Complex Formation in Dilute Aqueous Solutions of Cupric Chloride. Spectrophotometric Determination of Equilibria Involving Slight Complex Formation in Electrolytic Solution

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In a recent paper by the present author [1], the complex formation between cupric and sulphate ions in aqueous solutions was investigated spectrophotometrically. In that article a method for the determination of the thermodynamic complexity constant and the activity coefficient in systems of slight complexity was described. This method has since been further developed. In the following, the improved method is applied to the determination of the thermodynamic dissociation constant and the activity coefficient of the first cupric chloride complex.

EXPERIMENTAL

The light absorption measurements were carried as before out with a Beckman Quartz Spectrophotometer Model DU. 1 cm and 5 cm cells were used. The chemicals were of the best quality obtainable and were used without purification. Concerning further experimental details, the reader is referred to the previous papers by the present author [1,2].

METHOD OF CALCULATION

In dilute aqueous solutions of cupric chloride, the complex ion $Cu(H_2O)_3Cl^+$ is practically the only one present [3]. The equilibrium expression, according to the law of mass action, is

$$f_{Cu^{++}} [Cu^{++}] f_{Cl^-}[Cl^-] / f_{CuCl^+} [CuCl^+] = K_0 \tag{1}$$

which may be rewritten:

$$[Cu^{++}] \; [Cl^-] \, / \, [CuCl^+] = K/_0 F = K \tag{2}$$

where

$$F = f_{Cu^{++}} f_{Cl^-} / f_{CuCl^+} \tag{3}$$

For the determination of the thermodynamic constant K_0 and the activity coefficient F, a series of dilute cupric chloride solutions with varying amounts of hydrochloric acid were prepared. At wavelengths near 300 mμ, the light absorption of hydrochloric acid solution is negligible and that of cupric ions is very small, but that of the complex is considerable. From Beer's law we obtain:

$$\varepsilon = E/d - \varepsilon_{Cu^{++}} [Cu^{++}] = \varepsilon \, [CuCl^+] \tag{4}$$

where E is the extinction, d the thickness of the absorbing layer in cm, $\varepsilon_{Cu^{++}}$ the molecular extinction coefficient of cupric ion and ε that of the complex. Inserting (4) into (2) gives:

$$\frac{(c_{Cu} - e/\varepsilon)x}{e/\varepsilon} = K_0/F = K \tag{5}$$

or

$$\varepsilon - K_0 e/F c_{Cu} x - e/c_{Cu} = 0 \tag{6}$$

where $x = [Cl^-]$ and c_{Cu} is the total copper concentration. The concentration of chloride ion is approximately the same as the stoichiometric concentration. After the equilibrium constant has been determined, however, it is possible to calculate the concentration of the complex from

$$[CuCl^+] = c_{Cu} c_{Cl} / (K + c_{Cu} + c_{Cl} - [CuCl^+]) \tag{7}$$

by the iterative method. The accurate chloride ion concentration is now obtained from

$$[Cl^-] = c_{Cl} - [CuCl^+] \tag{8}$$

The activity coefficient in equation (6) may be calculated from the Debye-Hückel equation

$$pF = \frac{2.04 \; \sqrt{I}}{1 + a \sqrt{I}} - BI \tag{9}$$

where I is the ionic strength. The parameters a and B are unknown. We, therefore, assign them the values in alkalipechlorate solutions and after the molecular extinction coefficient ε has been calculated from equations (6) by the method of least squares, it is possible to calculate more accurate values for a and B by means of equation (5). This method of calculation is much less laborious than that presented in the previous paper by the present author[1].

The activity coefficient of the first cupric chloride complex, in alkali perchlorate solutions, may be determined as follows. In dilute cupric chloride solutions, with no alkali chloride or hydrochloric acid the concentration of the complex is very small compared to the total copper concentration. Therefore, we obtain from the law of mass action:

$$\frac{2\ c_{Cu}^2}{e/\varepsilon} = K_0/F \qquad (10)$$

or

$$p(e/2c_{Cu}^2) = p(\varepsilon/K_0) + pF \qquad (11)$$

By means of this equation it is possible to calculate the activity coefficient from the extinction of a series of cupric chloride solutions, where the ionic strength is varied by addition of alkali perchlorate. In addition the quotient ε/K_0 is obtained. For the determination of the activity coefficient in this case it is thus unnecessary to know either the molecular extinction coefficient or the thermodynamic dissociation constant. Although the method has been described with reference to a particular system, it can easily be adapted to any other such system.

RESULTS

In Table 1 a series of measurements in mixed solutions of cupric chloride and lithium perchlorate is presented. The values

$$\varepsilon/K_0 = 1625 \ (\lambda = 272 \ m\mu), \ a = 1.788 \ \text{and} \ B = 0.212$$

were obtained from equation (11) by the method of least squares. The activity coefficient function may thus be represented by the equation:

$$Fp = \frac{2.04\ \sqrt{I}}{1 + 1.788\ \sqrt{I}} - 0.212\ I \qquad (12)$$

This equation expresses very satisfactorily the data over the whole range of ionic strengths investigated. The maximum deviation is 0.006 and the average deviation 0.003. The error caused by the approximation $[Cu^{++}] = c_{Cu}$ is at most of the same order of magnitude as the average deviation.

The results in mixed solutions of cupric chloride and hydrochloric acid are recorded in Table 2. By using equation (6) the values

$$K_0 = 0.90 \text{ and } \varepsilon = 1478 \ (\lambda = 272 \text{ m}\mu)$$

Table 1. The activity coefficient of the first cupric chloride complex in lithium perchlorate solutions. $c_{Cu} = 0.01000$.

$\sqrt{I}$	e ($\lambda = 272$ mμ)	$p(e/2c^2) - p(\varepsilon/K_0)$	ΔpF (Deviation)
0.123	0.0544	0.1971	+ 0.0047
0.173	0.1750	0.2691	− 0.0058
0.222	0.1566	0.3173	− 0.0032
0.272	0.1430	0.3568	+ 0.0005
0.297	0.1368	0.3760	+ 0.0013
0.343	0.1268	0.4090	− 0.0004
0.383	0.1206	0.4308	+ 0.0018
0.453	0.1114	0.4652	+ 0.0017
0.513	0.1044	0.4934	− 0.0033
0.616	0.0990	0.5165	+ 0.0010
0.705	0.0960	0.5298	+ 0.0011
0.783	0.0960	0.5298	+ 0.0058
0.854	0.0960	0.5298	+ 0.0049
0.981	0.0980	0.5209	+ 0.0015
1.094	0.1020	0.5035	− 0.0023
1.128	0.1046	0.4926	+ 0.0003
1.196	0.1080	0.4787	− 0.0045
1.346	0.1224	0.4243	− 0.0024
1.537	0.1494	0.3378	− 0.0019
1.611	0.1644	0.2962	+ 0.0004
1.673	0.1794	0.2583	+ 0.0033

were obtained by the method of least squares. The maximum deviation of an individual value of the thermodynamic complexity constant is 0.03, and that of the molecular extinction coefficient 60. The average deviations are 0.01 and 20, respectively. The accuracy obtained is thus very satisfactory. In this case, the quotient of the molecular extinction coefficient and the thermodynamic dissociation constant is 1650, in satisfactory agreement with the above

Table 2. Determination of the thermodynamic dissociation constant and the activity coefficient of the first cupric chloride complex at 25° C. λ = 272 mμ.

$c_{Cu} \cdot 10^3$	x	e	$\sqrt{I}$	pF	K_0 ($\varepsilon = 1478$)	ε ($K_0 = 0.896$)
5.00	0.0100	0.0516	0.1225	0.2041	0.889	1490
10.00	0.0200	0.173	0.173	0.2670	0.929	1425
7.50	0.0402	0.238	0.219	0.3162	0.885	1497
5.83	0.0958	0.354	0.319	0.4008	0.889	1490
8.890	0.1300	0.658	0.373	0.4360	0.904	1466
3.333	0.259	0.419	0.512	0.5003	0.880	1502
2.500	0.341	0.377	0.587	0.5218	0.903	1468
2.000	0.509	0.417	0.715	0.5405	0.893	1483
1.667	0.675	0.438	0.823	0.5418	0.897	1477
1.229	0.763	0.357	0.875	0.5379	0.904	1468
1.304	0.880	0.438	0.939	0.5297	0.884	1494

independently determined value 1625. The activity coefficient in hydrochloric acid solutions may be expressed by the equation:

$$pF = \frac{2.04 \sqrt{I}}{1 + 1.645 \sqrt{I}} - 0.252 \, I \qquad (13)$$

The previous data on cupric sulphate solutions were recalculated using the improved method described above. The results in lithium sulphate solution were

$$pK = 2.149 - \frac{4.05 \sqrt{I}}{1 + 1.536 \sqrt{I}} + 0.0576 \, I \qquad (14)$$

The results are otherwise the same as before, except for the value of pK_0 which is 0.05 higher. This obviously arises from the uncertainty in the determination of the derivative "d log ε/d log [SO_4]" required in the old method.

In Fig. 1 the activity coefficient of the first cupric chloride complex is represented as a function of the ionic strength in lithium perchlorate solution.

DISCUSSION

The thermodynamic dissociation constant of $CuCl^+$ is, according to a recent investigation by J. Bjerrum [3], greater than or approximately equal to unity. This is thus in agreement with the value $K_0 = 0.90$ obtained in the present paper. The activity coefficient has not been previously determined.
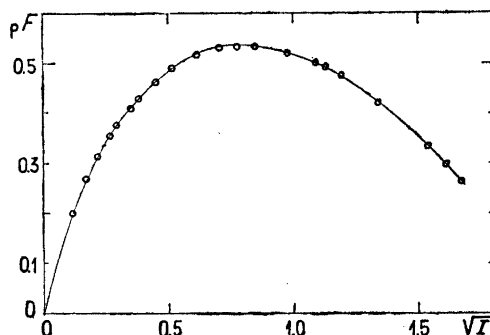
Fig. 1. Activity coefficient of the first cupric chloride complex in lithiumperchlorate solutions.

Some series of measurements were carried out at different wavelengths in the investigation of the effect of the higher complexes when hydrochloric acid is added. The measurements showed that the higher complexes do not interfere when the chloride ion concentration is smaller than 0.25. When the concentration of hydrochloric acid exceeds this value, the values of the activity coefficient obtained from the measurements, at different wavelengths, gradually begin to differ.

SUMMARY

Methods for the spectrophotometric determination of the thermodynamic complexity constants and the activity coefficient of complexes in systems of slight complexity are described.

The thermodynamic dissociation constant and the activity coefficient of the first cupric chloride complex are determined in hydrochloric acid and lithium perchlorate solutions. The Debye-Hückel equation expresses the results in lithium perchlorate solutions very accurately over wide ranges of ionic strength. In hydrochloric acid solutions the higher complexes begin to interfere when the concentration of hydrochloric acid is higher than 0.25.

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