

A Calorimetric Study of Copper(II) Chloride Complexes in Aqueous Solution

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The complex formation between copper(II) and chloride ion in 5 M Na(ClO₄,Cl) medium at 25 °C has been investigated with a flow microcalorimetric technique. By using equilibrium constants determined earlier, the enthalpy changes for the formation of the species CuCl⁺, CuCl₂ and CuCl₃⁻ were obtained.

The weak complex formation between copper(II) and chloride ion in aqueous solution has been investigated mainly by spectrophotometric methods.^{1–17} Other methods which have been used are

ion-exchange,²² ion exchange paper chromatography,²³ kinetics,² solvent extraction²⁵ and calorimetry.^{10,16,18–21} Some of the results, obtained under conditions similar to those in the present investigation, are given in Table 1. The β_n and ΔH_n values refer to the reactions $\text{Cu}^{2+} + n\text{Cl}^- \rightleftharpoons \text{CuCl}_n^{(2-n)}$ with $n=1-4$. The existence of these complexes was first established by Bjerrum¹ already in 1946 and has been confirmed by later investigators.⁸

The main objective of the present work has been to determine reliable ΔH -values for the formation

Table 1. Some literature data for the system Cu(II) chloride at 25 °C.

Ref.	Method	Medium	β_1 M ⁻¹	β_2 M ⁻²	β_3 M ⁻³	β_4 M ⁻⁴	ΔH_1 kJ mol ⁻¹
2	spectr.	1 M HClO ₄	1.30±0.03	0.23±0.15	—	—	—
5,	spectr.	2 M NaClO ₄	1.22	—	—	—	6.6
18	calorim.						
23	paper chromat.	3 M HClO ₄	0.94±0.05	0.16±0.07	0.05±0.08	—	—
19	calorim.	2 M NaClO ₄	0.96±0.01	—	—	—	8.2±0.2
24	kinetics	1 M NaClO ₄	1.30±0.27	—	—	—	—
10	spectr.	3 M NaClO ₄	0.87±0.08	—	—	—	9.3±0.2
	calorim.						
21	calorim.	3 M LiClO ₄	0.83	—	—	—	12.1
11	spectr.	4 M NaClO ₄	1.52±0.02	—	—	—	—
		5 M NaClO ₄	1.86±0.04	—	—	—	—
12	spectr.	5 M NaClO ₄	4.0±0.7	4.7±0.6	1.96±0.25	0.23±0.05	—
14	spectr.	4 M NaClO ₄	1.3±0.1	—	—	—	—
		6 M NaClO ₄	1.85±0.1	—	—	—	—
15	spectr.	5 M NaClO ₄	1.5	0.63	0.088	0.0032	—
16	spectr.	4 M LiClO ₄	0.92±0.07	—	—	—	13.6
	calorim.						
17	spectr.	3 M NaClO ₄	0.99±0.15	0.40±0.06	—	—	—

of copper(II) chloride complexes in 5 M Na(ClO₄, Cl) medium.

Several difficulties are encountered when weak complexes, such as those between copper(II) and chloride, are studied. The most serious of these is introduced by the need to substitute ligand (Cl⁻) for a great part of medium — in this case perchlorate — in order to promote complex formation. Assignment of activity coefficients to facilitate interpretation of the data is complicated by this variation of the medium.

Another difficulty, when studying weak complexes with calorimetry, derives from the small heat effect obtained. However, the technique used in this investigation, flow microcalorimetry, is, from our experience, well suited for the measurement of small heat effects with good accuracy.

EXPERIMENTAL

Chemicals. The copper(II) perchlorate stock solution was prepared²⁶ from CuO (Merck *p.a.*) and perchloric acid (Merck *p.a.*). The solution was analyzed for copper by electrodeposition²⁷ and for H⁺ potentiometrically.

Sodium perchlorate stock solution was prepared²⁸ from Na₂CO₃ (Merck *p.a.*) and perchloric acid (Merck *p.a.*).

Sodium chloride (Merck *p.a.*) was recrystallized in water, the crystals were dried at 200 °C and stored in a desiccator.

The compositions of the solutions used in the calorimetric measurements were

Solution *a* 5 M NaClO₄
 ≈ 0.015 M HClO₄

Solution *b* *A* M Cu(ClO₄)₂
 (5 - 2*A*) M NaClO₄
 ≈ 0.015 M HClO₄

Solution *c* *B* M NaCl
 (5 - *B*) M NaClO₄
 ≈ 0.015 M HClO₄

The solutions were acidified to suppress the hydrolysis of copper(II).

Apparatus. For the measurements an LKB Flow microcalorimeter (10700-1) was used. The thermal output was amplified by a Keithley 150 B Microvolt amplifier and recorded on a potentiometric recorder.

The reactants were passed through the mixing cell by means of two peristaltic pumps (LKB Vario Perplex II). The pumps were calibrated frequently by weighing the amount of water pumped in a known amount of time. It was found that the flow rates changed less than 0.2 % during an experiment, usually about five hours. The flow, ϕ (cm³ h⁻¹), of the mixing reactants covered a range of values between 1.5 and 25 cm³ h⁻¹.

The mixing cell used was a 24-carat gold channel, about 0.7 cm³ in volume. The detector sensitivity was 0.07 μ V/ μ W and the calibration current had an accuracy of ± 0.1 %.

Calorimetric procedure. The calorimetric measurements were performed in the following way. The base line output potential was taken when solution *a* (ionic medium) and solution *c* (chloride solution) were pumped through the cell. When a stable base line was obtained, solution *a* was replaced by solution *b* (copper(II) solution). In this way the heat of dilution of chloride into the medium was automatically corrected for. The base line shift obtained then had to be corrected for the heat of dilution of the metal ion [copper(II)], which had to be determined in separate experiments.

For copper(II) concentrations less than about 0.40 M, it was found that

$$\Delta H_{\text{dilution}} (\text{J mol}^{-1}) = -1030 \Delta [\text{Cu}^{2+}]$$

where $\Delta [\text{Cu}^{2+}]$ is the difference between the final and initial copper(II) concentration when a Cu(ClO₄)₂ solution (medium 5 M ClO₄⁻) is diluted in 5 M NaClO₄.

RESULTS AND CALCULATIONS

The calorimetric data obtained are collected in Table 2. The range of copper concentration covered is 0.004–0.35 M and of chloride 0.03–3.5 M. The measured heat effect corrected for the heats of dilution is Q_{exp} .

The calorimetric data were treated with the least-squares computer program LETAGROP/KALLE³⁰ and also with a new version of LETAGROP,³¹ linked with SUBHTF³² (a subroutine form of HALTAFALL).

The results of the calculations are given in Table 3. The ΔH -values were obtained using the equilibrium constants given by Bjerrum and Skibsted.¹⁵ A poorer fit to the experimental data was obtained

Table 2. Calorimetric data for the $\text{Cu}^{2+} - \text{Cl}^-$ system in 5 M $\text{Na}(\text{ClO}_4, \text{Cl})$ at 25 °C. Q_{calc} is the heat effect calculated with the β and ΔH_p values in Table 3.

$[\text{Cu}^{2+}]$ M	ϕ_{Cu} ml/h	$[\text{Cl}^-]$ M	ϕ_{Cl} ml/h	Q_{exp} J/h	$Q_{\text{calc}} - Q_{\text{exp}}$ J/h	
0.394	11.69	0.300	1.43	1.78	+0.02	
	22.76		4.42	5.25	+0.06	
	19.33		4.32	5.10	0.00	
	11.57		4.30	4.66	-0.02	
	6.87		4.53	4.20	-0.01	
	14.42		10.53	9.39	+0.01	
	5.55		4.28	3.70	+0.05	
	5.03		4.37	3.70	-0.04	
	4.69		7.66	4.82	-0.08	
	4.75		4.53	3.69	-0.04	
0.0146	5.26	1.00	4.96	0.188	-0.003	
	4.99		6.59	0.203	0.000	
	5.29		8.35	0.229	0.000	
	5.00		1.72	0.299	-0.011	
0.0734	5.00		1.72	1.35	+0.03	
0.0146	11.46	3.00	4.66	0.724	+0.006	
	4.58		4.85	0.466	-0.008	
	4.66		11.46	0.57	+0.01	
	11.46		4.66	1.58	+0.04	
	11.44		5.00	4.63	2.04	+0.06
	4.58		3.00	4.85	0.86	0.00
0.0365	11.85	5.00	6.40	5.86	-0.02	
0.0146	4.67	3.00	11.48	0.965	+0.021	
	4.58	5.00	4.85	1.01	0.00	
0.0365	10.05		18.46	5.80	0.00	
0.0146	4.66		11.46	1.09	0.00	

when the equilibrium constants given by Schwing-Weill¹² were used.

From the present data it was not possible to determine ΔH for the formation of CuCl_4^{2-} . It is seen from Fig. 1 that CuCl_4^{2-} does not exist in noticeable amounts in the region studied by us.

In the calculations, it has been assumed that the activity coefficients are constant, although part of the experimental data have been obtained in a region where a large fraction of the medium ions has been replaced by chloride ions. The good fit of the data over the whole concentration range gives some support to this assumption.

Some ΔH_1 -values that have been reported in the literature are listed in Table 1. Several of these

values^{16,21} are comparable to the ΔH_1 -value determined by us. This agreement may be coincidental however; in the earlier investigations^{16,21} it was assumed that only the monoligated complex was formed. Furthermore the ionic media used were not the same as used by us.

It is of interest to note as well that the present investigation of the $\text{Cu(II)} - \text{Cl}$ system seems to be the first in which the ΔH for the formation of CuCl_2 and CuCl_3^- as well as CuCl^+ has been determined.

In Table 4 the thermodynamic parameters ΔG° , ΔH° and ΔS° for the formation of $\text{Cu}^{2+} - \text{Cl}^-$ complexes are given.

In Table 5 the $\log K$ and ΔH° -values for some metal-chloride complexes are compared. The trend

Table 3. Results from the calculations made with the LETAGROP program on data of Table 2. The given uncertainties are 3σ . The calculations gave $\sigma(Q_{\text{calc}} - Q_{\text{exp}}) = 0.032 \text{ J}$.

β_i	ΔH_i kJ mol^{-1}
$\beta_1 = 1.5^a$	$\Delta H_1 = 12.30 \pm 0.1$
$\beta_2 = 0.63^a$	$\Delta H_{\beta_2} = 23.0 \pm 1.5$
$\beta_3 = 0.088^a$	$\Delta H_{\beta_3} = 11 \pm 4$

^aFrom Ref. 15.

in the stepwise $\log K$ and ΔH° values for Cu(II) is similar to the trend observed in these parameters for Zn(II) and is to be expected for the interaction between a typical (a)-acceptor ("hard") and the

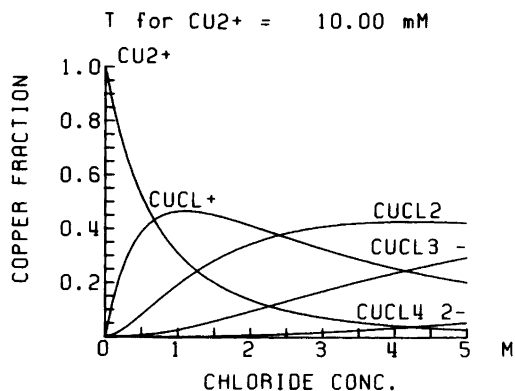


Fig. 1. Distribution of copper species as a function of chloride concentration in 5 M Na(ClO₄, Cl) at 25 °C. Plot produced by the SOLGASWATER²⁹ program with the equilibrium constants from Ref. 15.

Table 4. Calculated values of ΔG° , ΔH° , and ΔS° for the stepwise complex formation $\text{Cu}^{2+} - \text{Cl}^-$ in 5 M Na(ClO₄, Cl) at 25 °C.

Complex	K M^{-1}	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° $\text{J mol}^{-1} \text{K}^{-1}$
CuCl^+	1.5 ^a	-1.0	12.3	44.6
CuCl_2	0.42 ^a	+2.2	10.7	28.5
CuCl_3^-	0.14 ^a	+4.9	-12.0	-56.7

^aFrom Ref. 15.

Table 5. $\log K$ and ΔH -values for the stepwise formation of chloride complexes of Zn(II), Cd(II), Hg(II) and Cu(II) at 25 °C.

Metal ion	Complex	$\log K$	ΔH kJ mol^{-1}	Medium	Ref.
Zn^{2+}	ZnCl^+	0.147	17 ± 2	4 M LiClO ₄	33
	ZnCl_2	0.418	12 ± 1.4		
	ZnCl_3^-	0.212	-3.4 ± 7		
Cd^{2+}	CdCl^+	1.58	-0.42	3 M NaClO ₄	34
	CdCl_2	0.64	0.08		
	CdCl_3^-	0.18	7.74		
	CdCl^+	1.77	-2.8	4 M Li(ClO ₄ , Cl)	35
	CdCl_2	0.70	-2.7		
	CdCl_3^-	0.64	6.28		
	CdCl_4^{2-}	-0.55	24.7		
Hg^{2+}	HgCl^+	7.07	-24.2 ± 1.0	3 M NaClO ₄	36
	HgCl_2	6.91	-27.2 ± 1.5		
	HgCl_3^-	1.08	-4.3 ± 0.9		
	HgCl_4^{2-}	1.09	-6.2 ± 1.0		
Cu^{2+}	CuCl^+	0.18	12.3 ± 0.1	5 M Na(ClO ₄ , Cl)	This work
	CuCl_2	-0.38	10.7 ± 1.5		
	CuCl_3^-	-0.85	-12 ± 4		

chloride ion. For comparison, data are also given in the Table for a representative (b)-acceptor, Hg(II) and for a "mild" (b)-acceptor, Cd(II).

It should also be added that the analysis of the Cu(II)-Cl thermodynamic data summarized in Table 4 could possibly be further refined. One could attempt to take into account the proportion of inner and outer sphere complexes formed.³⁷ However, attempts that have been made to estimate the formation constant for outer and inner sphere CuCl^+ complexes^{20,21} are somewhat speculative. Therefore we have not considered it worthwhile to re-interpret our thermodynamic data for $\text{Cu}^{2+} - \text{Cl}^-$ by estimating the proportion of inner and outer sphere complexes which must necessarily be based on an uncertain estimate of their respective formation constants.

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