0.036	0.0345	0.034	0.032
0.00595	7.12	0.167	0.170	0.171	0.169	0.164	0.166	0.163
0.00202	8.23	0.490	0.505	0.502	0.505	0.494	0.496	0.486
0.000100	9.17	0.755	0.770	0.765	0.775	0.765	0.765	0.764
0.000402	10.19	0.893	0.897	0.895	0.908	0.899	0.896	0.887
0.000396	11.24	0.951	0.912	0.940	0.960	0.949	0.950	0.944
0.000407	12.13	0.972	0.960	0.960	0.976	0.966	0.967	0.967

$CoCl_2 - CaCl_2 - H_2O$

	ε_4	279	380	372	550	600		
C_{CoCl_2}	C_{CaCl_2}	610	624	641	662	690 nm	α_4 (exp)	α_4 (calc)[a]
0.0999	2.000	0.00179	0.00116	0.00108	0.00069	0.00047	0.0004	0.0001
0.1007	2.495	0.00265	0.00195	0.00193	0.00138	0.00113	0.001	0.0006
0.0408	2.999	0.0056	0.0047	0.0046	0.0040	0.0036	0.003	0.0025
0.00964	3.538	0.0182	0.0175	0.0172	0.0165	0.0156	0.015	0.012
0.00302	4.001	0.0534	0.0545	0.0540	0.0530	0.0513	0.051	0.045
0.00149	4.503	0.162	0.167	0.167	0.165	0.162	0.162	0.136
0.00103	4.999	0.323	0.335	0.335	0.338	0.332	0.335	0.332
0.00103	5.567	0.512	0.535	0.535	0.540	0.533	0.536	0.568

[a] 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.*[12] 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,[20] it has also been found necessary to assume that the ratio of the activity coefficients for the chloro complexes, $f(CoCl_{n-1}{}^{3-n})/f(CoCl_n{}^{2-n})$, 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 $\gamma_\pm$ for solvated strong electrolytes increases linearly with the molar concentration for high concentrations of the salt.[20,21] Thus the following relationships are approximately valid for chloride concentrations higher than 3 to 5 M:

$$\log \gamma_{(HCl)}{}^{(C)} = -0.42 + 0.18\ C_{Cl^-}$$

$$\log \gamma_{(CaCl_2)}{}^{(C)} = -0.55 + 0.20\ C_{Cl^-}$$

($\gamma^{(C)}$ 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:

$$a_{Cl^-} = [Cl^-] \times 10^{B[Cl^-]-0.5}$$

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:

$$K_n = \frac{[CoCl_n{}^{2-n}]}{[CoCl_{n-1}{}^{3-n}]a_{Cl^-}}, \quad n = 1,2,3,4$$

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 tetrachloro complex. In the terminology of Marcus [21] 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:

$$\alpha_4 = \beta_4 a_{Cl^-}{}^4 / \sum_0^4 \beta_n a^n{}_{Cl^-}, \text{ where } \beta_n = K_1 K_2 \cdots K_n$$

Since most of the determinations of α_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 ≈ 5 to 8 M. K_1 was tentatively taken to be 0.1 l mol⁻¹, and values of β_4 calculated by means of the expression

$$\beta_4 \approx \alpha_4/(1-\alpha_1)a_{Cl^-}{}^4$$

with $1-\alpha_1$ inserted for α_0. 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 β_4. β_4 itself was found to be $\approx 10^{-6.6}$ l⁴ mol⁻⁴, and K_4 was estimated to be $10^{-1.3}$ l mol⁻¹ from the values of α_4 for chloride concentrations > 11 M, where $\alpha_4 \rightarrow 1$. 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.

$$\sum_i \frac{[\alpha_4(calc)_i - \alpha_4(obs)_i]^2}{\sigma_i^2}$$

The σ_i are the tentatively assumed uncertainties in the values of α_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 ± 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 ± 0.02 gave unchanged values for the constants with nearly unchanged uncertainties in K_2 and K_3 but with somewhat higher uncertainties (about 60 %) in K_1, K_4,

Table 2. Results of calculations of the stability constants with different fixed values for the parameter B.

B	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log \beta_4$
0.16	-1.33 ± 0.28	-2.40 ± 0.81	-1.64 ± 0.78	-1.17 ± 0.14	-6.54 ± 0.16
0.17	-1.05 ± 0.31	-2.73 ± 0.97	-1.49 ± 0.97	-1.33 ± 0.11	-6.60 ± 0.23
0.18	-0.82 ± 0.42	-2.71 ± 0.68	-1.65 ± 0.68	-1.46 ± 0.10	-6.63 ± 0.37

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

Reference	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log \beta_4$
This paper [a]	-1.05 ± 0.38	-2.69 ± 0.90	-1.54 ± 0.89	-1.34 ± 0.13	-6.62 ± 0.24
Zeltmann *et al.*[12] [b]	-0.77 ± 0.19	-2.77 ± 0.12	-2.51 ± 0.15	-2.06 ± 0.09	-8.11
Belousov *et al.*[15] [c]	$+0.64 \pm 0.03$	0.13	-0.01	-0.57	0.20 ± 0.12

[a] C_{LiCl} var., calc. with $a_{Cl^-} = [Cl^-] \times 10^{(0.170 \pm 0.005)[Cl^-]-0.5}$ [b] m_{HCl} var., calc. with $a_{Cl^-} = m_{HCl}\gamma_\pm (HCl)/a_{H_2O}$
[c] 9 M $H(ClO_4)$, calc. with $a_{Cl^-} = [Cl^-]$.

and β_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 α_4 corresponding to the constants, with B taken as 0.170 ± 0.005, are shown in Table 1 and it can be seen that the agreement with the experimental values is satisfactory. The values of α_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 α_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 α_4 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 α_4(calc) in Table 1. The points plotted (+ for HCl and × 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 $CaCl_2$
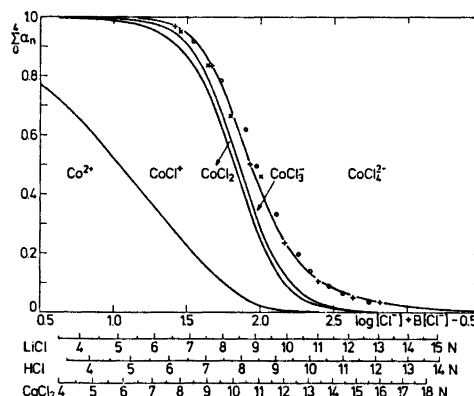

Fig. 3. Plots of the fractions α_n for various complexes $CoCl_n^{2-n}$ *versus* the logarithm of the chloride ion activity function: $a_{Cl^-} = [Cl^-] \times 10^{B[Cl^-]-0.5}$. The full curves show graphically the distribution of the complexes, calculated using the stability constants valid for LiCl solutions with the parameter $B = 0.170$. The experimental values for α_4 (HCl, +; $CaCl_2$, ×) shown are plotted *versus* $\log a_{Cl^-}$ 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 α_4 and C_{HCl} from the paper of Zeltmann *et al.*[12] (converted from molal to molar concentrations) are indicated by O points in the figure.

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 α_4 obtained by Zeltmann *et al.*[12] 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,[22–24] as well as the measurements of Zeltmann *et al.*,[12] provide evidence that the molar absorptivity of the trichloro 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 trichloro 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 in Table 3 with the activity-corrected constants obtained by Zeltmann *et al.*[12] and with the concentration constants estimated by Belousov *et al.*[15] 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 β_4 are most probably too high, considering the fine agreement between their values of α_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.*[15] 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.*,[15] 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 per cent. The spectrum of such a solution (0.125 M $CoCl_2$ in 8.05 M $HClO_4$) with $\alpha_4 = 0.078$ is, as already mentioned, shown in Fig. 1. Assuming that the distribution of the complexes for a given value of α_4 is the same as in Fig. 3, this solution is estimated to have $\alpha_0 = 0.2$, $[Cl^-] \cong 0.10$ M and $\beta_4 = \alpha_4/(\alpha_0 [Cl^-]^4) \cong 10^{3.6}$. Another solution (0.050 M $CoCl_2$ in 8.99 M $HClO_4$) with $\alpha_4 \cong 0.027$ was estimated to have $\alpha_0 \cong 0.28$, $[Cl^-] \cong 0.057$ M and $\beta_4 \cong 10^4$. Using the constants given by Belousov *et al.* one calculated $\alpha_4 \sim 0.0006$ for the same solution. Such a value for α_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 $10^{-6.6}$ 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 β_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[25] to be ≈ 350. The fourth power of this figure for $\gamma_{\pm}{}^{(C)}$ is as high as 1.5×10^{10}, which supports our estimate of the value of β_4 in 9 M $HClO_4$.

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