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Stability Constants for Chloride Complexes of Copper(II) in Sulphuric Acid Solution

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Spectrophotometric methods have been used to determine the stability constants of copper(II) chloride complexes in an ionic medium of 9 M sulphuric acid at 25 °C. The total molarity was held constant at 9 M.

Preliminary constants were obtained by graphical methods and were then refined with the generalized least squares program "LETAGROP". The experimental data could best be explained in terms of the following equilibria and stability constants:

$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ log $\beta_1 = 1.03 \pm 0.03$
$Cu^{2+} + 2Cl^- \rightleftharpoons CuCl_2$ log $\beta_2 = 1.60 \pm 0.07$
$Cu^{2+} + 3Cl^- \rightleftharpoons CuCl_3^-$ log $\beta_3 = 1.77 \pm 0.19$
$Cu^{2+} + 4Cl^- \rightleftharpoons CuCl_4^{2-}$ log $\beta_4 = 2.21 \pm 0.08$

The errors given correspond to an error of 3σ, where σ is the standard deviation in log β.

The formation of complexes between copper(II) ions and chloride ions in aqueous solution has mainly been studied by spectrophotometric methods, but a few investigators have used ion exchange or freezing point methods. The formation of complexes between Cu(II) ions and chloride ions cannot be investigated potentiometrically using a copper amalgam electrode or a silver chloride electrode, as both these electrodes reduce Cu(II) to Cu(I) in the presence of chloride ions.

The values of the stability constants (*cf.* Table 1) determined in the various investigations differ from each other, owing to different ionic media and methods of measurement. Some of the constants have been extrapolated to zero ionic strength.[1,3,8,11] From the values given in Table 1, it is evident that the complexes are very weak, the stability constant, β_1, for the reaction $Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ having an approximate value of 1.[1–6,9,11] Some authors have found a higher value for β_1.[7,8,10] This can be attributed to a more concentrated ionic medium, to the neglection of the second complex, or to the method of calculation. The uncertainty of the stability constant, β_2, for the reaction $Cu^{2+} + 2Cl^- \rightleftharpoons CuCl_2$ is larger than that of β_1, but its value is probably less than 1.[1,2]

It has been claimed that copper(II) forms four mononuclear complexes with chloride ions, namely $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$.[1,6,10] On account of the weak complexity, it has, however, proved difficult to determine the stability constants of the higher complexes. Using spectrophotometric measurements, with different metal chlorides as ionic media, Bjerrum[1] was, however, able to determine approximate values for β_3 and β_4. The values determined by Morris and Short[10] differ, however, considerably from those determined by Bjerrum.

In this work, the copper(II) chloride system has been studied spectrophotometrically in 9 M sulphuric acid at 25 °C, sulphuric acid being chosen as medium since it seemed likely that the copper(II) complexes would be stronger in 9 M sulphuric acid than in dilute aqueous solution. Sulphuric acid medium has, moreover, industrial interest, since anhydrous chlorides of the transition metals can be obtained by the distillation of such solutions.

Table 1. Survey of reported values for the stability constants of copper(II) chloride complexes.

Author	Ref.	Method	Medium	Temp. °C	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
Bjerrum	1	spectr.	extrap. to 0	22	1	0.2	8×10^{-3}	8×10^{-5}
McConnell and Davidsson	2	spectr.	1 M $HClO_4$	25.2	1.3	0.3		
Näsänen	3	spectr.	extrap. to 0	25	1.2			
Kruh	4	spectr.	1 M $HClO_4$	22	0.27			
Lister and Rosenblum	5	spectr.	2 M $NaClO_4$	25	1.22			
Andreev and Sapozhinkova	6	spectr.	HCl		1			
Libus	11	spectr.	extrap. to 0	25	1.63			
Faucherre and Crego	7	fp	sat. KNO_3		2.70			
Kenttämaa	8	fp	sat. $KClO_3$		1.50			
		fp	sat. $KClO_4$		4.60			
			extrap. to 0		8.90			
Tre'millon	9	ion exch.	1.5 M $NaNO_3$		0.4			
Morris and Short	10	ion exch.	0.69 M $HClO_4$	20	9.6	4.92	3.52	1.0
Ohlson and Vannerberg		spectr.	9 M H_2SO_4	25	10.7	39.6	59	163

EXPERIMENTAL

Chemicals and analysis. Stock solutions of copper(II) sulphate were prepared by dissolving *copper(II) sulphate* (Merck *p.a.*) in 9 M sulphuric acid and the copper content was determined electrogravimetrically.[13] *Sulphuric acid* was prepared by dilution of conc. sulphuric acid (Merck *p.a.*) and its concentration was calculated from the experimental density,[14] determined with an areometer, graduated from 1.470 to 1.520 g cm^{-3} (accuracy ± 0.001 g cm^{-3}). *Sodium chloride* (Merck *p.a.*) was dried at 110 °C and weighed.

The light absorption measurements in the range 350 – 385 nm were made with a Beckman spectrophotometer, Model DU-2. The measurements in the ultraviolet range 260 – 300 nm were made on a Gilford 240 spectrophotometer. Matched quartz cells of path lengths 0.1, 0.2, 0.5, 1.0 cm were employed, these being calibrated before use. During the measurements, the sample compartment was thermostated to 25.0 ± 0.1 °C.

Four series of solutions of copper(II) chloride were prepared by adding accurately weighed sodium chloride to a solution of copper(II) sulphate. In each series, the total copper ion concentration (B) was kept constant (B: 0.005, 0.010, 0.020, 0.050 M), while the total chloride concentration (A) was varied between 0.004 and 0.600 M. The total molarity was held constant at 9 M by the addition of sulphuric acid.

In one and the same series of measurements, B and l were kept constant and in the different series of measurements the product lB was kept constant.[15]

The wave lengths employed, the numbers of solutions and the numbers of measurements are given in Table 2.

Table 2. The wave lengths used, the numbers of solutions and the chloride concentrations.

Wave lengths (nm)	Number of solutions	Number of measured values	Chloride concentration (M)
260, 265, 270, 275, 280, 290, 300	63	354	0.004 – 0.064
350, 355, 360, 365, 370, 375, 380, 385	113	658	0.0192 – 0.600

LIST OF SYMBOLS

A	total concentration of chloride ions, Cl^-
a	free » » » » »
B	total » » copper ions, Cu^{2+}
b	free » » » » »
A_s	absorbance
l	optical path length
ε	apparent molar absorptivity
β_i	equilibrium constant for the reaction $Cu^{2+} + iCl^- \rightleftharpoons CuCl_i^{(2-i)+}$
ε_i	molar absorptivity for the complex $CuCl_i^{(2-i)+}$
$\bar{n}$	mean ligand number

MEASUREMENTS

The measurements were performed spectrophotometrically, the method of corresponding solutions [1,15-18] being used. In order to find suitable wave lengths, spectra were recorded for copper chloride solutions with constant B and varying A. The spectra showed absorption maxima at 250, 375, and 800 – 900 nm (Figs. 1, 2). The absorption of the Cu^{2+} ion, which probably exists as a sulphate complex in the sulphuric acid solution, increases with decreasing wave length in the UV range, and shows an absorption maximum at 810 nm (Fig. 1). The absorption bands of the complexes are displaced towards longer wave lengths with increasing chloride concentrations, their band widths also increasing considerably. Solutions with low A show one isosbestic point at 224 nm.

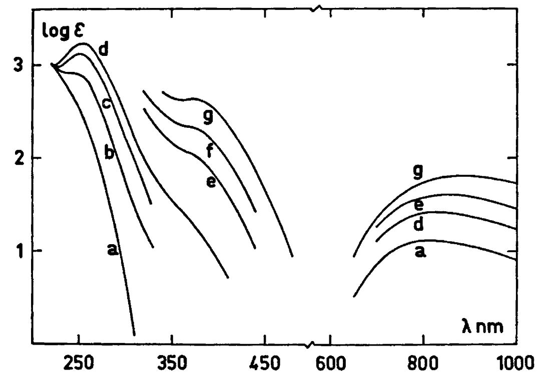

Fig. 1. log ε as a function of λ for copper(II) chloride solutions. $B = 0.010$ M and the following values of A were used: a. 0 M; b. 0.024 M; c. 0.060 M; d. 0.100 M; e. 0.300 M; f. 0.500 M; g. 1.000 M.

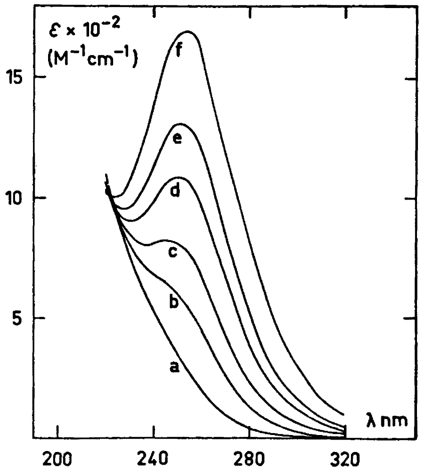

Fig. 2. ε data as a function of λ for solutions with $B = 0.010$ M and different values of A a. 0 M; b. 0.012 M; c. 0.024 M; d. 0.044 M; e. 0.060 M; f. 0.100 M.

The majority of the measurements (658 values) have been carried out in the range 350 – 385 nm, where the higher complexes can be detected. Another advantage of this range is that the Cu^{2+} ion does not absorb there. The remaining 354 measurements were made in the 260 – 300 nm range (Table 2). Only the stability constants of the two first complexes, $CuCl^+$ and $CuCl_2$, could be determined from measurements in the latter range, owing to the strong absorption of both the Cu^{2+} ion and the copper(II) chloride complexes. No measurements have been carried out in the 800 – 900 nm range, because of the small absorptivities of the complexes. The absorption of chloride ions is negligible.

TREATMENT OF THE DATA

The absorbance, A_s, of a solution is the product of the apparent molar absorptivity, ε, the optical path length, l, and the total concentration of the absorbing substance, B,

$$A_s = l\varepsilon B = l \sum_{i=0}^{N} \varepsilon_i [BA_i] = l \sum_{i=0}^{N} \varepsilon_i \beta_i b a^i \qquad (1)$$

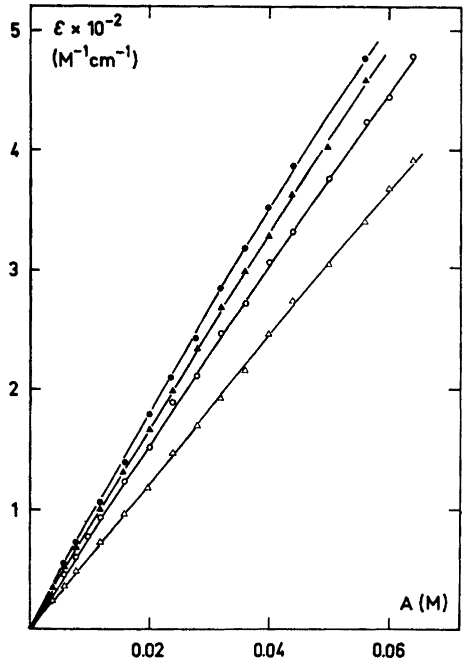

Fig. 3. The function $\varepsilon(A)$ at different values of B at 280 nm. △$B=0.05$ M; ○$B=0.02$ M; ▲$B=0.01$ M; ●$B=0.005$ M.

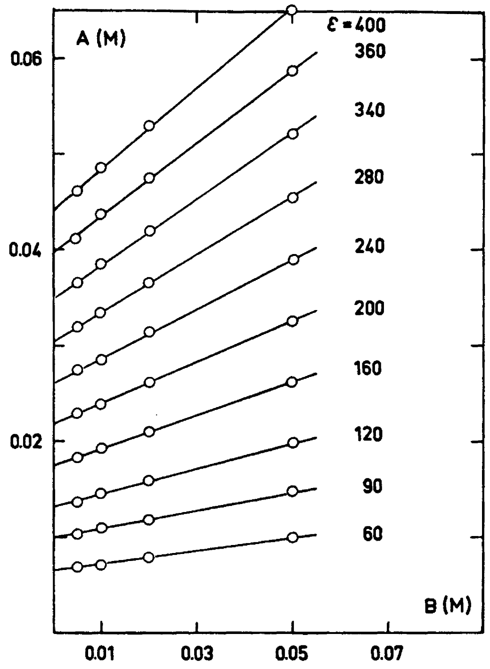

Fig. 4. A versus B at different ε at 280 nm.

where ε_0, ε_1, . . . , ε_N are the molar absorptivities for Cu^{2+}, $CuCl^{+}$, . . . , $CuCl_N^{(2-N)+}$, respectively.

The apparent molar absorptivity is defined as

$$\varepsilon = \frac{\sum_{i=0}^{N} \varepsilon_i[\mathrm{BA}_i]}{B} = \left[\sum_{i=0}^{N} \varepsilon_i \beta_i a^i\right] \Big/ \left[1 + \sum_{i=1}^{N} \beta_i a^i\right] \qquad (2)$$

From eqn. (2) it is seen that ε is solely a function of a, if only mononuclear complexes are present. The mean ligand number $\bar{n}$ is defined as

$$\bar{n} = \frac{A-a}{B} = \left[\sum_{i=1}^{N} i\beta_i a^i\right] \Big/ \left[1 + \sum_{i=1}^{N} \beta_i a^i\right] \qquad (3)$$

and $\bar{n}$ is thus only a function of a, this gives

$$A = a + \bar{n}B \qquad (4)$$

Table 3. Corresponding values of B, A, a and $\bar{n}$ obtained from the $\varepsilon(A)$-curve for $\lambda = 280$ nm.

	A M						
B M ε	0.005	0.01	0.02	0.05	a	$-\log a$	$\bar{n}$
60	0.0068	0.0071	0.0079	0.0099	0.0064	2.19	0.07
90	0.0103	0.0108	0.0117	0.0148	0.0098	2.01	0.10
120	0.0137	0.0145	0.0158	0.0198	0.0132	1.88	0.13
160	0.0183	0.0192	0.0211	0.0262	0.0174	1.76	0.18
200	0.0229	0.0239	0.0262	0.0325	0.0219	1.66	0.21
240	0.0274	0.0286	0.0314	0.0389	0.0261	1.58	0.26
280	0.0319	0.0335	0.0366	0.0454	0.0304	1.52	0.30
340	0.0388	0.0411	0.0448	0.0554	0.0373	1.43	0.36
360	0.0411	0.0437	0.0475	0.0587	0.0398	1.40	0.38
400	0.0460	0.0488	0.0531	0.0654	0.0447	1.35	0.41

Table 4. Corresponding values of log a and $\bar{n}$, obtained from $\varepsilon(A)$-curves for 15 different wave lengths, followed by $(\bar{n}_{\text{calc}}-\bar{n})\times 10^3$, which has been calculated with the "LETAGROP VRID" program.

λ nm			
385	-0.9340	0.93000	4.99
	-0.8780	0.99000	45.53
	-0.8330	1.11000	13.05
	-0.7930	1.17000	36.20
	-0.7610	1.30000	-23.49
	-0.7030	1.43000	-17.17
	-0.6560	1.60000	-68.17
	-0.6130	1.69000	-42.68
	-0.5930	1.71000	-6.89
	-0.5750	1.78000	-25.61
	-0.5410	1.86000	-6.15
	-0.5110	1.92000	24.13
	-0.4840	2.00000	27.10
	-0.4580	2.08000	28.23
	-0.4340	2.15000	33.92
	-0.4100	2.20000	60.09
	-0.3890	2.29000	36.90
	-0.3680	2.36000	33.65
	-0.3490	2.48000	-26.18
	-0.3310	2.55000	-39.54
380	-1.2030	0.57000	-8.75
	-1.1500	0.66000	-37.66
	-1.0930	0.72000	-25.60
	-1.0410	0.79000	-23.66
	-0.9730	0.88000	-9.89
	-0.9120	0.94000	33.42
	-0.8690	1.06000	-7.46
	-0.8280	1.12000	13.16
	-0.7910	1.20000	10.50
	-0.7590	1.27000	11.02
	-0.7330	1.36000	-19.13
	-0.7060	1.45000	-44.51
	-0.6830	1.52000	-57.47
	-0.6410	1.63000	-58.59
	-0.6050	1.74000	-70.51
	-0.5710	1.80000	-34.08
	-0.5390	1.88000	-20.20
	-0.5100	1.93000	17.17
	-0.4830	2.00000	30.20
	-0.4590	2.10000	5.09
	-0.4360	2.19000	-12.41
	-0.4140	2.24000	7.38
	-0.3930	2.33000	-15.82
	-0.3720	2.37000	10.95
	-0.3540	2.45000	-11.99
	-0.3350	2.54000	-42.09
375	-1.1970	0.58000	-12.10
	-1.0910	0.69000	7.06
	-1.0160	0.83000	-26.84
	-0.9530	0.87500	27.87
	-0.9070	0.98000	2.34
	-0.8630	1.06000	4.01
	-0.8250	1.11000	29.27
	-0.7660	1.31000	-44.70
	-0.7140	1.44000	-53.92
	-0.6710	1.58000	-86.98
	-0.6310	1.65000	-51.78
	-0.5940	1.71000	-9.71
	-0.5620	1.77000	22.03
	-0.5330	1.83000	47.70
	-0.5040	1.91000	55.50
	-0.4790	2.00000	42.62
	-0.4560	2.11000	4.51
	-0.4340	2.20000	-16.08
	-0.4130	2.26000	-9.45
	-0.3920	2.29000	27.36
	-0.3730	2.43000	-52.22
370	-0.9910	0.84000	1.52
	-0.9410	0.92000	3.04
	-0.9000	1.02000	-25.05
	-0.8610	1.07000	-2.14
	-0.8260	1.13000	7.23
	-0.7960	1.21000	-10.21
	-0.7660	1.28000	-14.70
	-0.7400	1.33000	-5.47
	-0.7150	1.38000	3.67
	-0.6940	1.46000	-24.98
	-0.6720	1.50000	-9.54
	-0.6530	1.53000	9.69
	-0.6170	1.64000	-3.68
	-0.6010	1.70000	-19.36
	-0.5850	1.73000	-4.22
	-0.5540	1.80000	15.44
	-0.5260	1.90000	-1.29
	-0.4980	1.96000	23.89
	-0.4740	2.04000	18.18
	-0.4500	2.11000	23.39
	-0.4280	2.20000	2.93
	-0.4060	2.29000	-17.19
	-0.3870	2.41000	-76.73
	-0.3670	2.48000	-83.17
	-0.3470	2.50000	-39.87
365	-1.1690	0.60000	-0.19
	-1.0920	0.70000	-4.27
	-1.0270	0.76000	26.78
	-0.9710	0.82000	53.34
	-0.8910	1.01000	1.38
	-0.8270	1.19000	-54.80
	-0.7700	1.28000	-23.61
	-0.7230	1.40000	-35.49
	-0.6770	1.47000	7.71
	-0.6410	1.58000	-8.59
	-0.6060	1.69000	-23.30
	-0.5750	1.76000	-5.60
	-0.5440	1.84000	4.94
	-0.5160	1.90000	28.93
	-0.4910	2.00000	5.45
	-0.4670	2.08000	0.03
	-0.4440	2.14000	12.31
	-0.4210	2.20000	25.14
360	-1.3280	0.47000	-32.53
	-1.2660	0.52000	-24.51
	-1.2140	0.57000	-20.75
	-1.1690	0.62000	-20.19
	-1.1300	0.67000	-23.15
	-1.0600	0.72000	19.34
	-1.0070	0.81000	6.79
	-0.9590	0.86000	32.93
	-0.9210	0.92000	37.53
	-0.8870	1.00000	18.76
	-0.8540	1.06000	21.43
	-0.8230	1.11000	33.36
	-0.7970	1.19000	7.65
	-0.7480	1.30000	6.06
	-0.7030	1.37000	42.82
	-0.6670	1.48000	23.29
	-0.6320	1.58000	15.53
	-0.6000	1.68000	3.44
	-0.5700	1.77000	-1.19
	-0.5410	1.85000	3.85
	-0.5140	1.92000	15.00
	-0.4890	2.00000	11.62
	-0.4640	2.06000	29.42
	-0.4410	2.11000	51.78
	-0.4180	2.16000	74.67
355	-1.2490	0.50800	4.53
	-1.1620	0.59400	14.03
	-1.0960	0.67700	13.44
	-1.0390	0.74200	27.23
	-0.9910	0.80300	38.52
	-0.9520	0.88700	17.54
	-0.9170	0.95700	7.56
	-0.8830	1.00000	26.18
	-0.8520	1.01700	68.34
	-0.8260	1.11900	18.23
	-0.8000	1.16200	29.28
350	-1.6780	0.21300	-2.97
	-1.6070	0.23400	10.64
	-1.5480	0.26100	16.34
	-1.4750	0.33300	-9.66
	-1.4110	0.38300	-13.75
	-1.3570	0.42400	-11.54
	-1.3160	0.46800	-19.79
	-1.2910	0.47100	0.33
	-1.2530	0.50000	8.48
300	-2.1900	0.06300	4.57
	-2.0730	0.07900	8.90
	-1.9120	0.11700	8.84
	-1.7170	0.19100	2.03
	-1.6500	0.22100	2.10
	-1.5900	0.25200	1.67
	-1.5390	0.27600	6.67
	-1.4940	0.30500	5.74
	-1.4170	0.36100	3.71
	-1.3840	0.39200	-1.68
	-1.3520	0.41200	4.68
290	-2.1760	0.06800	1.73
	-2.0560	0.08800	3.31
	-1.9670	0.11100	0.38
	-1.8880	0.12600	6.71
	-1.8240	0.14500	7.81
	-1.7750	0.16800	2.13
	-1.7280	0.18700	1.48
	-1.6880	0.21000	-4.45
	-1.6520	0.22500	-2.86
	-1.6160	0.24100	-1.03
	-1.5880	0.26500	-10.24
	-1.5560	0.27700	-4.32
	-1.5300	0.29500	-6.91
	-1.5020	0.31000	-4.43
	-1.4790	0.33400	-13.35
	-1.4560	0.34800	-11.60
	-1.4270	0.35100	6.25
	-1.4090	0.37900	-8.22
280	-2.2680	0.05800	-1.35
	-2.1920	0.07000	-2.74
	-2.1220	0.08000	-1.25
	-2.0610	0.09000	0.29
	-2.0100	0.10000	1.20
	-1.9620	0.11000	2.62
	-1.8800	0.13100	4.07
	-1.8120	0.15000	6.89
	-1.7600	0.17500	0.79
	-1.7080	0.19300	3.84
	-1.6600	0.21300	5.35
	-1.6200	0.23400	3.93
	-1.5830	0.25500	2.48
	-1.5480	0.27600	1.34
	-1.5170	0.30000	-3.91
	-1.4840	0.32400	-6.69
	-1.4550	0.34000	-2.90
	-1.4280	0.35900	-2.48
	-1.4000	0.37500	2.71
	-1.3760	0.39700	-0.23
	-1.3500	0.41400	4.38
275	-2.1980	0.06500	1.36
	-2.1480	0.07700	-2.73
	-2.0950	0.08300	0.67
	-2.0200	0.10000	-1.03
	-1.9470	0.11400	2.44
	-1.8870	0.13200	1.00
	-1.8350	0.15000	-0.84
	-1.7890	0.16800	-3.00
	-1.7460	0.18600	-4.76
	-1.6690	0.21400	0.15
	-1.6030	0.24800	-1.26
	-1.5740	0.26200	0.46
	-1.5200	0.30200	-7.78
	-1.4710	0.34400	-17.95
270	-2.3190	0.05300	-2.53
	-2.2130	0.06300	1.15
	-2.1290	0.07200	5.52
	-2.0030	0.09900	3.79
	-1.9010	0.12500	3.95
	-1.8170	0.15300	2.17
	-1.7490	0.18000	0.06
	-1.6850	0.21200	-5.12
	-1.6290	0.24000	-6.61
	-1.5790	0.26700	-7.32
	-1.5540	0.27900	-5.16
	-1.5300	0.29000	-1.91
265	-2.2330	0.06000	1.32
	-2.1010	0.07800	4.55
	-2.0000	0.10000	3.48
	-1.9140	0.12100	4.29
	-1.7770	0.16000	9.38
	-1.7200	0.19200	-0.22
	-1.6720	0.23000	-17.23
260	-2.3040	0.05100	1.22
	-2.1650	0.06500	6.48
	-2.0660	0.08200	7.29
	-1.9800	0.10300	5.20
	-1.9400	0.11500	3.27
	-1.9030	0.12200	6.38
	-1.8690	0.12700	11.39
	-1.8350	0.14000	9.16

Solutions with the same ε have the same value of $\bar{n}$ and a, and such solutions are known as corresponding solutions.[1,15–18]

The function $\varepsilon(A)$ [15] was plotted for three or four given values of the total concentration B. From these curves pairs of values (B,A), corresponding to selected ε, were obtained.

If A was plotted against B at a constant value of ε, a straight line was obtained, indicating that only mononuclear complexes were present, $\bar{n}$ being obtained from the slope and a from the intercept on the A-axis. Measurements for $\lambda = 280$ nm illustrate this procedure (*cf.* Figs. 3, 4 and Table 3).

The stability constants were then calculated from the $\bar{n}(a)$ values by several different methods (*cf.* Table 4 and Fig. 6).

CALCULATIONS BASED ON THE DATA IN THE LOW UV RANGE

Curve fitting. In order to determine values of β_1 and β_2, the experimental curve in Fig. 5 was fitted to the following normalized curve:

$$\bar{n} = (Ru + 2u^2)/(1 + Ru + u^2) \qquad (5)$$

where $u = \beta_2^{\frac{1}{2}}a$ and $R = \beta_1\beta_2^{-\frac{1}{2}}$.[19] Functions $\bar{n}(\log u)_R$ were drawn for different constant R values and compared with the experimental ones.

Table 5. Spectrophotometric data in the low UV range for 40 solutions. *A* and *B* are given for each solution, followed by ε, $\varepsilon_{\text{calc}}$ and $\varepsilon_{\text{calc}} - \varepsilon$ for 7 wave lengths. The concentrations are expressed in M and the apparent absorptivities in M^{-1} cm^{-1}. Missing data is indicated by -1.

0.004000	0.005000							
15.300	15.301	0.001	34.300	34.516	0.216	81.300	80.787	-0.513
118.700	118.968	0.268	168.500	169.606	1.106	230.500	231.706	1.206
304.300	304.348	0.048						
0.006000	0.005000							
20.300	19.930	-0.370	43.700	43.307	-0.393	100.600	98.428	-2.172
143.500	142.974	-0.526	201.700	200.827	-0.873	272.400	270.532	-1.868
352.000	348.822	-3.178						
0.008000	0.005000							
24.680	24.736	0.056	52.150	52.316	0.166	116.900	116.075	-0.825
165.700	166.758	1.058	230.800	231.474	0.674	307.500	308.259	0.759
351.300	351.840	0.540						
0.010000	0.005000							
29.800	29.703	-0.097	61.600	61.522	-0.078	134.400	133.714	-0.686
192.000	190.315	-1.685	264.400	261.560	-2.840	347.000	344.925	-2.075
435.600	433.456	-2.144						
0.012000	0.005000							
34.800	34.820	0.020	71.000	70.908	-0.092	151.100	151.332	0.232
214.400	213.640	-0.760	292.400	291.094	-1.306	380.300	380.562	0.263
473.200	473.720	0.520						
0.016000	0.005000							
44.760	45.451	0.691	89.910	90.152	0.242	185.200	186.467	1.267
259.900	259.591	-0.308	349.000	348.558	-0.442	447.100	448.903	1.804
-1.000	-1.000	0.0						
0.020000	0.005000							
57.900	56.540	-1.360	113.400	109.923	-3.477	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.024000	0.005000							
67.600	68.006	0.406	130.500	130.110	-0.390	257.700	256.055	-1.644
350.200	348.631	-1.569	458.600	457.371	-1.229	572.600	574.722	2.122
-1.000	-1.000	0.0						
0.028000	0.005000							
78.720	79.780	1.060	148.800	150.619	1.819	288.300	290.385	2.086
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.032000	0.005000							
92.900	91.801	-1.099	173.000	171.365	-1.635	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.004000	0.010000							
15.400	14.838	-0.562	34.200	33.630	-0.570	79.800	78.984	-0.816
117.800	116.502	-1.298	165.400	166.382	0.982	227.800	227.674	-0.126
299.600	299.718	0.118						
0.006000	0.010000							
19.680	19.214	-0.466	42.350	41.954	-0.396	97.020	95.742	-1.278
139.600	139.334	-0.266	194.600	196.112	1.512	265.000	264.694	-0.306
341.700	342.148	0.448						
0.008000	0.010000							
23.950	23.754	-0.196	50.400	50.484	0.084	112.400	112.520	0.120
160.900	161.985	1.085	222.000	225.346	3.346	298.400	300.746	2.346
379.200	383.289	4.089						
0.012000	0.010000							
33.300	33.282	-0.018	68.400	68.097	-0.303	146.600	146.092	-0.508
207.200	206.723	-0.477	283.400	282.361	-1.039	369.800	370.062	0.262
459.600	461.875	2.275						
0.016000	0.010000							
42.150	43.335	1.185	84.890	86.346	1.456	176.400	179.614	3.214
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.020000	0.010000							
53.090	53.833	0.743	105.000	105.122	0.122	211.900	213.013	1.113
292.700	293.849	1.149	389.100	390.807	1.707	495.600	498.310	2.710
-1.000	-1.000	0.0						
0.024000	0.010000							
64.000	64.709	0.709	122.800	124.329	1.529	244.300	246.225	1.925
333.800	336.198	2.398	439.000	442.368	3.369	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.028000	0.010000							
76.240	75.899	-0.341	144.100	143.881	-0.219	279.600	279.196	-0.404
377.300	377.721	0.422	492.400	492.241	-0.159	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.032000	0.010000							
88.520	87.348	-1.171	165.000	163.701	-1.299	314.300	311.879	-2.420
420.900	418.412	-2.487	542.200	540.487	-1.713	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.036000	0.010000							
100.000	99.007	-0.993	183.600	183.721	0.121	345.400	344.235	-1.165
458.000	458.268	0.269	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0						
0.006000	0.020000							
18.100	17.985	-0.115	39.260	39.628	0.368	90.750	91.100	0.350
133.800	133.030	-0.770	186.900	187.930	1.030	253.400	254.542	1.142
331.000	330.531	-0.469						
0.008000	0.020000							
21.890	22.070	0.180	44.020	47.332	3.312	106.000	106.363	0.363
153.100	153.696	0.596	212.700	214.678	1.978	285.400	287.630	2.231
366.600	368.343	1.743						
0.010000	0.020000							
26.640	26.290	-0.350	55.010	55.208	0.198	122.700	121.656	-1.043
174.800	174.235	-0.565	241.100	241.052	-0.048	321.300	319.971	-1.328
406.600	405.154	-1.446						

Table 5. Continued.

0.012000	0.020000								
31.070	30.638	-0.432	63.480	63.243	-0.237	138.700	136.971	-1.729	
195.500	194.641	-0.859	268.200	267.057	-1.143	353.200	351.584	-1.616	
442.800	440.994	-1.806							
0.016000	0.020000								
39.840	39.682	-0.158	80.050	79.750	-0.300	168.500	167.629	-0.871	
235.700	235.045	-0.655	320.800	317.977	-2.822	415.600	412.698	-2.901	
512.100	509.867	-2.233							
0.020000	0.020000								
48.590	49.145	0.555	96.570	96.770	0.200	197.600	198.279	0.679	
273.700	274.882	1.182	367.800	367.476	-0.324	471.400	471.114	-0.286	
575.100	575.173	0.073							
0.024000	0.020000								
59.440	58.973	-0.467	116.400	114.226	-2.174	-1.000	-1.000	0.0	
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0	
-1.000	-1.000	0.0							
0.028000	0.020000								
68.370	69.115	0.745	132.100	132.051	-0.049	257.400	259.340	1.941	
352.100	352.775	0.675	462.200	462.358	0.158	581.500	580.377	-1.122	
694.900	695.864	0.964							
0.032000	0.020000								
79.920	79.528	-0.392	151.700	150.182	-1.518	292.300	289.662	-2.638	
395.000	390.801	-4.199	-1.000	-1.000	0.0	-1.000	-1.000	0.0	
-1.000	-1.000	0.0							
0.036000	0.020000								
88.550	90.171	1.621	165.700	168.561	2.861	317.800	319.792	1.993	
425.900	428.198	2.298	550.900	551.999	1.100	680.500	680.366	-0.133	
-1.000	-1.000	0.0							
0.004000	0.050000								
12.290	12.370	0.080	28.540	28.884	0.344	68.850	69.240	0.390	
103.400	103.124	-0.276	147.300	148.839	1.539	203.500	205.658	2.158	
273.500	274.398	0.898							
0.006000	0.050000								
15.300	15.397	0.097	34.260	34.699	0.439	81.230	81.159	-0.071	
118.900	119.477	0.577	168.000	170.272	2.272	229.400	232.538	3.138	
301.700	305.303	3.603							
0.008000	0.050000								
18.640	18.521	-0.119	40.440	40.644	0.204	94.360	93.131	-1.229	
136.000	135.791	-0.209	191.000	191.516	0.516	258.800	258.994	0.195	
335.900	335.627	-0.273							
0.012000	0.050000								
25.630	25.052	-0.578	52.600	52.905	0.305	117.600	117.216	-0.384	
168.600	168.288	-0.312	233.300	233.437	0.137	309.600	310.662	1.062	
393.300	394.573	1.273							
0.016000	0.050000								
32.440	31.935	-0.505	65.930	65.627	-0.303	142.100	141.461	-0.639	
202.600	200.596	-2.004	277.500	274.608	-2.892	362.400	360.713	-1.687	
453.000	451.316	-1.684							
0.020000	0.050000								
39.290	39.141	-0.149	77.720	78.769	1.049	162.700	165.834	3.134	
230.100	232.695	2.595	311.700	315.036	3.336	-1.000	-1.000	0.0	
-1.000	-1.000	0.0							
0.024000	0.050000								
47.290	46.645	-0.645	94.380	92.294	-2.085	191.900	190.305	-1.595	
265.700	264.568	-1.132	358.800	354.727	-4.073	459.400	456.161	-3.239	
559.100	558.506	-0.594							
0.028000	0.050000								
54.760	54.422	-0.338	106.800	106.168	-0.632	215.100	214.845	-0.255	
295.000	296.199	1.200	394.200	393.688	-0.512	501.900	501.653	-0.247	
-1.000	-1.000	0.0							
0.032000	0.050000								
62.520	62.450	-0.070	119.700	120.357	0.657	239.300	239.427	0.127	
324.900	327.574	2.675	430.000	431.927	1.927	-1.000	-1.000	0.0	
-1.000	-1.000	0.0							
0.036000	0.050000								
69.380	70.704	1.324	132.500	134.829	2.329	-1.000	-1.000	0.0	
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0	
-1.000	-1.000	0.0							

The best fit was obtained when $R=1.5$ and $\log u=1$ and $\log a=1.83$ (*cf.* Fig. 5). This gave $\beta_1=10.1$ M^{-1} and $\beta_2=45.7$ M^{-2}.

"LETAGROP" CALCULATIONS

The experimental data from the low UV-range were also processed with the spectrophotometric version "SPEFO" of the "LETAGROP" program.[22] U is the error squares sum, defined as $U=\sum(\varepsilon_{\text{calc}}-\varepsilon)^2$.

The "best values" for β_1 and β_2 obtained were:

$\beta_1=11.60\pm0.22$ M^{-1}
$\beta_2=39.17\pm6.21$ M^{-2}

and $U=490.2$ for 231 values for $A<0.04$ M. The errors given are σ, where σ is the standard deviation in β. The corresponding ε_1 and ε_2 values are given in Table 7 and Fig. 8. These ε_1 and ε_2 values were also confirmed by graphical methods. In Table 5 experimental and calculated data are presented.

CALCULATIONS BASED ON THE COMPLETE DATA SET

Fronæus' method.[17,20] The function used was

$$\bar{n}=\frac{\mathrm{d}\phi_0/\phi_0}{\mathrm{d}a/a}=\frac{\mathrm{d}\ln\phi_0}{\mathrm{d}\ln a} \tag{6}$$

Integrating (6) between the limits 0 and a_i, gives

$$\ln\phi_0(a_i)=\int_0^{a_i}\bar{n}\,\mathrm{d}\ln a \tag{7}$$

ϕ_0 is determined from eqn. (7).

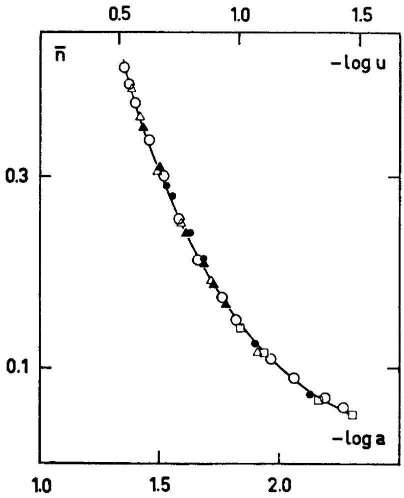

Fig. 5. $\bar{n}$ as a function of log a in the UV range. △300 nm; ▲290 nm; ○280 nm; ●270 nm; □260 nm.

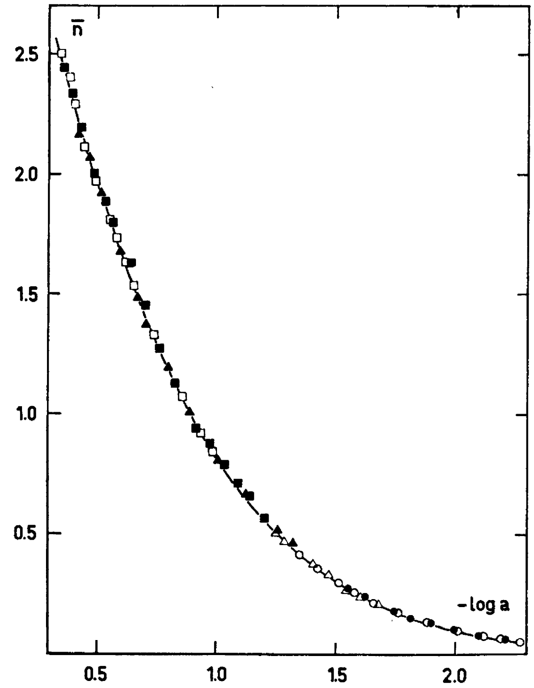

Fig. 6. The function $\bar{n}(\log a)$ at different wave lengths. ○280 nm; ●300 nm, △350 nm; ▲360 nm; □370 nm; ■380 nm.

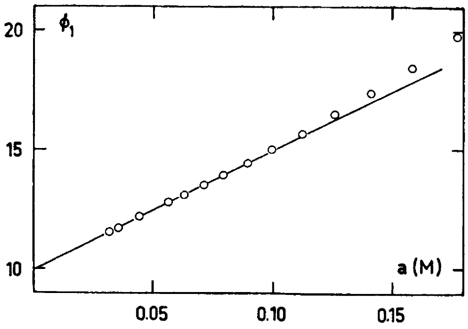

Fig. 7a. ϕ_1 as a function of a.

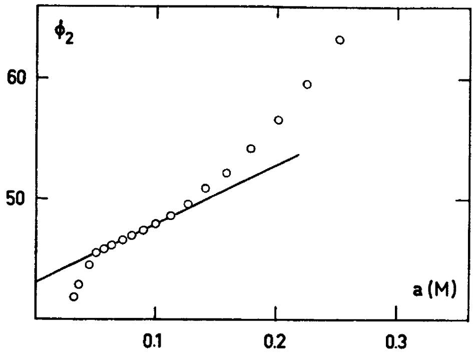

Fig. 7b. ϕ_2 as a function of a.

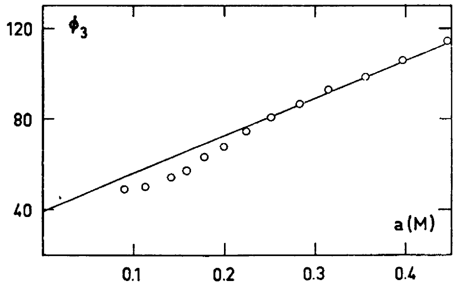

Fig. 7c. ϕ_3 as a function of a.

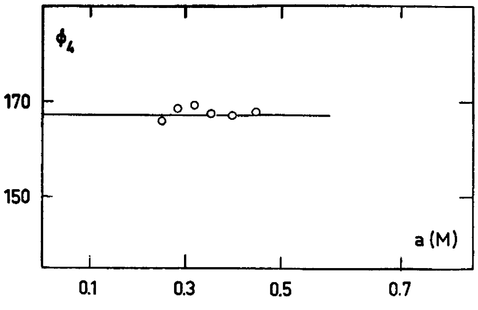

Fig. 7d. ϕ_4 as a function of a.

Table 6. The intercepts and the slopes of the different graphical functions for the calculation of the β-values.

	Function	Intercept	Slope	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
All data	ϕ_1	10	50	10	43	39	167
	ϕ_2	43	49				
	ϕ_3	39	167				
	ϕ_4	167	–				
Data in the range 350 – 385 nm	ϕ_1	11.5	42.5	11.5	40.5	46	177
	ϕ_2	40.5	43				
	ϕ_3	46	177				
	ϕ_4	177	–				
All data	F_1	10	46	10	36	42	161
	F_2	36	75				
	F_3	41.5	161				
	F_4	161	–				
All data	G_3	43	38	11	38	43	–
	G_2	43	11				

$$\phi_1 = \frac{\phi_0 - 1}{a} = \beta_1 + \beta_2 a\left(+ \sum_{i=3}^{N} \beta_i a^{i-1}\right) \tag{8}$$

At very low values of a, the first two complexes, BA and BA_2, predominate, and the function $\phi_1(a)$ becomes a straight line of slope β_2 and with intercept β_1. A value of any constant β_i may be obtained by using a generalization of eqn. (8).

The disadvantage of this method is that any errors in the values of $\beta_1, \ldots, \beta_{i-1}$ will accumulate in the value of β_i.

In Figs. 7a – d, the different functions $\phi_i(a)$ have been plotted, and the slopes and intercepts of these four functions are listed in Table 6. The approximate values of the stability constants obtained were:

$\beta_1 = 10\ M^{-1}$ $\quad$ $\beta_3 = 39\ M^{-3}$
$\beta_2 = 43\ M^{-2}$ $\quad$ $\beta_4 = 167\ M^{-4}$

The values of the constants based on the 350 – 385 nm data, only, were somewhat different. This can be attributed to the selection of the tail of the $\bar{n}(\log a)$ curve. The values obtained were:

$\beta_1 = 11.5\ M^{-1}$ $\quad$ $\beta_3 = 46\ M^{-3}$
$\beta_2 = 40.5\ M^{-2}$ $\quad$ $\beta_4 = 177\ M^{-4}$

(*cf.* Table 6).

Rossotti's method.[21] The function

$$F_1 = \frac{\bar{n}}{(1-\bar{n})a} = \beta_1 + \beta_2 \frac{2-\bar{n}}{1-\bar{n}} a + \sum_{i=3}^{N} \frac{i-\bar{n}}{1-\bar{n}} \beta_i a^{i-1} \tag{9}$$

may be derived from eqn. (3). The plot of $\bar{n}(1-\bar{n})/a$ against $(2-\bar{n})\ a/(1-\bar{n})$ becomes a straight line of slope β_2 and intercept β_1, as $a \to 0$.

A value of any constant β_i may be obtained by using a generalization of eqn. (9).

The slopes and the intercepts of the four functions F_i are given in Table 6. The following values of the stability constants were obtained:

$\beta_1 = 10\ M^{-1}$ $\quad$ $\beta_3 = 42\ M^{-3}$
$\beta_2 = 36\ M^{-2}$ $\quad$ $\beta_4 = 161\ M^{-4}$

The reciprocal method of Rossotti.[21] The constants may also be obtained by extrapolation to $a^{-1} = 0$, using the function

$$G_N = \frac{\bar{n}a^{-N}}{N-\bar{n}} = \beta_N + \beta_{N-1} \frac{N-1-\bar{n}}{N-\bar{n}} a^{-1} + \sum_{i=1}^{N-2} \frac{i-\bar{n}}{N-\bar{n}} \beta_i a^{i-N} \tag{10}$$

In this case no value can be obtained for β_4 (*cf.* Table 6). The values obtained were:

$\beta_1 = 11\ M^{-1}$ $\quad$ $\beta_3 = 43\ M^{-3}$
$\beta_2 = 38\ M^{-2}$

Table 7. Molar absorptivities, ε_i, in M^{-1} cm^{-1} calculated with the "LETAGROP" program. The errors given are σ, where σ is the standard deviation in ε.

λ nm	ε_0	ε_1	ε_2	ε_3	ε_4
260	210.9	2417 ± 10	1754 ± 199	–	–
265	150.6	2055 ± 7	2164 ± 111	–	–
270	105.4	1597 ± 7	2926 ± 100	–	–
275	70.3	1190 ± 5	3083 ± 67	–	–
280	45.6	847 ± 5	2913 ± 64	–	–
290	17.7	390 ± 4	2276 ± 53	–	–
300	6.6	195 ± 2	1434 ± 28	–	–
350	–	8.8 ± 0.7	171 ± 3	222 ± 18	513 ± 15
355	–	5.9 ± 0.6	157 ± 2	190 ± 16	503 ± 13
360	–	4.1 ± 0.6	145 ± 2	141 ± 12	533 ± 8
365	–	2.5 ± 0.4	129 ± 2	122 ± 13	534 ± 9
370	–	1.0 ± 0.4	114 ± 2	110 ± 11	536 ± 7
375	–	0.9 ± 0.4	98 ± 2	85 ± 12	549 ± 8
380	–	0.6 ± 0.3	84 ± 2	62 ± 12	550 ± 8
385	–	0.5 ± 0.3	71 ± 2	47 ± 13	530 ± 9

Table 8. Spectrophotometric data in the range 350 – 385 nm for 11 solutions and 8 wave lengths. A and B are given for each solution, followed by ε, ε_{calc}, and $\varepsilon_{calc} - \varepsilon$. The concentrations are expressed in M and the apparent absorptivities in M^{-1} cm^{-1}. $\beta_1 = 10.7$ M^{-1} and $\beta_2 = 39.6$ M^{-2} were kept constant during the calculation.

```
 0.019200   0.010000
    3.200      3.176    -0.024     2.550     2.554     0.004     2.050     2.085     0.035
    1.650      1.668     0.018     1.250     1.317     0.067     1.100     1.101     0.001
    0.850      0.882     0.032     0.650     0.714     0.064
 0.025600   0.010000
    4.750      4.769     0.019     3.850     3.914     0.064     3.300     3.241    -0.059
    2.600      2.647     0.047     2.100     2.150     0.050     1.800     1.797    -0.003
    1.400      1.448     0.048     1.100     1.169     0.069
 0.032000   0.010000
    6.750      6.551    -0.199     5.650     5.453    -0.197     4.750     4.561    -0.189
    3.850      3.776    -0.074     3.150     3.123    -0.027     2.650     2.610    -0.040
    2.150      2.111    -0.039     1.700     1.702     0.002
 0.038400   0.010000
    8.600      8.483    -0.117     7.250     7.138    -0.112     6.050     6.014    -0.036
    5.050      5.028    -0.022     4.250     4.212    -0.038     3.600     3.520    -0.080
    2.900      2.853    -0.047     2.300     2.298    -0.002
 0.020400   0.020000
    3.040      3.057     0.017     2.440     2.454     0.014     2.000     2.000     0.000
    1.600      1.557    -0.003     1.300     1.257    -0.043     1.100     1.052    -0.048
    0.850      0.842    -0.008     0.700     0.682    -0.018
 0.027200   0.020000
    4.540      4.600     0.060     3.690     3.768     0.078     3.040     3.116     0.076
    2.540      2.541     0.001     2.040     2.059     0.019     1.700     1.721     0.021
    1.400      1.386    -0.014     1.150     1.120    -0.030
 0.034000   0.020000
    6.400      6.331    -0.069     5.300     5.263    -0.037     4.450     4.397    -0.053
    3.750      3.635    -0.115     3.100     3.002    -0.098     2.550     2.509    -0.041
    2.100      2.028    -0.072     1.750     1.635    -0.115
 0.040800   0.020000
    8.330      8.218    -0.112     6.950     6.906    -0.084     5.890     5.813    -0.077
    4.890      4.855    -0.035     4.140     4.061    -0.079     3.440     3.394    -0.046
    2.750      2.750    -0.040     2.240     2.215    -0.025
 0.020000   0.050000
    2.050      2.168     0.118     1.660     1.709     0.049     1.270     1.374     0.104
    1.030      1.075     0.045     0.830     0.822    -0.008     0.640     0.687     0.047
    0.540      0.547     0.007     0.440     0.444     0.004
 0.040000   0.050000
    5.690      5.841     0.151     4.760     4.838     0.078     3.930     4.032     0.102
    3.240      3.322     0.082     2.650     2.731     0.081     2.160     2.283     0.123
    1.770      1.844     0.074     1.470     1.487     0.017
 0.060000   0.050000
   10.330     10.536     0.206     8.760     8.939     0.179     7.430     7.574     0.144
    6.300      6.380     0.080     5.310     5.396     0.086     4.430     4.508     0.078
    3.590      3.661     0.071     2.900     2.946     0.046
```

THE "LETAGROP" CALCULATIONS

The values obtained by the different graphical methods were refined using the computer program "LETAGROP VRID".[23] The "best values" for β_1, β_2, β_3, and β_4 obtained were:

$$\beta_1 = 10.69 \pm 0.25 \text{ M}^{-1} \qquad \beta_3 = 58.53 \pm 8.37 \text{ M}^{-3}$$
$$\beta_2 = 39.60 \pm 2.10 \text{ M}^{-2} \qquad \beta_4 = 163.3 \pm 9.66 \text{ M}^{-4}$$

and $U = \sum(\bar{n}_{calc} - \bar{n})^2 = 0.13946$. 246 $\bar{n}(\log a)$-values were used. The errors given are σ, where σ is the standard deviation in β.

The original experimental data in the range 350 – 385 nm were also processed with the spectrophotometric version "SPEFO" of the "LETAGROP" program.[22] U is the error squares sum, defined as $U = \sum(\varepsilon_{\rm calc} - \varepsilon)^2$. It appeared to be somewhat hazardous to determine the stability constants with the "SPEFO" program, owing partly to the large number of parameters and partly to the low molar absorptivity of $\rm CuCl^+$.

Table 9. Spectrophotometric data in the range 350 – 385 nm for 74 solutions. A and B are given for each solution, followed by ε, $\varepsilon_{\rm calc}$, and $\varepsilon_{\rm calc} - \varepsilon$ for 8 wave lengths. The concentrations are expressed in M, the apparent absorptivities in $\rm M^{-1}\ cm^{-1}$. $\beta_1 = 10.7\ \rm M^{-1}$, $\beta_2 = 39.6\ \rm M^{-2}$, $\beta_3 = 59\ \rm M^{-3}$ and $\beta_4 = 163\ \rm M^{-4}$ were kept constant during the calculation. Missing data is indicated by −1.

```
 0.240000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0      99.000     98.885    -0.115
   -1.000     -1.000     0.0      85.000     84.918     -0.082    -1.000     -1.000     0.0
   -1.000     -1.000     0.0      -1.000     -1.000      0.0
 0.270000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     115.800    115.122    -0.678
  108.000    107.238    -0.792   101.000    100.337     -0.663    93.800     93.281    -0.519
   86.400     85.727    -0.673    -1.000     -1.000      0.0
 0.285000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     123.300    123.244    -0.056
  115.300    115.138    -0.162   108.100    108.140      0.040   101.100    100.949    -0.151
   93.300     93.147    -0.153    84.500     84.684      0.184
 0.300000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     131.400    131.338    -0.062
  123.400    123.068    -0.332   116.300    115.970     -0.330   109.400    108.679    -0.721
  101.000    100.657    -0.343    91.800     91.791     -0.009
 0.315000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     138.700    139.383     0.683
  130.300    130.976     0.676   123.100    123.801      0.701   115.700    116.443     0.743
  107.100    108.229     1.129    98.300     98.975      0.675
 0.330000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     146.400    147.360     0.960
  137.800    138.841     1.041   130.400    131.611      1.211   123.400    124.216     0.816
  114.800    115.835     1.035   105.000    106.209      1.209
 0.345000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     154.600    155.253     0.653
  146.600    146.645     0.045   139.000    139.379      0.379   132.000    131.976    -0.024
  123.200    123.452     0.252   113.200    113.468      0.268
 0.360000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     161.800    163.047     1.247
  153.700    154.370     0.670   146.100    147.087      0.987   139.300    139.701     0.401
  130.300    131.056     0.756   119.900    120.729      0.829
 0.375000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     171.300    170.727    -0.573
  163.200    162.002    -1.198    -1.000     -1.000      0.0      -1.000     -1.000     0.0
  139.800    138.627    -1.173   128.800    127.972     -0.828
 0.390000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     178.500    178.283    -0.217
  169.800    169.527    -0.273   162.600    162.258     -0.342   155.600    154.973    -0.627
  146.200    146.147    -0.053   135.600    135.178     -0.422
 0.405000   0.005000
   -1.000     -1.000     0.0      -1.000     -1.000      0.0     185.300    185.706     0.406
  176.500    176.935     0.435   169.700    169.693     -0.007   162.400    162.488     0.088
  153.100    153.599     0.499   142.300    142.330      0.030
 0.076800   0.010000
   24.000     23.761    -0.239    21.200     20.948     -0.252    18.400     18.561     0.161
   16.000     16.182     0.182    -1.000     -1.000      0.0      -1.000     -1.000     0.0
   -1.000     -1.000     0.0      -1.000     -1.000      0.0
 0.089600   0.010000
   29.600     29.641     0.041    26.200     26.293      0.093    23.100     23.395     0.295
   20.200     20.534     0.334    17.600     17.873      0.273    -1.000     -1.000     0.0
   -1.000     -1.000     0.0      -1.000     -1.000      0.0
 0.102400   0.010000
   36.000     35.816    -0.184    32.100     31.926     -0.174    28.400     28.515     0.115
   25.000     25.175     0.175    22.000     22.081      0.081    19.000     19.339     0.339
   16.400     16.682     0.282    -1.000     -1.000      0.0
 0.115200   0.010000
   41.800     42.235     0.435    37.300     37.804      0.504    33.600     33.883     0.283
   29.700     30.075     0.375    26.200     26.561      0.361    22.900     23.364     0.464
   19.800     20.256     0.456    16.900     17.447      0.547
 0.128000   0.010000
   48.800     48.860     0.060    43.750     43.890      0.140    39.600     39.472    -0.128
   35.300     35.211    -0.089    31.400     31.295     -0.105    27.600     27.651     0.051
   24.000     24.097     0.097    20.700     20.853      0.153
 0.140800   0.010000
   55.400     55.659     0.259    50.000     50.155      0.155    45.300     45.258    -0.042
   40.600     40.561    -0.039    36.200     36.265      0.065    32.200     32.191    -0.009
   28.200     28.200    -0.000    24.300     24.517      0.217
 0.153600   0.010000
   62.500     62.602     0.102    56.250     56.573      0.323    50.800     51.220     0.420
   45.800     46.108     0.308    41.400     41.454      0.054    36.800     36.972     0.172
   32.400     32.555     0.155    28.200     28.435      0.235
 0.166400   0.010000
   69.800     69.665    -0.135    63.150     63.121     -0.029    57.400     57.340    -0.060
   51.900     51.835    -0.065    47.200     46.847     -0.353    42.200     41.979    -0.221
   37.400     37.153    -0.247    32.800     32.599     -0.201
 0.179200   0.010000
   77.000     76.824    -0.176    70.000     69.777     -0.223    63.800     63.599    -0.201
   57.800     57.725    -0.075    52.800     52.428     -0.372    47.400     47.201    -0.199
   42.200     41.983    -0.217    37.200     37.000     -0.200
 0.192000   0.010000
   83.600     84.058     0.458    76.000     76.522      0.522    69.500     69.980     0.480
   63.300     63.761     0.461    57.700     58.181      0.481    52.200     52.621     0.421
   46.800     47.032     0.232    41.300     41.625      0.325
 0.204800   0.010000
   90.800     91.347     0.547    83.050     83.336      0.286    75.800     76.466     0.666
   69.600     69.928     0.328    63.600     64.089      0.489    57.800     58.226     0.426
   52.000     52.284     0.284    46.000     46.461      0.461
 0.217600   0.010000
   97.800     98.672     0.872    89.700     90.203      0.503    82.500     83.040     0.540
   75.800     76.207     0.407    69.700     70.135      0.435    -1.000     -1.000     0.0
   57.500     57.724     0.224    51.300     51.494      0.194
```

Table 9. Continued.

0.230400	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	88.900	89.687	0.787
81.800	82.583	0.783	75.500	76.301	0.801	-1.000	-1.000	0.0
62.800	63.336	0.536	56.100	56.706	0.606			
0.240000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	95.600	94.709	-0.891
87.800	87.418	-0.382	81.000	80.995	-0.005	74.800	74.446	-0.354
67.900	67.646	-0.254	60.700	60.724	0.024			
0.243200	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	96.000	96.389	0.389
88.000	89.039	1.039	82.200	82.571	0.371	75.600	75.970	0.370
68.800	69.101	0.301	61.600	62.082	0.482			
0.256000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	102.400	103.132	0.732
95.200	95.559	0.359	88.400	88.927	0.527	-1.000	-1.000	0.0
74.600	75.002	0.402	67.300	67.604	0.304			
0.268800	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0	95.100	95.352	0.252	87.900	88.401	0.501
80.600	81.021	0.421	73.100	73.254	0.154			
0.270000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	111.100	110.535	-0.565
103.100	102.744	-0.356	96.100	95.957	-0.143	89.500	88.993	-0.507
82.100	81.590	-0.510	74.200	73.789	-0.410			
0.285000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	119.200	118.479	-0.721
110.800	110.483	-0.317	103.600	103.556	-0.044	96.600	96.440	-0.160
89.000	88.780	-0.220	80.600	80.561	-0.039			
0.300000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	127.000	126.414	-0.586
119.200	118.240	-0.960	111.800	111.201	-0.599	104.600	103.967	-0.633
96.400	96.075	-0.325	87.600	87.453	-0.147			
0.315000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	133.600	134.319	0.719
125.200	125.095	0.795	-1.000	-1.000	0.0	112.100	111.547	-0.553
-1.000	-1.000	0.0	95.100	94.439	-0.661			
0.330000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	142.500	142.175	-0.325
133.700	133.726	0.026	127.000	126.529	-0.471	118.400	119.155	0.755
110.900	110.880	-0.020	101.800	101.494	-0.306			
0.345000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
141.000	141.414	0.414	134.900	134.170	-0.730	126.400	126.770	0.370
118.200	118.339	0.139	108.800	108.593	-0.207			
0.360000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	158.200	157.674	-0.526
148.800	149.043	0.243	141.800	141.770	-0.030	134.400	134.369	-0.031
126.500	125.805	-0.695	116.200	115.714	-0.486			
0.375000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	164.900	165.288	0.388
156.700	156.595	-0.105	149.200	149.311	0.111	142.100	141.934	-0.166
133.300	133.258	-0.042	122.700	122.834	0.134			
0.390000	0.010000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	173.100	172.795	-0.305
162.600	164.060	1.460	157.000	156.778	-0.222	150.500	149.447	-1.053
141.400	140.678	-0.722	130.600	129.937	-0.663			
0.081600	0.020000							
23.200	23.174	-0.026	20.500	20.416	-0.084	17.900	18.081	0.181
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0			
0.095200	0.020000							
29.100	28.992	-0.108	25.800	25.701	-0.099	22.700	22.859	0.159
19.800	20.050	0.250	17.300	17.437	0.137	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0			
0.108800	0.020000							
35.400	35.121	-0.279	31.500	31.291	-0.209	27.800	27.937	0.137
24.500	24.649	0.149	21.600	21.602	0.002	18.700	18.912	0.212
16.200	16.304	0.104	-1.000	-1.000	0.0			
0.122400	0.020000							
41.200	41.513	0.313	36.900	37.141	0.241	33.200	33.277	0.077
29.400	29.520	0.120	26.000	26.052	0.052	22.800	22.904	0.104
19.700	19.846	0.146	16.800	17.086	0.286			
0.136000	0.020000							
47.600	48.126	0.526	42.800	43.215	0.415	38.700	38.851	0.151
34.500	34.638	0.138	30.600	30.765	0.165	27.000	27.170	0.170
23.500	23.664	0.164	20.200	20.467	0.267			
0.149600	0.020000							
55.100	54.929	-0.171	49.800	49.481	-0.319	45.000	44.634	-0.366
40.400	39.982	-0.418	36.000	35.725	-0.275	31.900	31.697	-0.203
28.000	27.751	-0.249	24.300	24.115	-0.185			
0.163200	0.020000							
62.200	61.891	-0.309	56.200	55.914	-0.286	51.000	50.607	-0.393
46.000	45.536	-0.464	41.200	40.917	-0.283	36.800	36.475	-0.325
32.500	32.101	-0.399	28.300	28.025	-0.275			
0.176800	0.020000							
69.200	68.985	-0.215	62.600	62.489	-0.111	56.900	56.748	-0.152
51.800	51.280	-0.520	46.800	46.323	-0.477	41.900	41.491	-0.409
37.300	36.703	-0.597	32.600	32.191	-0.409			
0.190400	0.020000							
76.000	76.188	0.188	69.200	69.185	-0.015	63.000	63.041	0.041
57.200	57.198	-0.002	51.700	51.928	0.228	46.500	46.731	0.231
41.200	41.548	0.348	36.700	36.602	-0.098			
0.204000	0.020000							
84.000	83.479	-0.521	76.400	75.981	-0.419	69.900	69.466	-0.434
63.700	63.275	-0.425	-1.000	-1.000	0.0	52.400	52.182	-0.218
-1.000	-1.000	0.0	41.800	41.248	-0.552			
0.217600	0.020000							
90.900	90.835	-0.065	83.200	82.857	-0.343	76.000	76.008	0.008
69.600	69.491	-0.109	63.600	63.670	0.070	57.700	57.827	0.127
51.900	51.909	0.009	46.400	46.115	-0.285			
0.231200	0.020000							
98.500	98.237	-0.263	89.800	89.794	-0.006	82.500	82.648	0.148
75.800	75.832	0.032	70.000	69.773	-0.227	63.700	63.650	-0.050
57.400	57.396	-0.004	51.600	51.190	-0.410			

Table 9. Continued.

0.244800	0.020000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	90.500	89.370	-1.130
83.400	82.279	-1.121	76.600	76.006	-0.594	70.300	69.634	-0.666
63.900	63.066	-0.834	57.100	56.455	-0.645			
0.258400	0.020000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	97.000	96.158	-0.842
89.500	88.816	-0.684	82.900	82.354	-0.546	76.100	75.760	-0.340
69.500	68.900	-0.600	62.400	61.895	-0.505			
0.272000	0.020000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
96.500	95.425	-1.075	89.400	88.797	-0.603	82.500	82.011	-0.489
75.400	74.881	-0.519	67.800	67.490	-0.310			
0.285600	0.020000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0	95.600	95.318	-0.282	88.400	88.369	-0.031
80.800	80.989	0.189	73.400	73.224	-0.176			
0.360000	0.020000							
169.000	167.532	-1.468	156.800	155.561	-1.239	146.300	147.408	1.108
139.400	138.888	-0.512	132.000	131.657	-0.343	124.100	124.262	0.162
115.600	115.881	0.281	105.700	106.252	0.552			
0.390000	0.020000							
181.700	182.766	1.066	169.300	170.199	0.899	162.200	162.223	0.023
152.600	153.552	0.953	145.400	146.271	0.871	137.600	138.881	1.281
128.700	130.248	1.548	118.600	119.957	1.357			
0.420000	0.020000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	177.700	176.691	-1.009
168.900	167.940	-0.960	161.300	160.667	-0.633	154.500	153.367	-1.133
144.900	144.557	-0.343	133.700	133.654	-0.046			
0.140000	0.050000							
38.200	38.183	-0.017	34.000	34.091	0.091	30.600	30.490	-0.110
27.000	26.974	-0.026	23.700	23.721	0.021	20.700	20.809	0.109
17.800	17.983	0.183	-1.000	-1.000	0.0			
0.120000	0.050000							
30.600	30.431	-0.169	27.200	27.012	-0.188	23.700	24.047	0.347
20.800	21.123	0.323	18.000	18.406	0.406	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0			
0.100000	0.050000							
23.400	23.190	-0.210	20.400	20.431	0.031	17.800	18.094	0.294
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0	-1.000	-1.000	0.0			
0.160000	0.050000							
46.200	46.362	0.162	41.900	41.592	-0.308	37.600	37.358	-0.242
33.700	33.265	-0.435	29.400	29.497	0.097	26.200	26.018	-0.182
22.500	22.630	0.130	19.300	19.549	0.249			
0.180000	0.050000							
55.100	54.894	-0.206	49.600	49.449	-0.151	45.000	44.604	-0.396
40.400	39.955	-0.445	36.000	35.700	-0.300	31.900	31.673	-0.227
28.000	27.730	-0.270	24.200	24.096	-0.104			
0.200000	0.050000							
64.100	63.720	-0.380	57.900	57.607	-0.293	52.300	52.185	-0.115
47.100	47.008	-0.091	42.600	42.299	-0.301	38.000	37.754	-0.246
33.500	33.271	-0.229	29.200	29.082	-0.118			
0.220000	0.050000							
73.200	72.786	-0.414	66.400	66.020	-0.380	60.400	60.061	-0.339
54.400	54.392	-0.008	49.800	49.266	-0.534	44.400	44.237	-0.163
39.400	39.238	-0.162	34.700	34.495	-0.205			
0.240000	0.050000							
81.200	82.045	0.845	73.600	74.643	1.043	67.800	68.199	0.399
61.600	62.073	0.473	56.600	56.569	-0.031	51.200	51.099	-0.101
45.700	45.610	-0.090	40.600	40.320	-0.280			
0.260000	0.050000							
92.000	91.453	-0.547	83.800	83.435	-0.365	77.000	76.560	-0.440
70.200	70.018	-0.182	64.400	64.176	-0.224	58.200	58.308	0.108
52.400	52.361	-0.039	46.700	46.533	-0.167			
0.280000	0.050000							
101.000	100.968	-0.032	92.300	92.358	0.058	84.700	85.112	0.412
77.600	78.192	0.592	71.500	72.051	0.551	65.400	65.833	0.433
59.200	59.462	0.262	53.100	53.105	0.005			
0.300000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	93.900	93.819	-0.081
86.200	86.560	0.360	79.800	80.161	0.361	73.000	73.640	0.640
66.400	66.878	0.478	59.500	60.007	0.507			
0.320000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
94.700	95.089	0.389	88.300	88.468	0.168	81.400	81.692	0.292
74.300	74.575	0.275	66.700	67.204	0.504			
0.360000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
-1.000	-1.000	0.0	105.000	105.533	0.533	97.700	98.383	0.683
-1.000	-1.000	0.0	-1.000	-1.000	0.0			
0.420000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	147.600	147.488	-0.112
138.700	138.967	0.267	131.900	131.736	-0.164	124.400	124.341	-0.059
116.100	115.957	-0.143	106.700	106.325	-0.375			
0.440000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	155.900	156.392	0.492
147.600	147.773	0.173	141.600	140.503	-1.097	134.000	133.101	-0.899
125.500	124.558	-0.942	115.500	114.523	-0.977			
0.460000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	165.400	165.217	-0.183
157.500	156.525	-0.975	-1.000	-1.000	0.0	141.700	141.862	0.162
132.900	133.187	0.287	123.200	122.767	-0.433			
0.480000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	-1.000	-1.000	0.0
164.800	165.200	0.400	157.100	157.920	0.820	149.600	150.598	0.998
-1.000	-1.000	0.0	130.400	131.027	0.627			
0.500000	0.050000							
-1.000	-1.000	0.0	-1.000	-1.000	0.0	183.400	182.544	-0.856
174.900	173.778	-1.122	166.900	166.522	-0.378	159.000	159.281	0.281
150.700	150.417	-0.283	-1.000	-1.000	0.0			

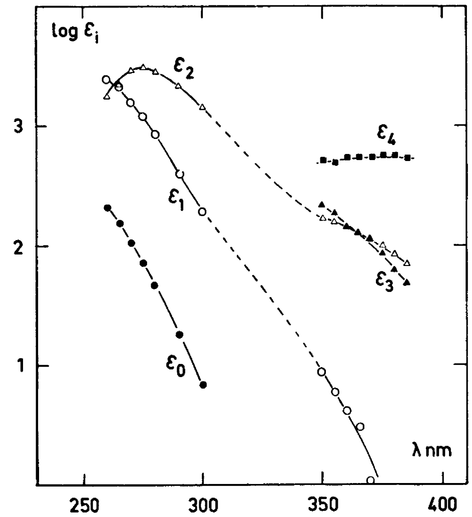

Fig. 8. The log ε_i values obtained from the "LETAGROP" program. ε_0 measured directly.

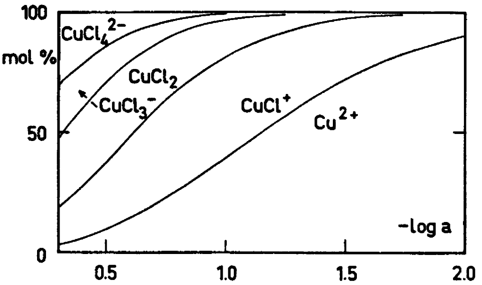

Fig. 9. The distribution of copper(II) chloride complexes as a function of log a for $B = 0.010$ M.

The values of the stability constants were determined from the $\bar{n}(\log a)$-curve by means of the program "LETAGROP VRID".[23] The values of the constants were then inserted in the "SPEFO" version to calculate the ε_i values. The program requires that ε_1 is determined. By inserting the values of β_1 and β_2 and processing the experimental data obtained at low chloride ion concentration ($A < 0.06$ M), it was possible to obtain approximate values for ε_1 in the range 350 – 385 nm. ε_1 was then fixed, and ε_2, ε_3, and ε_4 were calculated (*cf.* Table 7). All the ε_i values were then fixed, and the stability constants were calculated with the "SPEFO" program in the range 370 – 385 nm (*cf.* Table 10). The values for β_1, β_2, β_3 and β_4 obtained were:

$\beta_1 = 10.43 \pm 0.42$ M^{-1} $\quad \beta_3 = 56.54 \pm 2.13$ M^{-3}

$\beta_2 = 39.13 \pm 0.92$ M^{-2} $\quad \beta_4 = 160.0 \pm 4.86$ M^{-4}

and $U = 67.55$ for 274 values for $A \leq 0.5$ M. The errors given are σ, where σ is the standard deviation. The errors are probably underestimated since it was necessary to hold the ε_i values constant during the calculation. The experimental data, which were processed with the "SPEFO" program are presented in Tables 8 and 9.

RESULTS AND DISCUSSION

The refinement of the constants thus gave the following values which are regarded as being the "best values":

$\log \beta_1 = 1.03 \pm 0.03$ $\quad \log \beta_3 = 1.77 \pm 0.19$

$\log \beta_2 = 1.60 \pm 0.07$ $\quad \log \beta_4 = 2.21 \pm 0.08$

Table 10. Survey of the values for the stability constants, β, obtained by the different methods of calculation.

Calculation method	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
Curve fitting	10.1	45.7	–	–
LETAGROP "SPEFO"	11.6 ± 0.2	39.2 ± 6.2	–	–
Fronæus' method	10	43	39	167
	11.5	41	46	177
Rosotti's method	10	36	42	161
Rosotti's reciprocal method	11	38	43	–
LETAGROP VRID	10.7 ± 0.3	39.6 ± 2.1	59 ± 8	163 ± 10
LETAGROP "SPEFO"	10.4 ± 0.4	39.1 ± 0.9	57 ± 2	160 ± 5

These were obtained from the "LETAGROP VRID" calculations based on the $\bar{n}(\log a)$ data (*cf.* Table 10).

The errors given are 3σ, where σ is the standard deviation in $\log \beta$. The third complex shows a greater error than the others. In Fig. 9 a distribution curve has been drawn from the above values of the constants. The narrow band of existence for the third complex shows that it only exists in comparatively small quantities.

The recorded spectra show absorption bands at 250, 375, and 800 – 900 nm. According to Andreev *et al.*[6] and Eswein *et al.*,[12] the absorption band at 250 nm indicates the formation of the lower complexes at these low concentrations. The absorption bands at 375 nm and 800 – 900 nm should indicate $CuCl_4^{2-}$. The fourth complex also absorbs in the low UV range.

The different ε_i values have been calculated with the "LETAGROP" program (*cf.* Fig. 8). The maximum for $CuCl_2$ is at 275 nm, which is in accordance with Andreev *et al.* The molar absorptivity, ε_4, for $CuCl_4^{2-}$ at 375 nm is about 530 M^{-1} cm^{-1} which agrees with the findings of Eswein *et al.*[12] The value of ε_2 (approximately 100 M^{-1} cm^{-1}) is also similar to the value calculated by Eswein *et al.*

The coordination of the Cu^{2+} ion in aqueous solution is tetragonally distorted octahedral, and of $CuCl_4^{2-}$ probably distorted tetrahedral. As can be seen from Fig. 8, the absorption maximum at 375 nm is characteristic for the $CuCl_4^{2-}$ complex, only. Thus there is evidence that this complex has a different symmetry from the lower ones. However, it should be borne in mind that, although only $CuCl_4^{2-}$ has an absorption maximum at 375 nm, the absorptivities of the other complexes cannot be neglected.

It is obvious that the stepwise stability constants in sulphuric acid solution are greater by a factor of 10 than those obtained in perchlorate medium. Without a knowledge of the entropies and heats of formation of the complexes in the perchlorate and sulphuric acid media, it is not worthwhile to speculate on the reason for this.

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REFERENCES

1. Bjerrum, J. *Kgl. Dan. Vidensk. Selsk. Mat. Phys. Medd. 22* No. 18 (1946).
2. McConnell, H. and Davidsson, N. *J. Amer. Chem. Soc. 72* (1950) 3164.
3. Näsänen, R. *Suom. Kemistilehti 26* (1953) 37.
4. Kruh, R. *J. Amer. Chem. Soc. 76* (1954) 4865.
5. Lister, M. W. and Rosenblum, P. *Can. J. Chem. 38* (1960) 1827.
6. Andreev, S. N. and Sapozhnikova, O. V. *Zh. Neorg. Khim. 13* (1968) 1548.
7. Faucherre, J. and Crego, A. *Bull. Soc. Chim. Fr.* (1962) 1820.
8. Kenttämaa, J. *Suom. Kemistilehti B 32* (1959) 68.
9. Trémillon, B. *Bull. Soc. Chim. Fr.* (1958) 1483.
10. Morris, D. F. C. and Short, E. L. *J. Chem. Soc.* (1962) 2672.
11. Libus, Z. *Inorg. Chem. 12* (1973) 2972.
12. Eswein, R. P., Howald, E. S., Howald, R. A. and Keeton, D. P. *J. Inorg. Nucl. Chem. 29* (1967) 437.
13. Vogel, A. I. *Quantitative Inorganic Analysis*, Longmans, London 1961, p. 608.
14. Domke, J. and Bein, W. *Z. Anorg. Chem. 43* (1905) 125/81, 176; (after Gmelin 8 Ed., Part 9, B2, 656).
15. Fronæus, S. *Acta Chem. Scand. 7* (1953) 21.
16. Olerup, H. *Järnkloridernas komplexitet* (Diss.), Lund 1944.
17. Fronæus, S. *Komplexsystem hos koppar* (Diss.), Lund 1948.
18. Elding, L.-I. and Leden, I. *Acta Chem. Scand. 20* (1966) 706.
19. Rossotti, F. J. C. and Rossotti, H. S. *The Determination of Stability Constants*, McGraw-Hill, New York 1961, p. 89.
20. *Ibid.*, p. 108.
21. *Ibid.*, p. 110.
22. Sillén, L.-G. and Warnquist, B. *Ark. Kemi 31* (1969) 365.
23. Ingri, N. and Sillén, L.-G. *Ark. Kemi 23* (1964) 97.

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