

Determination of Small Stability Constants. A Spectrophotometric Study of Copper(II) Chloride Complexes in Hydrochloric Acid

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The four stability constants in the copper(II) chloride system have previously been determined by the author for solutions of various highly soluble metal chlorides. The constants were calculated with the assumption that the tetrachloro complex is the only complex absorbing at 436 nm, and the necessary activity corrections were derived from the measurements themselves. New spectrophotometric measurements described in the present paper confirm that the constants are reliable and that the assumptions made are correct. They are used in this work to resolve the measured absorption curves of the UV, visible and near-infrared region into spectra for each of the four chloro complexes.

It is also established that some authors who have determined stability constants for the four copper(II) chloro complexes in 5 M Na (Cl, ClO₄) have not taken into consideration the fact that maintaining a high constant ionic strength is not the same as maintaining a constant salt medium. For this reason, and because of the weak complex formation, they can only calculate reliable values for the first two stability constants at relatively small chloride concentrations.

The principle of using a constant salt medium with a strong dominant electrolyte has been very useful in obtaining mass action constants in the case of strong complex formation. For weak aniono complex formation it is, however, necessary to include the complex-forming electrolyte in high and varying concentrations, making it impossible to maintain a constant salt medium. It is possible to maintain a constant ionic strength, but this is of little value when the ionic strength is much higher than 0.1 M. In the case of high ionic strength, the logarithm of the activity coefficients in a mixture of two electrolytes varies linearly with the mole fraction of the electrolyte according to Harned's rule. These changes, which depend to a great extent on the hydration of the species, introduce an uncertainty which can be very large in the case of weak complex formation.¹

For this reason, a treatment differing from that

involving a constant ionic strength was introduced, and the weak complex formation in CuCl₂,^{2,3} CoCl₂⁴ and FeCl₃⁵ solutions was studied for small concentrations of the complex-forming metal chloride in solutions containing increasing concentrations of a single, highly soluble chloride such as HCl, LiCl or CaCl₂.

The logarithm of the mean activity coefficient on a molar basis, $\gamma^{(c)}$, is a linear function of the concentration of chloride ion molarities higher than 3 M, as shown for some strong electrolytes in Fig. 1. This fact makes it possible to substitute the ligand concentration with an effective ligand activity derived from the measurements themselves in cases where a determination of the concentration of at least one of the complexes can be made over a large ligand concentration interval. If this is not possible, the activity, in lack of better, can be replaced by the product of the ligand concentration and the mean activity coefficient

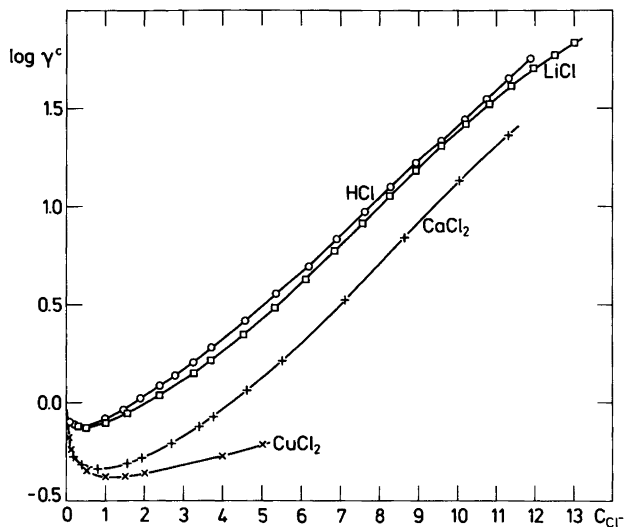


Fig. 1. Plots of the logarithm of the mean activity coefficients on a molar basis vs. the chloride ion concentration for some electrolytes at 25 °C.⁶

for the dominant electrolyte, as done by Bjerrum and Lukes.⁵

The copper(II) chloride system

In the CuCl_2 system, the absorption at the blue mercury line at 436 nm at low chloride concentration increases as the fourth power of the chloride concentration.^{2,8} This indicates that CuCl_4^{2-} is the only species absorbing at this wavelength, and further support for this assumption is given in the present paper. Making this assumption, the extended Bodländer relation⁷ can be written as

$$\frac{d \log \epsilon_{436}}{d \log [\text{Cl}^-]} = 4 - \bar{n}. \quad (1)$$

In order to use this equation for very high chloride concentrations, an effective chloride activity, $a_{\text{Cl}^-} = F[\text{Cl}^-]$, was introduced for $[\text{Cl}^-]$ in eqn. (1) by means of the expression:

$$\log F = A + B[\text{Cl}^-]$$

where A and B are individual constants for the various chlorides used. The introduction of a single mean activity coefficient F presupposes that

$$F \sim \frac{f_{\text{Cu}^{2+}} f_{\text{Cl}^-}}{f_{\text{CuCl}^+}} \sim \frac{f_{\text{CuCl}^+} f_{\text{Cl}^-}}{f_{\text{CuCl}_2}} \sim \frac{f_{\text{CuCl}_2} f_{\text{Cl}^-}}{f_{\text{CuCl}_3^-}} \sim \frac{f_{\text{CuCl}_3^-} f_{\text{Cl}^-}}{f_{\text{CuCl}_4^{2-}}}$$

This approximation corresponds to the assumption that $\log f_{\text{CuCl}_n^{2-n}}$ changes smoothly from $f_{\text{Cu}^{2+}}$ to $f_{\text{CuCl}_4^{2-}}$ and is quite reasonable in the case of concentrated solutions for which chemical similarity between the ions rather than their charges determined the activity coefficients.

Replacing $d \log [\text{Cl}^-]$ in eqn. (1) with $d \log F[\text{Cl}^-]$ and introducing

$$\frac{d \log F}{d[\text{Cl}^-]} = B$$

leads to the following relationship:²

$$\frac{d \log \epsilon_{436}}{d[\text{Cl}^-]} = \left(\frac{0.4343}{[\text{Cl}^-]} + B \right) (4 - \bar{n}). \quad (2)$$

Using this relationship, values of B and \bar{n} were obtained for C_{Cl^-} higher than 3 M. The following values for B were obtained for the various chloride media:² HCl 0.20, LiCl 0.23, MgCl_2 0.18 and CaCl_2 0.21. It is remarkable that these B values differ only little from those for the pure electrolytes HCl, LiCl and CaCl_2 , for which the following approximate relations derived from Fig. 1 apply for chloride concentrations higher than 3 M:

$$\begin{aligned} \log \gamma_{\text{HCl}}^{(e)} &= -0.45 + 0.187[\text{Cl}^-] \\ \log \gamma_{\text{LiCl}}^{(e)} &= -0.53 + 0.190[\text{Cl}^-] \\ \log \gamma_{\text{CaCl}_2}^{(e)} &= -0.90 + 0.22[\text{Cl}^-]. \end{aligned}$$

The stability constants in the CuCl_2 system were calculated from the values of B and corresponding values of \bar{n} and $[\text{Cl}^-]$ obtained by use of eqn. (2). For the effective chloride activity $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{A+B[\text{Cl}^-]}$, the undetermined constant A , with reference to the above expressions for $\gamma_{\text{HCl}}^{(c)}$ and $\gamma_{\text{LiCl}}^{(c)}$, was taken to be -0.5 . On this basis^{2,3} the estimated values for the consecutive activity constants were as follows:

$$K_1 \cong 1, K_2 \cong 0.4, K_3 \cong 0.06, K_4 \cong 0.01.$$

Experimental

Reagents and solutions. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (pro analysi) and iron-free 37% hydrochloric acid were employed. The stock solutions of HCl were analysed by acid-base titration and the CuCl_2 solutions by Volhard titration. The various solutions were prepared in volumetric flasks by adding from burettes or pipetting from stock solutions.

Spectrophotometric measurements in the UV and visible regions were made on a Cary 118 spectrophotometer, and in the near-infrared on a Zeiss DMR 21 spectrophotometer. The instruments were in both cases thermostatted at 25.0°C . Owing to the high UV-absorption of the

solutions, most of the measurements were made in 0.1 cm silica cells. The reference cell was in all cases filled with corresponding copper-free solution. This was especially necessary in the near-infrared, where aqueous HCl solutions have considerable absorption with maxima at 1200 nm and between 1000 and 950 nm.

Results and discussion

A new estimate of K_4 and of the absorption of the trichloro and tetrachloro complexes in the blue region of the visible spectrum. As mentioned,^{2,3} the stability constants were obtained with the assumption that CuCl_4^{2-} is the only species absorbing at 436 nm. In order to independently test this assumption, measurements were made on three solutions, composed as shown in Table 1, in the wavelength range from 440 to 390 nm. The molar absorbances of the solutions were carefully measured at intervals of 5 nm. The average value of the ratio between the absorbance differences $(\epsilon_{\text{I}} - \epsilon_{\text{II}})/(\epsilon_{\text{I}} - \epsilon_{\text{III}})$ was calculated to be 0.444 ± 0.015 on the basis of 11 determinations. This shows that the absorbances of solutions I–III fulfil, within experimental uncertainty, the conditions for an isobestic system of the complexes CuCl_3^- and CuCl_4^{2-} . The fourth consecutive constant, K_4 , could therefore be calculated from the previously derived equation:⁵

$$\frac{(a_{\text{Cl}^-})_{\text{I}} - (a_{\text{Cl}^-})_{\text{II}} + \{(a_{\text{Cl}^-})_{\text{I}}(a_{\text{Cl}^-})_{\text{II}} - (a_{\text{Cl}^-})_{\text{II}}(a_{\text{Cl}^-})_{\text{III}}\} K_4}{(a_{\text{Cl}^-})_{\text{I}} - (a_{\text{Cl}^-})_{\text{III}} + \{(a_{\text{Cl}^-})_{\text{I}}(a_{\text{Cl}^-})_{\text{III}} - (a_{\text{Cl}^-})_{\text{II}}(a_{\text{Cl}^-})_{\text{III}}\} K_4} = 0.444$$

Table 1. Composition of three solutions used for the determination of K_4 and of the absorption spectra of the trichloro and tetrachloro copper(II) complexes in the wavelength range from 440 to 390 nm.

No.	C_{CuCl_2}	C_{HCl}	a_{Cl^-}	α_3	α_4
I	4.83×10^{-4}	11.98	947 ^a	0.094	0.906
			718 ^b	0.097	0.903
II	4.83×10^{-4}	10.00	316 ^a	0.237	0.763
			261 ^b	0.228	0.772
III	4.83×10^{-4}	8.34	138 ^a	0.416	0.584
			119 ^b	0.392	0.608

^a $[\text{Cl}^-] \times 10^{-0.5 + 0.20[\text{Cl}^-]}$; α_4 calculated with $K_4 = 0.0102$.

^b $[\text{Cl}^-] \gamma_{\text{HCl}}^{(c)}$; α_4 calculated with $K_4 = 0.013$.

by using the expression $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{-0.5 + 0.20[\text{Cl}^-]}$ derived for hydrochloric acid solutions. For comparison, K_4 was also calculated with the activity of the electrolyte used, i.e. $a_{\text{Cl}^-} = [\text{Cl}^-] \gamma_{\text{HCl}}^{(c)}$. The values of K_4 in the two cases (0.0102 and 0.013), as well as the values of α_3 and α_4 calculated from these constants neglecting lower chloro complexes, are given in Table 1. The two values for K_4 are very similar, and it will be noticed that the value for K_4 calculated with $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{-0.5 + 0.20[\text{Cl}^-]}$ gives the best agreement with the previously estimated value of $K_4 \cong 0.01$.

The molar absorbances for the trichloro complex were calculated using $K_4 = 0.0102$ as well as 0.013 from the expression:

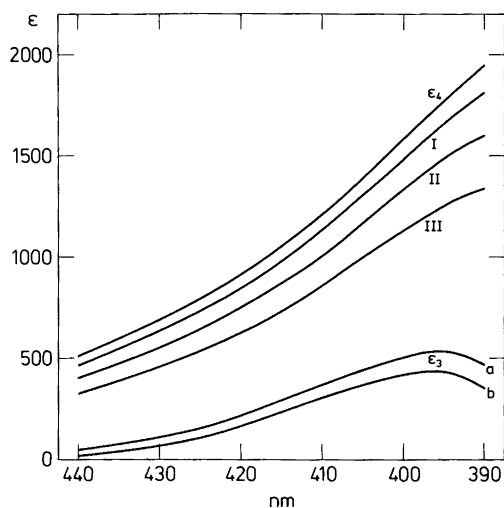


Fig. 2. The spectra of the trichloro (ϵ_3) and tetrachloro (ϵ_4) complexes at 25.0°C in the wavelength range 440–390 nm, calculated from the absorption curves for solutions I–III in Table 1. Curve a for the trichloro complex is calculated with $K_4 = 0.0102$ and curve b with $K_4 = 0.013$.

$$\epsilon_3 = \epsilon_{III} - (\epsilon_I - \epsilon_{III}) \frac{(\alpha_4)_{III}}{(\alpha_4)_I - (\alpha_4)_{III}}$$

and the molar absorptances for the tetrachloro complex were calculated from

$$\epsilon_4 = \epsilon_I - (\epsilon_I - \epsilon_{III}) \frac{1 - (\alpha_4)_I}{(\alpha_4)_I - (\alpha_4)_{III}}$$

Table 2. Composition of the solutions IV–VII calculated with the estimated stability constants $K_1 \cong 1$, $K_2 \cong 0.4$, $K_3 \cong 0.06$, $K_4 \cong 0.01$, and used for the determination of the spectra of the tetrachloro (ϵ_4), trichloro (ϵ_3) and dichloro (ϵ_2) complexes in the UV.

No.	C_{CuCl_2}	C_{HCl}	a_{Cl^-}	α_1	α_2	α_3	α_4	\bar{n}
IV	1.93×10^{-4}	11.58	758 ^a	–	–	0.116	0.881	3.88
			594 ^b	–	–	0.144	0.856	3.86
V	1.93×10^{-4}	8.78	158 ^a	–	0.039	0.372	0.588	3.55
			133 ^b	–	0.051	0.407	0.541	3.49
VI	9.65×10^{-4}	6.75	47.8 ^a	–	0.199	0.542	0.259	3.05
			43.6 ^b	–	0.220	0.543	0.237	3.00
VII	9.65×10^{-4}	3.645	6.18 ^a	0.217	0.537	0.199	0.012	1.94
			6.92 ^b	0.195	0.538	0.223	0.015	2.00

^a $a_{Cl^-} = [Cl^-] \times 10^{-0.5 + 0.20[Cl^-]}$, ^b $a_{Cl^-} = [Cl^-]_{HCl}^{(c)}$

The measured and calculated absorption curves are plotted in Fig. 2, and it will be noticed that the absorption of the trichloro complex is so small in the wavelength range 440–430 nm that it confirms the assumption that the tetrachloro complex is the only species absorbing at 436 nm within the experimental uncertainty. In the following, the calculated constants together with the activity expression:

$$a_{Cl^-} = [Cl^-] \times 10^{-0.5 + 0.20[Cl^-]}$$

are used to estimate the spectra of the four chloro complexes in the UV, visible and near-infrared.

Estimation of the UV-spectra. The absorption curves for solutions IV–VII (Table 2) were used to calculate the UV spectra of the individual chloro complexes. The analysis of the composition of these solutions was made using both approximations for a_{Cl^-} . The calculated values for α_n are not very different in the two cases, but only the values calculated with $a_{Cl^-} = [Cl^-] \times 10^{-0.5 + 0.20[Cl^-]}$, corresponding to the stability constants used, were applied. The computed spectra are shown in Fig. 3.

In the blue region of the visible, the curve for ϵ_4 and curve (a) for ϵ_3 are the same as those calculated for solutions I–III in Fig. 2. Curve (c) is based on an independent calculation of ϵ_3 made by combination of ϵ_4 with the molar absorptance of solution VI with α_4 0.259 and α_3 0.542, utilizing the fact that the absorption of the dichloro complex is completely negligible for $\lambda > 330$ nm. The

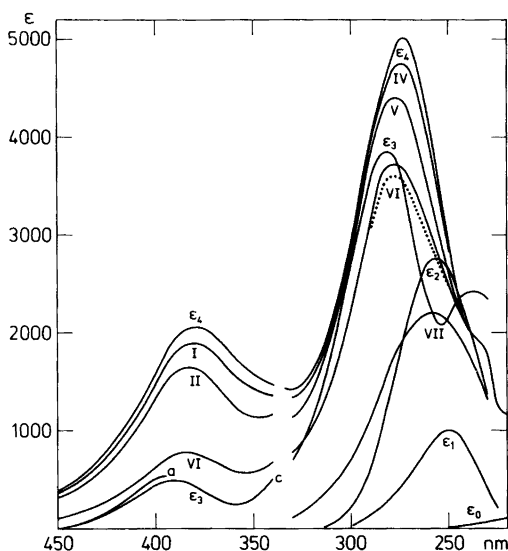


Fig. 3. The UV spectra at 25.0°C of the four chloro copper(II) complexes in hydrochloric acid solutions, calculated from the measured absorption curves for solutions I–VII in Table 2.

agreement between the two curves for ϵ_3 is seen to be excellent.

The UV spectra of the tetrachloro and trichloro complexes in the wavelength range 330–220 nm were calculated with $K_4 = 0.01$, assuming solutions IV and V to be part of an isosbestic system. The computed curves for these complexes are seen to follow nicely the curves for ϵ_4 and ϵ_3 for $\lambda > 330$ nm. The spectrum of the dichloro complex (ϵ_2) was obtained from the absorption curve for solution VII with $\bar{n} = 1.94$ by applying the computed values of ϵ_4 and ϵ_3 and using average values for ϵ_1 taken from the literature.⁹ The curve for the monochloro complex is reproduced

in Fig. 3 together with the absorption curve for the aqua copper (II) ion below 250 nm. A recalculation of the absorption curve for solution VI in the wavelength range 330–230 nm with the values obtained for the individual complexes (the dotted curve in Fig. 3) is seen to give good agreement with the curve measured directly.

The absorption curves in Fig. 3, measured for hydrochloric acid solutions, are all electron-transfer spectra and as such are dependent on the medium. The absorption in hydrochloric acid solutions is higher than in most other chloride salt solutions.^{2,5} This is in contrast to the low intensity of the ligand field bands in the near-infrared, which are much less dependent on the medium.

Estimation of the ligand field spectra. The absorption curves for solutions I–V (Table 3) shown in Fig. 4 were used to estimate the spectra of the individual chloro complexes in the visible and near-infrared. The chloride activity used to compute the distribution of the complexes was calculated from $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{-0.5 + 0.20[\text{Cl}^-]}$; for HCl concentrations smaller than 3 M, a_{Cl^-} was calculated using the $\gamma_{\text{HCl}}^{(c)}$ values for the electrolyte.

The measured and calculated spectra of the chloro complexes are shown in Fig. 4. The spectra of the tetrachloro (ϵ_4) and trichloro (ϵ_3) complexes were calculated assuming solutions I and II to be part of an isosbestic system. The spectrum of the dichloro complex (ϵ_2) was calculated from the absorption of solution III by use of the known values for ϵ_3 and ϵ_4 , applying independently estimated molar absorption values for the monochloro complex (ϵ_1) and the aqua ion (ϵ_0). These values were estimated using the molar absorptions of solutions IV and V. Corrections were made for the small concentrations of dichloro complex in IV and of the monochloro

Table 3. Composition of the solutions used for the determination of the ligand field spectra of the chloro copper(II) complexes in the visible and near-infrared by use of the constants $K_1 \cong 1$, $K_2 \cong 0.4$, $K_3 \cong 0.06$, $K_4 \cong 0.01$.

No.	C_{CuCl_2}	C_{HCl}	a_{Cl^-}	α_0	α_1	α_2	α_3	α_4	\bar{n}
I	0.00579	11.42	695 ^a	0	0	0	0.0126	0.874	3.87
II	0.00579	8.54	137.8 ^a	0	0	~0	0.421	0.579	3.57
III	0.00965	3.645	6.18 ^a	0	0.217	0.537	0.199	0.012	1.94
IV	0.01930	0.800	0.659 ^b	0.546	0.360	0.094	0	0	0.548
V	0.01930	0.019	0.058 ^c	0.966	0.034	0	0	0	0.034

^a $a_{\text{Cl}^-} = [\text{Cl}^-] \times 10^{-0.5 + 0.20[\text{Cl}^-]}$. ^b $a_{\text{Cl}^-} = [\text{Cl}^-] \gamma_{\text{HCl}}^{(c)}$. ^c $a_{\text{Cl}^-} = [\text{Cl}^-] \gamma_{\text{HCl}, \text{CuCl}_2}^{(c)}$.

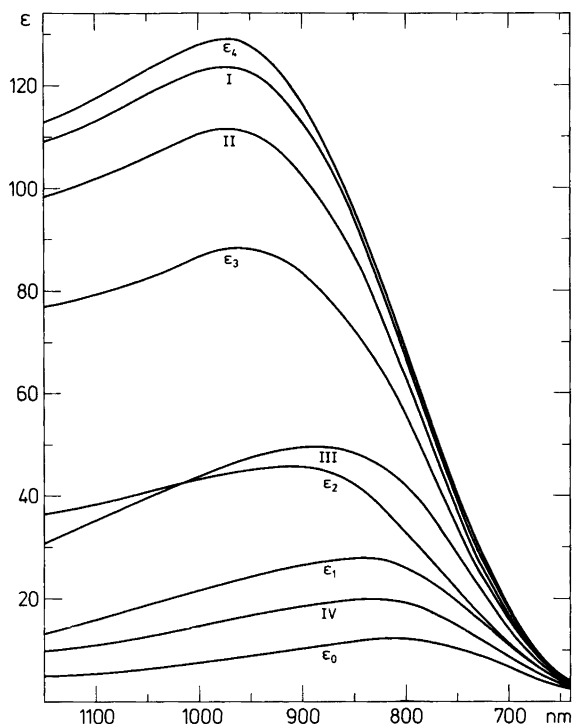


Fig. 4. The near-infrared spectra at 25.0°C of the four chloro copper(II) complexes in hydrochloric acid solutions, calculated from the measured absorption curves for solutions I–V in Table 3.

complex in V by applying the stability constants used.

The chloride ion is placed before water in the spectrochemical series, and, as would be expected, the absorption of the chloro complexes is displaced towards higher wavelengths than that of the aqua ion. As seen from Fig. 4, the shift is on average about 40 nm per chloride in the complex. At the same time, ϵ_{\max} increases rather smoothly from 12 for the aqua ion to 129 l mol⁻¹ cm⁻¹ for the tetrachloro complex.

Comparison with data in the literature. Schwing-Weill⁹ and Khan¹⁰ and Ramette^{11,12} have determined the four stability constants for the CuCl₂ system in 5 M Na (Cl, ClO₄) without taking into consideration the fact that 5 M NaCl is a medium which is quite different from 5 M NaClO₄, and further that even at this high chloride concentration only small amounts of the higher complexes are formed. Bjerrum and Skibsted¹³ have shown that the solubility of Ca(IO₃)₂ in this medium increases nearly linearly with the chloride concentration, and that the solubility in 5 M NaCl

is 2.5 times higher than in 5 M NaClO₄. Calcium chloride solutions do not contain inner-sphere complexes, but some ion-pair formation probably takes place with an association constant which must be rather small considering the high ionic strength. Assuming that the solubility of Cu(IO₃)₂ corrected for complex formation shows the same increase with the chloride-ion concentration as that of Ca(IO₃)₂, then the experimental solubility, *s*, of Cu(IO₃)₂ should be corrected according to the relation:

Table 4. Ramette's stability constants determined in 5 M Na (Cl, ClO₄) compared with values tentatively corrected for the medium effect so that *K*₃ and *K*₄ become negligible.

Ref.	<i>K</i> ₁	<i>K</i> ₂	<i>K</i> ₃	<i>K</i> ₄
Ramette ^a	2.49	0.46	0.79	0.028
Ramette ^b	2.36	0.63	0.46	0.080
(Ramette corr.)	~2.2	~0.55	~0	~0

^aRef. 11. ^bRef. 12.

Table 5. The calculated distribution of the chloro complexes in 5 M NaCl.

Ref.	α_0	α_1	α_2	α_3	α_4
Ramette ^a	0.006	0.073	0.168	0.662	0.092
Ramette ^b	0.006	0.070	0.219	0.504	0.202
(Ramette corr.)	0.024	0.260	0.716	—	—
This paper calc.	0.059	0.281	0.555	0.157	0.0077

^aRef. 11. ^bRef. 12.

$$s' = s(1 - 0.12 C_{Cl^-}).$$

A calculation shows that use of this equation gives too high a correction, resulting in negative values of K_3 and K_4 . However, by empirically introducing two thirds of this correction [$s' = s(1 - 0.08 C_{Cl^-})$], nearly zero values for K_3 and K_4 are obtained as well as values of K_1 and K_2 which are not very different from those determined by Ramette (see Table 4). This does not, however, mean that the higher chloro complexes are negligible in 5 M NaCl. The mean activity coefficient, $\gamma_{NaCl}^{(c)}$, in 5 M NaCl is 0.946, and the chloride activity $5 \times 0.946 = 4.73$, or the same as that in 3.08 M HCl. In Table 5, the distribution of the chloro complexes in 5 M NaCl calculated with the activity constants used in this paper is compared with that computed by Ramette.^{11,12} 5 M NaCl is seen to contain about 15 % trichloro complex and less than one per cent tetrachloro complex. This is in fine agreement with previous calculations for 3 M HCl (see diagram in Ref. 2, p. 32). According to Ramette's uncorrected constants, 5 M NaCl contains larger amounts of the higher complexes varying from 50 to 66 % of the trichloro and from 9 to 20 % of the tetrachloro complex, depending on the method of computation employed.

Schwing-Weill and Kahn^{9,10} have made a careful spectrophotometric study of the $CuCl_2$ system in 5 M Na (Cl, ClO_4) medium for the purpose of determining both the stability constants and the absorption spectra of the four chloro complexes. As pointed out by Bjerrum and Skibsted³ this is a very difficult task, and when one considers the influence of the medium effect in the salt solutions used it is quite understandable that they cannot determine reliable values for the higher complexes and find much too low a value for the molar absorbance of the tetrachloro complex. Bjerrum and Skibsted³ employed a more correct

value for the molar absorbance of the fourth complex in their measurements, and recalculated their data. This approach was criticized by Ramette,¹¹ but obtains support from the results obtained in the present study.

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