Estimation of Small Stability Constants in Aqueous Solution. The Chromium(III) Chloride System
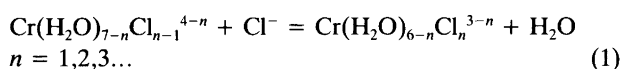
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The weak complex formation in the chromium(III) chloride system was studied by spectrophotometric measurements and by ion-exchange high-performance liquid chromatography (HPLC). The relative concentrations of $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_4Cl_2^+$ were directly determined from HPLC measurements and the average ligand numbers were estimated up to $\bar{n} \approx 3$ from the spectrophotometric measurements. The equilibria were studied at 25 °C in weakly acidic LiCl solutions up to 12.5 M. For solutions with an acidity of 0.1 M the equilibrium establishment takes up to 2000 h. The results were expressed in "semi-thermodynamic" activity constants corrected for both changes in LiCl activity and in water activity. The consecutive constants K_1 and K_2 were obtained from HPLC measurements, K_1, K_2 and K_3 from spectrophotometric measurements. Hypothetical values of K_4, K_5 and K_6 were estimated on the basis of certain assumptions.

The equilibrium in aqueous chromium(III) chloride solutions adjusts itself only slowly. In weakly acidic solutions weeks or months are required to establish equilibrium. The complex formation is small and even in 10 M LiCl less than three chloride ions are bound to the chromium. The green chromium(III) chloride hydrate was shown by Werner and Gubser[1] to be the dichloro complex. Niels Bjerrum[2,3] prepared the light-green monochloro salt and studied kinetically the formation and dissociation of the mono- and dichloro complexes in aqueous solution. In a dilatometric study he found that a 1 M Cr(III) chloride solution contains about 13 % monochloro and 85 % hexaaqua ions in equilibrium at 25 °C. Several authors[4] have, by the use of spectrophotometric and ion-exchange methods, determined the concentrations of the two chloro complexes in different chloride media and expressed their results using concentration mass-action expressions. Gates and King[5] give such values for K_1 and K_2 in 4.4 M $NaClO_4$ mixtures. Hale and King[6] introduce also a correction for the changes in the water activity in the concentration stability constants.

In the present paper the weak chloro complex formation is studied in LiCl solutions up to the highest possible concentration by spectrophotometric measurements and by ion-exchange high-performance liquid chromatography (HPLC). Under extreme conditions for which the interionic forces can be neglected,[7,8] the so-called stepwise "semi-thermodynamic" stability constants for reaction (1)

$$Cr(H_2O)_{7-n}Cl_{n-1}^{4-n} + Cl^- = Cr(H_2O)_{6-n}Cl_n^{3-n} + H_2O$$
$$n = 1,2,3... \tag{1}$$

$$K_n = \frac{[CrCl_n]a_{H_2O}}{[CrCl_{n-1}][Cl^-]\gamma_\pm^c}$$

are probably those which come closest to the true activity constants.[9] Besides introducing a correction for the changes in the water activity a_{H_2O} the chloride ion concentration in this expression is substituted by $[Cl^-]\gamma_\pm^c$, where $\gamma_\pm^c$ is the mean activity coefficient of the chloride salt (LiCl) in molar concentrations. By use of this expression K_1 and K_2 are obtained from a direct determination of the relative concentrations of the complex species by HPLC measurements, and K_1, K_2 and K_3 from spectrophotometric measurements.

Experimental

The chemicals used were of analytical grade. The chromium content in the 1 M stock solution of blue $CrCl_3 \cdot 6H_2O$ was analysed by atomic absorption spectrometry and the chloride concentration by potentiometric silver nitrate titration after disengagement of the complexly bound chloride.[2] The stock solution of nearly saturated LiCl was analysed by Volhard titration. The various solutions to be equilibrated were prepared in volumetric flasks by adding from burettes or pipetting from stock solutions. They were kept in a water bath thermostatted to 25.0 °C. The spectrophotometric measurements were carried out with a Cary 118 spectrophotometer also thermostatted to 25 °C.

Ion-exchange high-performance liquid chromatography was carried out on a Waters HPLC system. The system includes an M 6000 A solvent delivery unit, a U 6 K universal injector and a 990 photodiode array detector con-

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Table 1. Molar absorbances at selected wavelengths (nm) for the measured weakly acidic chromium(III)–LiCl solutions in equilibrium.[a]

No.	C_{LiCl}	650	605	450	430	Max 1	Max 2	Time at 25 °C/h
1	0	3.5	10.2	6.5	11.6	572, 13.2	405, 15.7	584
2	1.30	3.8	10.6	6.9	12.1	575, 13.0	408, 15.4	386
3	2.60	4.8	11.4	7.7	12.8	580, 13.2	411, 15.7	386
4	3.90	6.85	12.8	10.65	15.1	585, 13.7	417, 16.7	216
5	6.55	12.2	15.1	17.1	19.9	610, 15.7	432, 19.7	216
6	8.58	18.4	16.1	24.8	20.7	634, 19.0	449, 24.6	386
7	10.23	21.4	15.9	27.6	20.7	649, 21.3	458, 28.2	584
8	12.48	22.1	12.5	26.6	15.7	666, 23.3	471, 32.0	192
9	0	3.5	10.5	6.5	11.8	574, 12.9	408, 15.1	2496
10	1.30	4.9	11.6	8.1	13.2	579, 13.3	410, 15.7	696
11	2.60	4.9	11.7	8.4	13.6	581, 13.2	412.5, 15.6	2496
12	3.99	6.5	12.6	10.4	15.2	588, 13.3	418, 16.2	1656
13	6.50	19.3	23.2	27.8	29.7	615, 23.7	434.5, 30.2	2496
14	8.58	18.8	16.1	25.1	20.8	635, 19.3	451, 25.1	2016
15	11.27	22.3	13.4	28.0	18.0	663, 23.0	468, 31.7	1176
16	12.35	22.7	12.2	28.7	18.0	668.5, 24.3	472, 34.5	2016

[a] C_{CrCl_3} = 0.0394 M, C_{HCl} = 0.005 M (Nos. 1–8), 0.12 M (Nos. 9–16).

trolled by an NEC computer using Waters 990 software. The separations were performed using a strong cation-exchange column (Protein Pak SP 5 PW from Waters) with the dimensions 75 mm×7.5 mm internal diameter.

The separation of the different cationic chromium complexes in the equilibrium solutions was performed by injecting 2–10 µl samples (Hamilton syringes, 25 µl) followed by isocratic elution (1 ml min^{-1}) with either 0.08 or 0.03 M Na_2SO_4 acidified with H_2SO_4 to pH 2.3. All experiments were carried out at 25 °C. The elution profile was recorded from 0 to 30 min with a full spectrum (300–700 nm) obtained at 2 s intervals. All separations were repeated at least three times.

The equilibrium solutions. The CrCl$_3$–LiCl solutions were studied at two hydrochloric acid concentrations, viz. 0.005 and 0.12 M. The absorption spectra of the solutions were recorded several times during the equilibrium adjustment. The times of equilibration depend somewhat on the LiCl concentration, but our data show that equilibrium is reached after about 200 h for the solutions with C_{HCl} = 0.005 M and after 1000–2000 h for the solutions with C_{HCl} = 0.12 M. Table 1 contains the wavelength and molar absorbance (λ, ε) data for the two maxima and the molar absorbances at four selected wavelengths for sixteen equilibrium solutions. The equilibrium solutions with C_{HCl} = 0.005 M undoubtedly contain some hydrolytic oligomers. According to Stünze *et al.*[10] aged hexaaqua ion solutions at ca. pH 2.3 can contain as much as 10 % of the chromium as dimers and trimers. The somewhat lower wavelengths of the maxima found for solution 1 in Table 1 compared with that of solution 9 with ca. pH 1 must therefore be the result of the presence of oligomers.

Analysis of the equilibrium solutions by use of the spectra of the pure species of the complexes. The absorption spectra of

the hexaaqua and the two chlorochromium(III) ions was first measured by Bjerrum[11] and later by King and co-workers.[5,12] These latter authors succeeded in separating the *cis* and *trans* isomers of the dichloro complex. These studies were continued by Mønsted and Mønsted,[13] and their very reliable numerical data for the pure complexes are plotted in Fig. 1. They reported the spectra of both the *cis* and *trans* dichloro complexes,[13] but for our purpose, it is the *cis–trans* equilibrium spectrum of the dichloro complex under the same conditions (0.5 M $HClO_4$ and 25 °C) which is illustrated in Fig. 1. Values for the wavelengths and molar absorbances of the maxima as well as the molar absorbances at four selected wavelengths of the pure com-
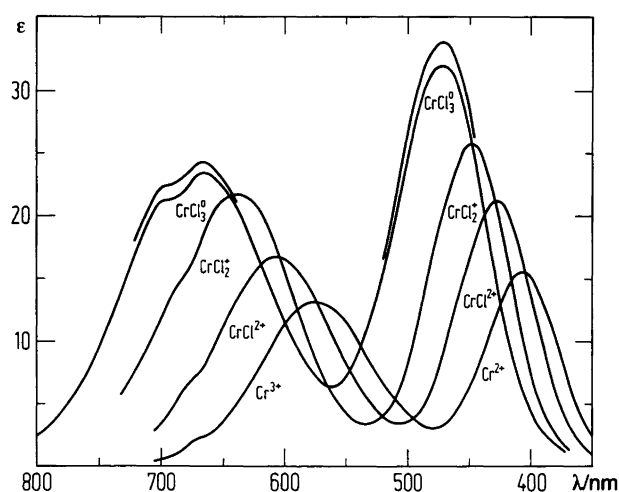

Fig. 1. The spectra of the hexaaqua, the monochloro and the *cis–trans* equilibrium spectrum of the dichloro complex in 0.5 M $HClO_4$ at 25 °C.[13] The spectra of solutions 8 and 16 in Table 1 with the average ligand number close to $\bar{n}$ = 3.0 are also shown in the figure.

Table 2. λ,ε data for the maxima of $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_5Cl_2^+$ in *cis–trans* equilibrium at 25 °C.

Parameter	$\lambda_1(max)$	$\varepsilon(max\ 1)$	$\lambda_2(max)$	$\varepsilon(max\ 2)$
ε_0 (11 M HCl)	575	15.8	408	21.6
(1 M HCl, 6 M LiCl)	575	15.8	407	21.6
(0.5 M HClO₄)	575	13.2	407	15.5
$\Delta\lambda$ /nm (1st red shift)	33		22	
ε_1 (0.5 M HClO₄)	608	16.8	429	21.2
$\Delta\lambda$ /nm (2nd red shift)	32		21	
ε_2 (0.5 M HClO₄)	640	21.6	450	25.6
$\Delta\lambda$ /nm (3rd, extrapolated)	31		20	
ε_3 (hypothetical)	671	(24)	470	(34)

plexes are given in Table 2. This table shows that the red shift (in nm per chloride ion substituting water molecules in the hexaaqua ions to the dichloro complex) is almost constant. The shifts in wavelength show a tendency to decrease somewhat in a manner which closely corresponds to constant energy differences in wavenumber. The red shift from the dichloro to the trichloro complex is therefore tentatively taken to have the same value in cm^{-1}.

High electrolyte concentrations deform the ligand field spectra to some extent and usually increase the molar absorbances. It can be seen from Table 2 that the wavelengths of the maxima of the hexaaqua ion at high electrolyte concentrations are rather independent of the ionic medium. The red shifts of the maxima of the pure species could therefore be used directly to estimate the average ligand numbers. Owing to the electrolyte dependence of the absorbances of the pure species they can therefore only be used to estimate the ligand numbers in the equilibrium solutions for LiCl concentrations that are not to high. The results of the calculations of the average ligand numbers in the equilibrium solutions numbered 2–8 and 10–16 in Table 1 are presented in Table 3.

Table 4 contains the values of the activity coefficients $\gamma_\pm^c$

and activities of water corresponding to the molar concentrations of (Li,H)Cl in the equilibrium solutions. The values are calculated from the values of $\gamma_\pm^m$ on a molal basis and the osmotic coefficients given by Robinson and Stokes.[14] The formation curve for the chloro complex formation is shown in Fig. 2. The average ligand numbers $\bar{n}$ (from Table 3) are plotted against the values of $\log a_{Cl^-}^* = \log (C_{LiCl}\ \gamma_\pm^c/a_{H_2O})$ given in Table 4.

Determination of the relative concentrations of $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_4Cl_2^+$ in the equilibrium solutions using HPLC. The relative amounts of the three cationic chromium complexes in the $CrCl_3$–LiCl equilibrium system were determined by HPLC. Samples of equilibrium solutions were injected into the HPLC column, and the mixture was separated into the individual complexes by elution with acidified solutions of Na_2SO_4. The elution order of the complexes was $Cr(H_2O)_4Cl_2^+$, $Cr(H_2O)_5Cl^{2+}$ and finally $Cr(H_2O)_6^{3+}$, as seen from the absorption spectra of the separated complexes. It was not possible to separate the dichloro complex into the *cis* and *trans* isomers.

The area under a peak in the chromatogram is related by the Lambert–Beer law to the total amount of the species that cause the peak. It is therefore possible to calculate the relative amounts of the complexes in the equilibrium solutions from the areas of the separated peaks if the molar absorbances of the individual complexes are known. The accuracy of the method was estimated by injecting known amounts of cobalt(III) complexes, such as Co en_3^{3+}, into the HPLC column. The results showed that the method was accurate to within 5 %. Errors arising from ligand exchange during the separation of the chromium complexes are negligible because of the short separation time (<30 min).

Separation with 0.08 M Na_2SO_4, H_2SO_4, pH 2.3, was used to obtain the relative amounts of $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$, whereas elution with 0.03 M Na_2SO_4, H_2SO_4, pH 2.3, was used to obtain the relative amounts of $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_4Cl_2^+$. The different eluents were chosen to obtain optimal conditions for determination

Table 3. Estimations of the average ligand numbers in the studied $CrCl_3$–LiCl solution from the red shifts of the maxima and the molar absorbances at the four wavelengths used.

No.	$\bar{n}_{\lambda_1}$	$\bar{n}_{\lambda_2}$	$\bar{n}_{650}$	$\bar{n}_{605}$	$\bar{n}_{450}$	$\bar{n}_{430}$	$\bar{n}_{av}$
2	~0	~0	0.040	0.024	0.054	0.047	0.04
3	0.15	0.15	0.162	0.144	0.136	0.120	0.14
4	0.30	0.42	0.42	0.37	0.43	0.36	0.40
5	1.06	1.14					1.10
6	1.82	1.95					1.88
7	2.29	2.40					2.34
8	2.84	3.05					2.94
11	0.18	0.21	0.19	0.19	0.21	0.21	0.20
12	0.41	0.48	0.38	0.34	0.41	0.37	0.38
13	1.21	1.26					1.23
14	1.84	2.05					1.94
15	2.74	2.90					2.82
16	2.92	3.10					3.01

Table 4. Values of the mean activity coefficients of LiCl on molar basis and the water activities of the studied Cr(III)–LiCl solutions at 25 °C calculated from isopiestic measurements.[14]

No.	$C_{(Li,H)Cl}$	$\gamma_\pm^c$	a_{H_2O}	$\log a_{Cl^-}$ [a]
1	0	(0.79)		
2	1.30	0.85	0.95	0.066
3	2.60	1.15	0.89	0.526
4	3.90	1.74	0.79	0.934
5	6.55	5.13	0.58	1.763
6	8.58	13.2	0.38	2.474
7	10.23	26.9	0.26	3.025
8	12.48	59.5	0.155	3.680
10	1.42	0.87	0.94	0.119
11	2.72	1.18	0.88	0.562
12	4.11	1.86	0.77	0.997
13	6.62	5.28	0.57	1.788
14	8.70	13.8	0.37	2.511
15	11.39	41.7	0.20	3.376
16	12.47	59.5	0.155	3.680

[a] $\log a_{Cl^-} = \log (C_{LiCl} \, \gamma_\pm^c / a_{H_2O})$.

of the relative areas of the involved peaks in the chromatogram. Examples of such chromatograms are shown in Fig. 3. The calculations were performed at two wavelengths. The wavelengths used for the separation of $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_6^{3+}$ were 420 and 580 nm, and for the separation of $Cr(H_2O)_4Cl_2^+$ and $Cr(H_2O)_5Cl^{2+}$ 440 and 620 nm. The area of the peak of a given species divided by the molar absorbance of the species represents the relative amount of this species in relation to other species. The ratio between the relative amounts of $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_6^{3+}$, which is the same as the ratio between their concentrations in the sample, was calculated directly from the areas in the chromatogram and the molar absorbances
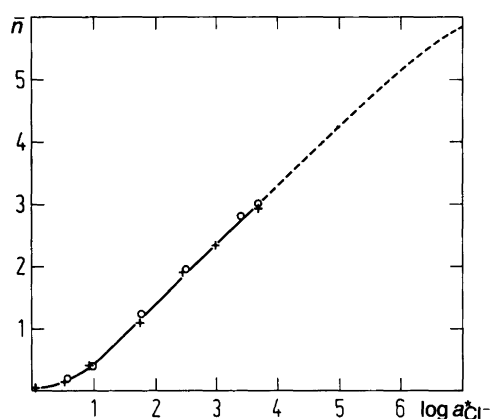
Fig. 2. The formation curve for the chromium(III) chloride system. The ligand numbers $\bar{n}$ versus $\log a_{Cl^-}$ are plotted from the data given in Tables 3 and 4. The points obtained for solutions 1–8 are indicated by +, and those for solutions 10–16 by O. The dotted line for $\bar{n} > 3$, which continues the curve up to $\bar{n} = 6$, is drawn symmetrical about the midpoint of the formation curve.
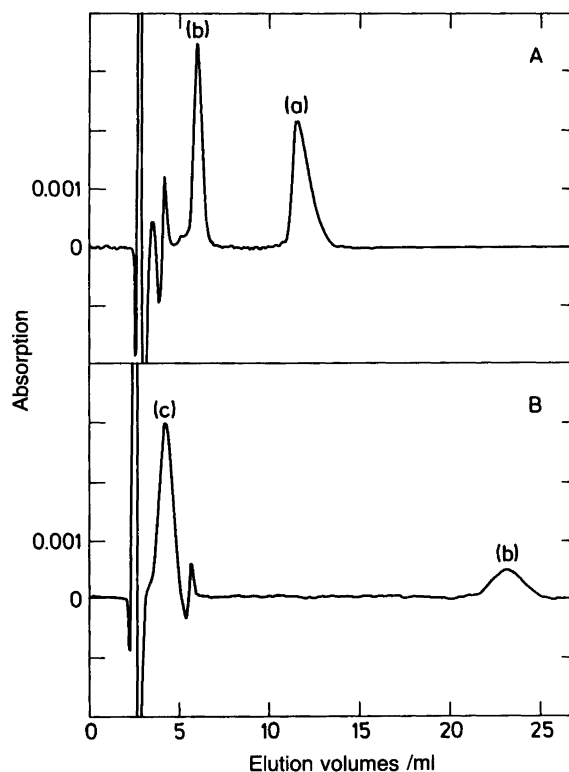
Fig. 3. HPLC chromatograms. (A) Separation of (a) $Cr(H_2O)_6^{3+}$ and (b) $Cr(H_2O)_5Cl^{2+}$ from equilibrium solution 12 in Table 1 at 420 nm. The chromatogram was obtained by injecting 8 µl sample and eluting with 0.08 M Na_2SO_4, pH 2.3. Flow rate 1.0 ml min⁻¹. Ordinate: absorbance unit 0.001. (B) Separation of (b) $Cr(H_2O)_5Cl^{2+}$ and (c) $Cr(H_2O)_4Cl_2^+$ from equilibrium solution 14 in Table 1 at 440 nm. The chromatogram was obtained by injecting 5 µl sample and eluting with 0.03 M Na_2SO_4, pH 2.3. Flow rate 1.0 ml min⁻¹. Ordinate: absorbance unit 0.001.

of the species given in Table 5. The relative amounts of $Cr(H_2O)_4Cl_2^+$ and $Cr(H_2O)_5Cl^{2+}$ were estimated using the same procedure. However, the peak from $Cr(H_2O)_4Cl_2^+$ was so close to the elution of the LiCl front that it was necessary to take special precautions in the calculations of the areas of this peak. The amount of $Cr(H_2O)_4Cl_2^+$ was calculated by subtracting the integral of the peak in the chromatogram at 520 nm [where the absorbance of $Cr(H_2O)_4Cl_2^+$ is at a minimum] from the integral of the peak at 440 or 620 nm (wavelengths where the absorbance of the complex ion is close to a maximum) in order to eliminate the contribution from the LiCl front. The molar absorbances to be used to calculate the amount of the complex from these corrected areas are accordingly the difference between the molar absorbances at 440 or 620 nm and the molar absorbance at 520 nm, $(\varepsilon_{440} - \varepsilon_{520})$ and $(\varepsilon_{620} - \varepsilon_{520})$, respectively. The results obtained at 440 and 620 nm normally agreed within 5 %. The tacit assumption for the calculation of the amounts of $Cr(H_2O)_4Cl_2^+$ that the contribution from the LiCl front is independent of the wavelength can be confirmed directly from observation of

Table 5. Molar absorbances of $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_4Cl_2^+$ in 0.5 M $HClO_4$ at 25 °C at the wavelengths used in the HPLC calculations.[a]

λ/nm	$\varepsilon Cr(H_2O)_6^{3+}$	$\varepsilon Cr(H_2O)_5Cl^{2+}$	$\varepsilon Cr(H_2O)_4Cl_2^+$
420	14.12	20.47	–
440	–	19.61	24.68
520	–	4.01	4.01
580	13.18	14.20	–
620	–	15.94	20.27

[a]Directly measured figures by courtesy of O. Mønsted.[13]

the chromatograms of $Cr(H_2O)_4Cl_2^+$ at 440, 620 and 520 nm shown in Fig. 4.

The results of the HPLC determinations of K_1 and K_2 from selected equilibrium solutions are shown in Table 6. The calculation of these "semi-thermodynamic" constants were performed by use of the estimated values of the ratios of the amounts of the complex ions, the chloride ion concentration and the values of $\gamma_\pm^c$ and a_{H_2O} given in Table 4.
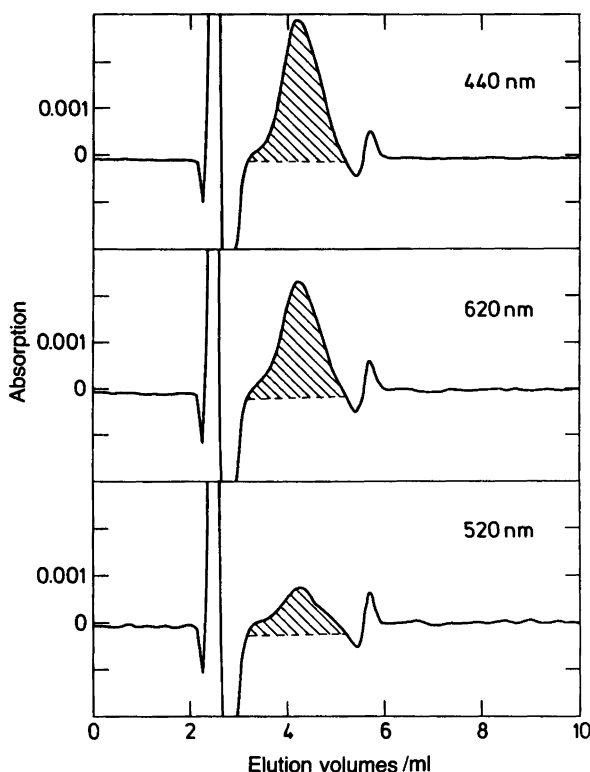

Fig. 4. Chromatograms $Cr(H_2O)_4Cl_2^+$ at 440, 620 and 520 nm from equilibrium solution 14. Shaded areas are the areas used to determine the amount of the dichloro complex as described in the text.

Table 6. Survey of the experimental HPLC data used to calculate the semi-thermodynamic stability constants K_1 and K_2. The figures in parentheses indicate the estimated uncertainty in the last digit.

Equil. sol. No.	λ/nm	Area ratio[a]	$\dfrac{[CrCl^{2+}]}{[Cr^{3+}]}$	K_1
10	420	0.133(3)	0.092(2)	0.070(2)
10	580	0.098(3)	0.091(2)	0.069(2)
11	420	0.299(3)	0.206(2)	0.0565(5)
11	580	0.217(2)	0.201(2)	0.0553(4)
12	420	0.78(2)	0.54 (1)	0.054(1)
12	580	0.552(7)	0.512(6)	0.00516(6)
13	420	4.5(2)	3.1 (1)	0.051(2)
13	580	3.05(6)	2.83 (5)	0.0462(8)
				Av. 0.0567

Equil. sol. No.	λ/nm	Area ratio[b]	$\dfrac{[CrCl_2^+]}{[CrCl^{2+}]}$	K_2
12	440	0.05(2)	0.05 (2)	0.005(2)
12	620	0.061(6)	0.060(6)	0.0060(6)
13	440	0.42(2)	0.40 (2)	0.0064(2)
13	620	0.38(2)	0.37 (2)	0.0061(3)
14	440	1.48(6)	1.40 (6)	0.0043(2)
14	620	1.29(5)	1.26 (5)	0.0039(2)
				Av. 0.0053

[a]The ratio of the area of the $Cr(H_2O)_5Cl^{2+}$ and the $Cr(H_2O)_6^{3+}$ peaks at the stated wavelength. [b]The ratio of the area of the $Cr(H_2O)_4Cl_2^+$ and $Cr(H_2O)_5Cl^{2+}$ peaks is corrected for the absorption due to the LiCl front.

Discussion of results

The formation curve in Fig. 2 derived from spectrophotometric measurements extends only to $\bar{n} = 3$. Chromium(III) systems are, however, known to have the coordination number 6; Werner and Gubser[1] have, under extreme conditions, prepared a red–violet compound $Rb_2[Cr(H_2O)Cl_5]$, while Hatfield *et al.*[15] have shown the presence of the octahedral hexachloro complex in the crystal structure of $[Crpn_3][CrCl_6]$. The chromium(III) chloride system is free from steric strain, and is a system in which no change in configuration and total spin quantum number occurs.[16,17] Systems with non-charged ligands such as the ammonia systems[16] usually have a rather constant ligand effect, and this is probably also the case for the Cr(III) chloride system. The formation of these complexes takes place at high ionic concentrations where the Coulombic forces can be neglected [compare with the Cu(II) chloride system[18,19]]. The formation curve in Fig. 2 is with this assumption tentatively prolonged up to $\bar{n} = 6$, assuming symmetry around the midpoint of the curve. The values of $-\log a_{Cl^-}^*$, -1.08, -2.10 and -3.16, from the experimental part of the curve for $\bar{n} = 0.5$, 1.5 and 2.5, respectively, represent preliminary constants, and the values of $\log K_n(\lambda, \varepsilon)$ shown in Table 7 are calculated from these constants by iteration as described in Ref. 16, p. 37. These stability

Table 7. Survey of the "semi-thermodynamic" stability constants for the Cr(III) chloride system at 25 °C calculated in various ways.

n	$-\log(a^{*}_{Cl^-})_{n=n-\frac{1}{2}}$	$\log "K_n"$	$\log K_n(\lambda,\varepsilon)$	$\log K_n$ (HPLC)
1	−1.08	−0.99	−1.20	−1.25
2	−2.10	−2.14	−2.07	−2.28
3	−3.16	−3.19	−3.16	
4	(−4.22)	−4.21	−	
5	(−5.30)	−5.26	−	
6	(−6.44)	−6.41	−	

constants are seen to compare nicely with the average values of log K_1 and log K_2 (in the last column of Table 7) calculated from the HPLC measurements from Table 6. This agreement makes us confident that the values of the stability constants presented in this paper are reasonably correct.

The "K_n" values in Table 7 are given by eqn. (1) and

$$\log "K_n" = -\log (a^{*}_{Cl^-})_{\bar{n}=3} + \log \left(\frac{7-n}{n}x^{7-2n}\right) \qquad (1)$$

calculated using the knowledge that log $(a_{Cl^-})_{\bar{n}=3} = 3.70$ and that the midpoint slope of the formation curve is given by eqn. (2).

$$\Delta = 0.4343 \left(\frac{d\bar{n}}{d\log a^{*}_{Cl^-}}\right)_{\bar{n}=3} = 0.408 \qquad (2)$$

The expression for "K_n" is derived under the assumption that the system has a constant ligand effect, and that the factor x is defined by the relationship given in Ref. 16, p. 46

$$\frac{K_n}{K_{n+1}} = \frac{(6-n+1)(n+1)}{(6-n)n}x^2 \qquad (3)$$

[eqn. (3)] where $(6-n+1)(n+1)/(6-n)n$ is the statistical ratio and 2 log x is the ligand effect.

For systems with coordination number 6, Δ is related to x by eqn. (4), given in Ref. 16, p. 31, from which relationship x is calculated to be 2.438.

$$\Delta = \frac{18 + 48\,x^5 + 30x^8}{2 + 12x^5 + 30x^8 + 20x^9} \qquad (4)$$

The "K_n" values in Table 7 are seen to agree rather nicely with the experimentally determined constants, and enable us at the same time to propose the order of magnitude of the extremely small stability constants K_n for $n > 3$, which cannot be determined experimentally in aqueous solution.

The rather good agreement between the calculated "K_n" values and the $-\log(a^{*}_{Cl^-})_{\bar{n}=n-\frac{1}{2}}$ values obtained from the tentatively prolonged formation curve is noteworthy.

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