Estimation of Small Stability Constants in Aqueous Solution. The Chromium(III)–Bromide System

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Weak complex formation in the chromium(III)–bromide system has been studied by spectrophotometric measurements and by ion-exchange high-performance liquid chromatography (HPLC). The equilibria were studied at 25 °C in weakly acidic LiBr solutions up to ≈ 11 M. The semi-thermodynamic constant $K_1 = [Cr(H_2O)_5Br^{2+}]a_{H_2O}/[Cr(H_2O)_6^{3+}][Br^-]\gamma^c_{LiBr}$, was found by HPLC to have the value 0.0024 ± 0.0004 M^{-1} in equilibrium solutions containing from 4.5 to 9.5 M LiBr. The uncorrected concentration constant varied in the same equilibrium solutions from 0.0128 to 1.02 M^{-1}. From the red shifts of the absorption spectra per ligand taken up the following values were estimated for the semi-thermodynamic constants: $K_1 \approx 0.0030$, $K_2 \approx 0.00035$ and $K_3 \approx 0.00004$ M^{-1}. The hydrolysis of the dichloro and dibromo complexes in 1 M acidic solutions is more than 100 times faster than the hydrolysis of the monohalogeno complexes. This fact was used to prepare pure solutions of the monohalogeneo ions which could be precipitated as Recoura's chloro- and bromosulfates.

The yellow–green chromium(III) bromide salt [CrBr$_2$(H$_2$O)$_4$]Br·2H$_2$O was first prepared by Recoura,[1] and the preparation was later modified by Werner et al.[2] and by N. Bjerrum.[3] In aqueous solution this salt is transformed via the monobromo complex to the hexaaqua ion, and the molar enthalpy for this dissociation is −11.6 kcal.[4,5] The complex formation in chromium(III)–bromide solutions has been studied by King and coworkers[6,7] by cation-exchange measurements. Using this method Espenson and King[6] isolated the monobromo species Cr(H$_2$O)$_5$Br^{2+} in solution and determined the formal concentration constant Q_1 for the inner-sphere complex formation in 2 M solution to be as low as 0.0022 M^{-1} at 25 °C. Spreer and King[7] determined by the same method both of the inner-sphere formal concentration constants Q_1 and Q_2 in concentrated aqueous hydrogen bromide solutions. They used elevated temperatures (45–75 °C), since equilibrium establishment at room temperature takes several weeks in these solutions. Using spectrophotometric measurements in the near-ultraviolet, Spreer and King[7] also studied the instantaneous and much greater outer-sphere association between the complex species and the bromide ion.

In the present work, which extends our study[8] of the chromium(III)–chloride system, the ratio between the concentrations of the monobromo complex and the hexaaqua ion in the lithium bromide solutions was determined by high-performance liquid chromatography (HPLC) measurements. The semi-thermodynamic stability constant K_1 is defined by eqn. (1), where a_{H_2O} is the activity of water and

$$K_1 = \frac{[CrBr(H_2O)_5^{2+}]a_{H_2O}}{[Cr(H_2O)_6^{3+}][Br^-]\gamma_\pm^c} \qquad (1)$$

$[Br^-]\gamma_\pm^c$ is the activity of lithium bromide on a molar basis. Use of this expression for K_1 led to a surprisingly high constancy of the value for this constant ($K_1 = 0.0024 \pm 0.0004$) over a large concentration range. The dibromo complex is so rapidly hydrolyzed in solution to the monobromo complex that it could not be determined quantitatively from the HPLC chromatograms, and for this reason K_2 could not be determined by this method. However, some information concerning the stability of the dibromo complex was obtained from the red shifts of the absorption bands in the equilibrium solutions ($K_2 \approx 0.00035$). The method used extensively by one of the authors[9] to estimate the value of the stability constant by analysis of the isosbestic spectra of equilibrium solutions was also applied, and is discussed in connection with the validity of the semi-thermodynamic expression defined in eqn. (1).

The rate of conversion of the dihalogeno to the monohalogeno complexes in 1 M acidic solutions is more than 100 times greater than the rate of hydrolysis of the monohalogeno complexes to the hexaaqua ion. This fact made it possible to prepare pure solutions of the monohalogeno complexes which could be precipitated with sulfuric acid to give very pure samples of Recoura's halogenosulfates, [Cr(H$_2$O)$_5$Cl]SO$_4$·H$_2$O[10] and [Cr(H$_2$O)$_5$Br]SO$_4$·H$_2$O,[11] respectively.

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Experimental

Materials and instruments. The chemicals used were of analytical grade. The anhydrous LiBr (Fluka, purum *p.a.*) was purified to remove a weak near-ultraviolet absorption by treatment with charcoal and recrystallization. The nearly saturated stock solution of LiBr was analyzed by Volhard titration. Solutions with low Cr(III) concentrations were prepared from a stock solution of hexaaquachromium(III) chloride analyzed by atomic absorption. The use of chromium chloride instead of chromium bromide had no influence on the precision of the measurements. The absorption was measured with a Cary 118 spectrophotometer and with a Perkin–Elmer Lambda diode array spectrophotometer suitable for rapid reactions.

Ion-exchange HPLC was performed on Waters HPLC equipment as described previously.[8] The separation was performed using a strong cation-exchange column (Protein Pak SP 5PW, Waters) of dimensions 75 mm × 7.5 mm i.d. This column material, containing the group $-CH_2CH_2CH_2SO_3^-$, is not suitable for operation below pH 2. The separations of the $Cr(H_2O)_5Br^{2+}$ and the $Cr(H_2O)_6^{3+}$ ions from the equilibrium solutions were performed by isocratic elution (1 ml min^{-1}) with 0.075 M Na_2SO_4 acidified with H_2SO_4 to pH 2.06. The elution profile from 0 to 27 min was recorded with a full spectrum (300–800 nm) obtained at 7 s intervals. All separations were carried out at 0 °C, achieved by cooling the column and inlet with ice, and were repeated at least three times.

Prepared salts. $[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$ was prepared by a method based on that described by Gutierrez de Cells[12] from chromium(VI) oxide and 50 % HBr. Before crystallization the reaction mixture was evaporated to a smaller volume than that specified.[12] The yellow–green salt was washed with alcohol and ether and dried over 80 % H_2SO_4. Yield 44 %. Anal. $CrBr_3 \cdot 6H_2O$: Cr, 13.02. Found Cr, 12.95.

$[Cr(H_2O)_5Br]SO_4 \cdot H_2O$ was first prepared by Werner and Huber[11] and later by N. Bjerrum *et al.*[13] from dibromochromium(III) bromide and sulfuric acid. The preparation used in the present work utilized the fact that a 1 M acidic solution of the yellow–green bromide is almost completely

converted into a solution of the monobromochromium(III) ion after about 1 h at room temperature. The procedure is as follows: 12 g of $[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$ (0.03 mol) was dissolved in 8 ml of 2 M H_2SO_4 and the solution was left to stand for 40 min at room temperature for crystallization to begin. 1 ml of conc. H_2SO_4 and 8 ml of ethanol were then added dropwise with cooling. After about 1 h the light-green crystals were isolated by filtration on a sintered glass filter, washed with diethyl ether and dried in a desiccator over 80 % H_2SO_4. Yield 6.8 g (65 %). Anal. $CrBrSO_4 \cdot 6H_2O$: Cr, 15.47; Br, 23.78. Found Cr, 15.43; Br, 23.72.

$[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ was first prepared by Recoura[10] from violet chromium(III) sulfate and concentrated hydrochloric acid. By exploiting the fact that a 1 M acid solution of dichlorochromium(III) chloride is essentially completely converted into a solution of the monochlorochromium(III) ion after about 24 h at room temperature, very pure samples of Recoura's chlorosulfate could be prepared as follows: 8 g of commercial (Riedel de Haen, rein) dichlorochromium(III) chloride (0.03 mol) was dissolved in 8 ml of 2 M H_2SO_4 and the solution was allowed to stand overnight. 2 ml of conc. H_2SO_4 and 8 ml of ethanol were then added dropwise with cooling. After about 1 h the light-green crystals was isolated by suction filtration on a sintered glass filter. Yield 3 g (34 %).

Results

Kinetics. The two-step hydrolysis of the dichlorochromium (III) complex to the hexaaqua ion studied by N. Bjerrum[14,15] in 1906 in weakly acidic (0.0005–0.01 M) HCl solutions. On the basis of rate experiments at 25 °C he arrived at the relationships of eqns. (2) and (3) for the dependence of the rate constants on the acid concentration. In these

$$k_{2,1} = 0.00227 + 0.0000162 \, [H^+]^{-1} \tag{2}$$

$$k_{1,0} = 10^{-7} \times (31 \, [H^+] + 0.005 \, [H^+]^{-2}) \tag{3}$$

expressions $k_{2,1}$ (min^{-1}) is the first-order rate constant for the reaction $Cr(H_2O)_4Cl_2^+ \rightarrow Cr(H_2O)_5Cl^{2+}$ and $k_{1,0}$ (min^{-1}) the corresponding rate constant for the reaction

Table 1. Some kinetic data for the two consecutive first-order hydrolyses of the dihalogenochromium(III) complexes to the hexaaqua ion.

T/°C	Medium	Cr(III) salt	$K_{2,1}$/min^{-1}	$K_{1,0}$/min^{-1}
25	1.04 M HBr	$[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$	0.160	
25	1.00 M HBr	$[Cr(H_2O)_5Br]SO_4 \cdot H_2O$		0.00041
25	0.107 M HBr	$[Cr(H_2O)_5Br]SO_4 \cdot H_2O$		0.00129
25	0.0107 M HBr	$[Cr(H_2O)_5Br]SO_4 \cdot H_2O$		0.0112
25	0.30 M NaClO$_4$[a]	$[Cr(H_2O)_5Br]SO_4 \cdot H_2O$	0.27	0.016
0.3	0.075 M Na$_2$SO$_4$[b]	$[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$	0.0084	
25	1.00 M HCl	$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	0.0028	
25	1.00 M HCl	$[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$		0.000023

[a]pH 2.3. [b]pH 2.06.

$Cr(H_2O)_5Cl^{2+} \rightarrow Cr(H_2O)_6^{3+}$. According to these expressions $k_{1,0}$ is strongly dependent on the acid concentration, in contrast to $k_{2,1}$, which is only very slightly dependent on the acid concentration below pH 2. Bjerrum did not make rate measurements at high acid concentrations, but our results with the chloro complexes in 1.0 M HCl in this study show that the expressions are also approximately valid at high acid concentrations (Table 1). Our results are collected in Table 1 and show that while $k_{2,1}$ is nearly independent, $k_{1,0}$ is inversely proportional to the hydrogen ion concentration. The estimated rate constants in Table 1 were calculated from the change in molar absorbance with time at selected wavelengths. The most rapid reactions could only be followed using the Perkin–Elmer spectrophotometer, which can record spectra at very short intervals. Table 2 gives data for the very rapid hydrolysis of the *trans*-dibromo to the monobromo complex. The dichlorochromium(III) salt $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ is known to dissolve as the *trans* isomer,[16] and there is much evidence that the same is the case for $[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$. The instantaneous spectrum of the *trans*-dibromo complex is shown in Fig. 1. The less rapid reactions were all monitored using the Cary spectrophotometer, and an example of the rate determinations is shown in Table 3. The high values found for the ratio between the rate constants $k_{1,0}$ and $k_{2,1}$ in both the bromo and the chloro systems form the basis for our preparations of the pure samples of Recoura's halogenosulfates. The ratio $k_{1,0}/k_{2,1}$ in 1 M acidic solutions is found to have the value 122 for the chloride and 390 for the bromide system. The higher value for the ratio in the bromide than in the chloride system is in agreement with the higher *trans* effect of the bromide ion than of the chloride ion.

Comparison of the absorption spectra of the equilibrium solutions with those of the pure complexes. The spectra of the pure bromide complexes are shown in Fig. 1 and those of the studied equilibrium solutions in Fig. 2. The composition and other data for the equilibrium solutions are given

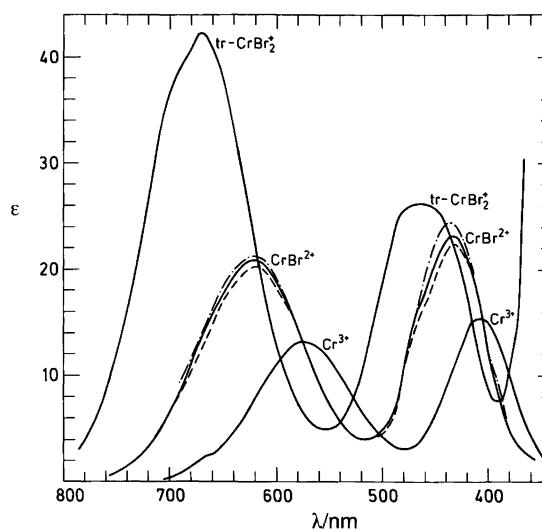Fig. 1. The (ε, λ) absorption spectra of the hexaaqua-, the monobromo- and the *trans*-dibromochromium(III) complexes in the two visible bands at 25 °C. The *trans*-dibromo spectrum is the extrapolated spectrum ($t = 0$) of $[CrBr_2(H_2O)_4]Br \cdot 2H_2O$ in 1 M HBr. The spectrum of the monobromo complex was measured (1) in a solution of $[CrBr(H_2O)_5]SO_4 \cdot H_2O$ in 0.36 M HBr (-----), (2) in 4.55 M LiBr and 0.36 M HBr (-·-·-) and (3) in a solution of $[CrBr_2(H_2O)_4]Br \cdot 2H_2O$ in 1 M HBr after about 1 h (———).

in Table 4. In order to ensure that equilibrium was established, the solutions were kept for several hundred hours at 25 °C. The activity coefficient on a molar basis, $\gamma_\pm^c$, for LiBr and the activity of water, a_{H_2O}, were calculated from the isopiestic measurement of Robinson and Stokes.[16]

What is assumed to be the *trans*-dibromo complex has a higher molar absorbance in the first band (with a maximum at 670 nm) than an equilibrium solution at the same wavelength. The unknown molar absorbance of the *cis* isomer must therefore necessarily be still lower. In contrast, in the second band it is the *cis* complex which has the higher molar absorbance. This is completely in agreement with the findings of Mønsted and Mønsted[17] in the chloride system, and supports our assumptions as to what is *cis* or *trans* in the bromide system. It is also noteworthy that the authors found that the *cis* and *trans* dichlorochromium(III) complexes have absorption maxima at the same wavelength.

Table 2. Data for the change in molar absorbance of a 0.0105 M solution of $[Cr(H_2O)_4Br_2] \cdot 2H_2O$ in 1.04 M HBr at 670 nm (close to ε_{max}) and with constancy at 618 nm (isosbestic wavelength) at 25 °C.

t/s	ε_{618}	ε_{670}	$1-\alpha$	$k_{2,1}/min^{-1}$
0[a]	21.0	42.3	1	
59	21.0	38.1	0.856	0.158
119	21.0	34.4	0.729	0.160
179	20.9	31.3	0.623	0.158
249	20.9	28.2	0.517	0.159
369	20.9	23.8	0.366	0.164
489	20.9	20.7	0.260	0.165
729	20.9	17.4	0.147	0.158
∞[b]	20.8	13.1	0	

Av. 0.160

[a]The spectrum of $Cr(H_2O)_4Br_2^+$ as found by extrapolation to $t = 0$.
[b]The spectrum of $Cr(H_2O)_5Br^{2+}$ as found after about 1 h.

Table 3. Data for the change in molar absorbance of a 0.0336 M solution of $[Cr(H_2O)_5Br]SO_4 \cdot 2H_2O$ in 1.00 M HBr at 620 nm (close to ε_{max}) and with constancy at 578 nm (the isosbestic wavelength) at 25 °C.

t/h	ε_{578}	ε_{620}	$1-\alpha$	$k_{1,0}/min^{-1}$
0[a]	13.1	19.80	1	
7	13.0	18.15	0.85	0.00039
21	12.9	15.33	0.596	0.00041
46	12.8	12.02	0.293	0.00044
∞[b]	13.1	8.80	0	

Av. 0.00041

[a]The spectrum of $Cr(H_2O)_5Br^{2+}$. [b]The spectrum of $Cr(H_2O)_6^{3+}$.
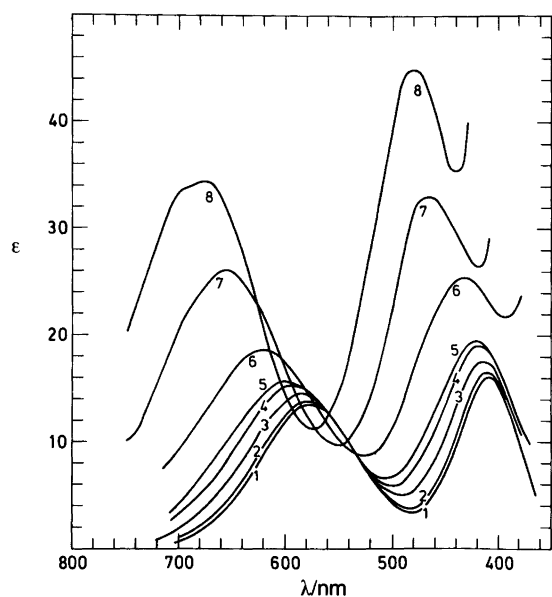
Fig. 2. The (ε,λ) absorption spectra of the studied Cr(III)–LiBr equilibrium solutions (Nos. 1–8, Table 4) in the two visible bands at 25 °C.

The same seems to be the case for the *cis*- and *trans*-dibromochromium(III) complexes, as judged from the spectra obtained for the equilibrium mixture of the dibromo complexes after isolation by HPLC. One can there-

fore equally well compare the red shift of the equilibrium solutions with the spectrum of the *trans*-dibromo complex as with the *cis–trans* equilibrium mixture of the dibromo complex.

In Table 5 the values of ε and λ for the absorption maxima of the equilibrium solutions are compared with those for the pure complexes. The red shift (in nm) on going from the mono- to the dibromo complex is a little higher than on going from the hexaaqua ion to the mono-bromo complex, but no more than that corresponding to a constant energy difference in cm^{-1}. It therefore seems reasonable to assume that the average ligand number in a given equilibrium solution is roughly proportional to the observed red shift in the spectrum of the solution, if the molar absorbances of the complexes in their maximum are not too different. The values of $\bar{n}$ in Table 5 are calculated according to these assumptions. The conclusions which can be drawn from a knowledge of the average ligand numbers are discussed in a later section of the paper.

Determination of the first stability constant from HPLC measurements. Information concerning the relative amounts of the complexes in an equilibrium mixture can, in the case of robust complexes, be obtained by ion-exchange HPLC. The area of a peak in a HPLC chromatogram is related by the Lambert–Beer law to the total amount of the complex giving rise to the peak. It is thus possible to

Table 4. Composition and activity data for the studied Cr(III)–bromide equilibrium solutions.

No.	$C_{Cr^{3+}}$	C_{HBr}	C_{LiBr}	$\gamma_\pm{}^c$	a_{H_2O}	$a^*_{Br^-}{}^a$	t/h^b
1	0.0394	0.0050	2.32	1.23	0.92	3.1	888
2	0.0394	0.0050	4.64	3.39	0.71	22.1	888
3	0.0394	0.0050	6.03	6.92	0.58	71.9	480
4	0.0394	0.0050	6.96	12.02	0.46	182	888
5	0.0394	0.0050	7.42	16.2	0.42	286	480
6	0.0394	0.0050	8.35	33.8	0.32	882	576
7	0.0394	0.0050	9.55	87.1	0.204	4077	600
8	0.0394	0.0050	10.86	199.5	0.110	19700	600

$^a a^*_{Br^-} = [LiBr]\gamma_\pm{}^c/a_{H_2O}$. ^{b}At 25 °C.

Table 5. Values of average ligand numbers $(\bar{n})$ estimated from the red shifts $(\Delta\lambda)$ of the maxima of the absorption curves compared with those for the pure bromide complexes.

No.	ε_{max1}	λ_{max1}	$\Delta\lambda_{max1}$	$\bar{n}$	ε_{max2}	λ_{max2}	$\Delta\lambda_{max2}$	$\bar{n}$	$\bar{n}_{av}$
0^a	13.2	575	0	0	15.6	407	0	0	
1	13.5	576	1	0.02	16.0	408	1	0.04	0.03
2	13.8	579	4	0.09	16.6	410	3	0.11	0.10
3	14.5	586	11	0.24	17.6	415	8	0.28	0.26
4	15.2	594	19	0.42	19.2	420	13	0.46	0.44
5	15.6	600	25	0.56	19.6	421	14	0.50	0.53
6	18.6	620	45	1.00	25.4	434	27	0.96	0.98
$\varepsilon_1{}^b$	20.9	620	45	1	23.1	435	28	1	
7	26.0	656	81	1.62	33.0	464	57	1.89	1.75
$\varepsilon_{2\ trans}{}^c$	42.3	670	95	2	26.2	465	58	2	
8	34.4	680	105	2.10	45.0	480	73	2.43	2.31

$^a\varepsilon_{max}$ for $Cr(H_2O)_6^{3+}$. $^b\varepsilon_{max}$ for $Cr(H_2O)_5Br^{3+}$. $^c\varepsilon_{max}$ for *trans*-$Cr(H_2O)_4Br_2^{3+}$.
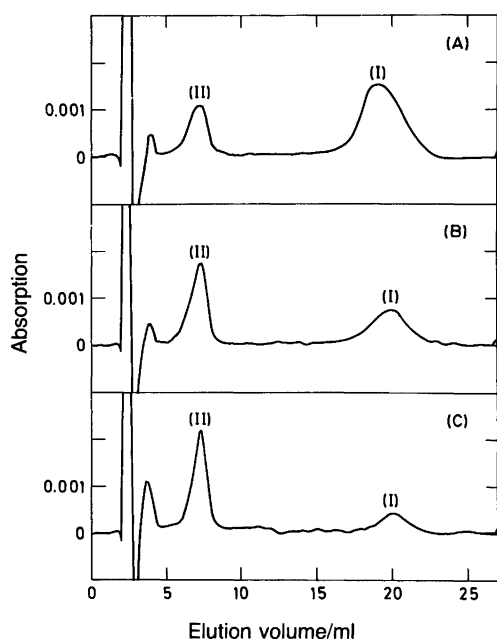
Fig. 3. HPLC chromatograms showing the separations of (I) $Cr(H_2O)_6^{3+}$ and (II) $Cr(H_2O)_5Br^{2+}$ for various equilibrium solutions in Table 4: (A) equilibrium solution No. 3 (12 µl), (B) equilibrium solution No. 5 (6 µl) and (C) equilibrium solution No. 6 (5 µl). The chromatograms recorded at 420 nm were obtained by injecting the indicated amount of the equilibrium solution and eluting with 0.075 M Na_2SO_4, pH 2.06. Flow rate 1.0 ml min^{-1}. Temperature 0 °C. Ordinate in absorption units.

calculate the relative amounts of two complexes in an equilibrium solution from the areas of the separated peaks in the chromatogram when the molar absorbances of the two complexes are known.

The individual cationic complexes $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$ in samples of the Cr(III)–LiBr equilibrium solutions (Nos. 2–7, Table 4) were separated by ion-exchange HPLC using Na_2SO_4 solutions acidified with H_2SO_4 as eluent. $Cr(H_2O)_5Br^{2+}$ was eluted before $Cr(H_2O)_6^{3+}$, as seen from the absorption spectra of the separated complexes. Examples of chromatograms obtained under conditions optimized for the separation of $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$ are shown in Fig. 3. The $Cr(H_2O)_4Br_2^{+}$ ion was not separated from the elution front of LiBr under the conditions used to separate $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$. Furthermore, no attempt was made to optimize the separation of the $Cr(H_2O)_4Br_2^{+}$ ion, since the high rate constant for the first-order hydrolysis of $Cr(H_2O)_4Br_2^{+}$ to Cr $(H_2O)_5Br^{2+}$, even under conditions optimized to suppress the hydrolysis, would make it difficult to obtain reliable determinations of the amount of $Cr(H_2O)_4Br_2^{+}$ relative to the amount of $Cr(H_2O)_5Br^{2+}$.

The ratio between the relative amounts of $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$, which is the same as the ratio between their concentrations in the sample, was calculated from the areas of the peaks in the chromatograms and the molar absorbances of the species. The calculations were performed at two wavelengths, viz. 420 and 600 nm, in order
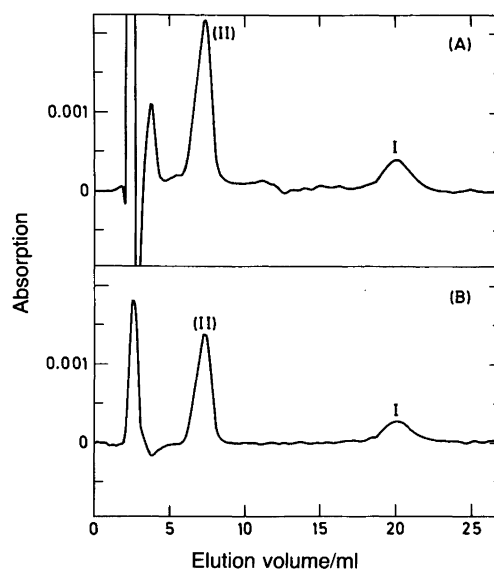

Fig. 4. HPLC chromatograms showing the separation of (I) $Cr(H_2O)_6^{3+}$ and (II) $Cr(H_2O)_5Br^{2+}$: (A) chromatogram at 420 nm, and (B) chromatogram at 420 nm after subtraction of the chromatogram at 500 nm (see text). The separation conditions were as indicated for Fig. 3(C).

to check for internal consistency. The calculations were further refined to reduce contributions from baseline noise by subtracting the chromatogram recorded at 500 nm, where the molar absorbances of $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$ are near minimum, from the chromatograms recorded at 420 and 600 nm, where the molar absorbances of the two complexes are near maximum. An example of the significance of such subtractions is shown in Fig. 4. The molar absorbances used to calculate the amounts of the complexes from these corrected areas are accordingly the differences between the molar absorbances at 420 and 600 nm and the molar absorbance at 500 nm ($\varepsilon_{420}-\varepsilon_{500}$ and $\varepsilon_{600}-\varepsilon_{500}$, respectively). The refinement had only a minor influence on the final results, but reduced the standard deviation on the mean value. The results obtained at 420 and 600 nm from a single separation were normally the same within 20 %. All separations were repeated at least three times.

Table 6. The constancy of the semi-thermodynamic constant K_1 calculated from HPLC measurements.

No.	C_{LiBr}	$[CrBr^{2+}]/[Cr^{3+}]$	Q_1 a	"K_1" b	K_1
2	4.64	0.0593	0.0128	0.003 77	0.002 68
3	6.03	0.185	0.0308	0.004 45	0.002 58
4	6.96	0.442	0.0635	0.005 28	0.002 43
5	7.42	0.641	0.0863	0.005 33	0.002 24
6	8.35	1.57	0.188	0.005 56	0.001 78
7	9.55	9.77	1.023	0.011 8	0.002 40

Av. 0.002 4
± 0.000 4

a Q_1 is the formal equilibrium quotient. b "K_1" is calculated without correction for the change in water activity.

Table 7. K_1 calculated from the data of Spreer and King[a] with estimated values for $\gamma_\pm^c$ and a_{H_2O} in HBr solutions.

C_{HBr}	Q_1 (25 °C)	$\gamma_\pm^c$	a_{H_2O}	K_1
2.10	0.0017	≈ 1	≈ 0.9	0.0018
8.92	0.19	≈ 40	≈ 0.4	0.0019

[a]Ref. 7.

Table 8. Estimation of K_1, K_2 and K_3 using eqn. (2) (see text).

n	$\log (a^*_{Br^-})_{n=\bar{n}+1/2}$	$(1/a^*_{Br^-})_{n=\bar{n}+1/2}$	K_n
1	2.42	0.003 80	0.002 97
2	3.45	0.000 354	0.000 35
3	4.40	0.000 040	0.000 04

Fig. 5. The formation curve for the chromium(III)–bromide system. The ligand numbers $\bar{n}$ vs. $\log (a^*_{Br})$ are plotted from the data given in Tables 4 and 5.

The results of the HPLC determination of the formal equilibrium quotient Q_1 for selected equilibrium solutions, together with the calculated semi-thermodynamic constant K_1, are shown in Table 6. The calculation of the semi-thermodynamic constant was performed using the values of the relative amounts of the two complexes $Cr(H_2O)_5Br^{2+}$ and $Cr(H_2O)_6^{3+}$, the bromide ion concentration and the values of $\gamma_\pm^c$ and a_{H_2O} shown in Table 4. The results in Table 6 show the very high constancy of the semi-thermodynamic constant corrected for the changes in the water activity for very large variations in the ratio between the complex ions. Our value of $K_1 = 0.0024 \pm 0.0004$ is in good agreement with the value which can be calculated from the estimation of Q_1 made by Spreer and King from ion-exchange measurements[7] in HBr solutions between 45 and 75 °C. Some of their data extrapolated to 25 °C from a plot of $\log Q_1$ versus $1/T$ are shown in Table 7.

Other estimations of the stability constants. Information concerning the stability constants can be obtained from the red shifts of the spectra of the equilibrium solutions. The formation curve $\bar{n}$ vs. $\log (a^*_{Br^-})$ is shown in Fig. 5 and is drawn on the basis of the data given in Tables 4 and 5. The values of $\log (a^*_{Br^-})$ for $\bar{n} = 0.5$, 1.5 and 2.5 can be read from the formation curve and form the basis for calculation of the constants. K_2 and K_3 are very nearly equal to the preliminary constants, and K_1 can with sufficient precision be calculated by the iteration formula of eqn. (4).
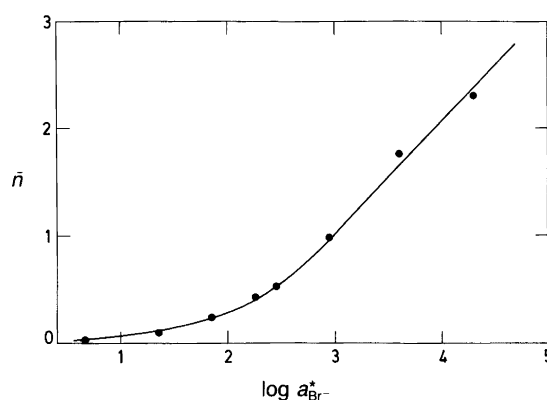
$$K_1 = \left(\frac{1}{a^*_{Br^-}}\right)_{\bar{n}=0.5} \left(\frac{1}{1 + 3K_2(a^*_{Br^-})_{\bar{n}=0.5}}\right) \tag{4}$$

The estimated values for the stability constants are given in Table 8. The value of $K_1 = 0.002\,97$ M^{-1} is in surprisingly good agreement with the value 0.0024 M^{-1} determined from the HPLC measurements. The estimated values for K_2 and K_3 furthermore provide the important information that the ratio K_n/K_{n+1} between successive constants is close to 10, as was also found to be the case in the chromium(III)–chloride system.

The method using isosbestic spectra of solutions containing mixtures of only two species, used previously by one of the present authors[9,18–20] to obtain information concerning stability constants in labile weak anionic systems, was also employed here for comparison purposes. The absorption of the first five equilibrium solutions seen in Fig. 2 corresponds very closely to that of mixtures of only two species. At least three solutions with molar absorbances decreasing in the order ($\varepsilon_c > \varepsilon_b > \varepsilon_a$) are necessary to calculate the stability constants. If more solutions are available they can be combined in various ways. The results of the calculations made are shown in Table 9. The semi-thermodynamic constant K_1 corrected for the change in water activity (Table 4) is calculated to be 0.0046 M^{-1}, whilst a value of 0.0034 M^{-1} is obtained if no correction is made for the change in water activity.

Table 9. Estimation of the first stability constant in the chromium(III)–bromide system by analysis of isosbestic absorption spectra.

Solutions used	$(\varepsilon_c-\varepsilon_b)/(\varepsilon_c-\varepsilon_a)$	"K_1"[a]	K_1
1, 3, 4	0.458±0.013	0.003 72±0.0009	0.005 01±0.0006
1, 3, 5	0.600±0.020	0.003 02±0.0010	0.004 24±0.0006
Av.		0.003 4	0.004 6

[a]"K_1" is calculated without correction for the change in water activity.

Discussion

As shown in a recent paper,[21] it is not possible to determine very small stability constants for labile complexes in mixed perchlorate medium at high constant ionic strength. It is therefore necessary to use solutions with strongly varying concentrations of the complex-forming salt when isosbestic spectra are used to determine constants with values $\ll 1$ M^{-1}. This leads to a systematic error in the method, as even in case of ligand field spectra the molar absorbances of the complex species are to some extent dependent on the salt concentration. However, on the whole the method using isosbestic spectra seems to give reasonable results for labile transition metal complexes, where no other method is available. The uncertainty in the method may perhaps explain the fact that more consistent results (Table 9) are obtained in some cases[9,20] when no correction for the change in water activity is introduced.

The best conditions for studying weak complex formation and testing the expressions for the semi-thermodynamic stability constants [eqn. (5)] apply when the com-

$$K_n = \frac{[ML_n]a_{H_2O}}{[ML_{n-1}][L]\gamma_\pm^c}; \; n = 1, 2, 3,.. \tag{5}$$

plexes are so robust that it is possible to determine the formal concentration constants Q_n by ion-exchange or HPLC measurements in equilibrium solutions. In the chromium(III)–chloride system[8] the complexes were sufficiently robust for both K_1 and K_2 to be determined by HPLC, and the results confirmed the usefulness of the activity-corrected mass action expression for the stability constants. In the present work only K_1 could be determined by HPLC, although over so large a concentration range that it provided a very convincing confirmation of the mass-action expression used (Table 6).

The wavelength shifts in the absorption spectra of well-defined transition metal complexes depend on the position of the ligand in the spectrochemical series, but it has been shown[8,22-25] for individual systems that the shift per ligand taken up is nearly constant. Assuming that the average ligand number in the system is roughly proportional to the wavelength shift observed in the equilibrium solution, a formation curve and a set of stability constants can be calculated on this basis. In this way it has been possible to estimate values for K_1, K_2 and K_3 in the chromium(III)–chloride[8] and in the chromium(III)–bromide systems (Table 8), and these values compare well with the values determined by HPLC. The values further show that the ratio between the consecutive constants K_n/K_{n+1} is close to ten. Swaddle and Guastalla[26] have estimated the very small stability constant for the weakly robust monoiodochromium(III) complex by ion-exchange measurements. In 2.3 M acidified potassium iodide solution they find Q_1 to have

the value 0.000038, corresponding to about 0.00003 M^{-1} for the activity-corrected constant.

The present authors consider these constants for inner-sphere complex formation, regardless of their smallness, to be good approximations to the true thermodynamic constants. The outer-sphere association studies of Spreer and King,[7] based on the UV spectra of chromium(III)–HBr solutions, have led to much higher values ($> 0.1 \; M^{-1}$), but the constants in question are not in the same way well-defined constants.

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