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THERMODYNAMIC STUDY ON THE FORMATION OF THE CUPRIC ION HYDROLYTIC SPECIES

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ABSTRACT

The formation constants of Cu(OH), $Cu_2(OH)_2$ and $Cu_3(OH)_4$ were determined by potentiometric measurements. The enthalpy changes were obtained by direct calorimetry. The species were individualized by statistic tests. The calculated entropy changes were correlated with the assumed structure of the species present in the solution.

INTRODUCTION

In order to continue our studies on the formation and stability of cupric ion mixed complexes in aqueous solution[1–5], it was necessary, chosen the ligands, to investigate a pH range such as to include the hydrolysis of the cupric ion. A number of authors[6–9] have determined both the various hydrolytic species and their constants. As they disagreed on the kind of species and did not work at an ionic strength of 0.1 M ($NaClO_4$) aqueous solution, we carried out the potentiometric measurements for determining stability constants.

We thought it right to determine the hydrolysis constant values and to contribute to the knowledge of hydrolytic species of cupric ion in a slightly acidic or neutral aqueous solution. For this reason we used the statistical analysis of our data. We also determined the enthalpy change by direct calorimetry, referred to the formation of the hydrolytic species of the cupric ion. In the literature we found only a thermochemical work[10] concerning the equilibrium $2Cu^{2+} + 2H_2O = Cu_2(OH)_2^{2+} + 2H^+$ at $I = 3$ M (Na)ClO_4. The enthalpy change value, found by Perrin[7], concerning the same equilibrium was obtained from temperature dependence of potentiometric data at $I = 0$.

EXPERIMENTAL

Reagents and solutions

Cupric perchlorate was obtained from cupric basic carbonate and perchloric acid, and was recrystallized many times before use. The $Cu(ClO_4)_2$ solutions were standardized by EDTA and murexide as indicator[11]. Preparation and standardization of NaOH and $HClO_4$ solutions were previously described[1]; $NaClO_4$ was obtained as reported by Grenthe[12]. The solutions were kept at constant ionic strength $I = 0.1 \pm 0.005$ M by the addition of $NaClO_4$.

Potentiometric measurements

The potentiometric measurements were carried out by an Amel potentiometer Model 332, with an Ingold 201 NS glass and 303 NS calomel electrodes system. The titrations were performed in a 100 ml glass cell, thermostated at 25 ± 0.1 °C by a Colora NB/DS 997 thermostat. The titrant was delivered by a 10 ml motorized burette Amel Model 233. Magnetic stirring was employed, CO_2 was removed by blowing nitrogen, presaturated with a 0.1 M $NaClO_4$ solution. The initial analytical concentrations of the ions in the solutions were:

$$[Cu]_T = 1\text{–}6\ \text{mM}, \qquad [H]_T = 2.5\text{–}5\ \text{mM}.$$

The first part of titration (pH <4) was used both to calculate the $E°$ values of the potentiometric system, and to refine the $[H]_T$ value, because a small systematic error in the $[H]_T$ value strongly affected the hydrolysis constants values. Six independent titrations with 114 points were performed. A pK_W value of 13.72 ± 0.02 was obtained by acid–base titrations.

Calorimetric measurements

The calorimetric measurements were performed at 25 ± 0.001 °C employing an LKB precision calorimeter Model 8700, and a 100-ml LKB titration vessel Model 8726-1, equipped with a 50-Ω standard resistance and a 2000-Ω thermistor incorporated in a d.c. Wheatstone bridge. The out of balance signal amplified by means of a d.c. null voltmeter (Hewlett-Packard, Model 419 A), was fed to a strip chart recorder (Leeds and Northrup, Model Speedomax W). Electrical calibration was made in such a way that the amount of heat used was as nearly identical as possible with that measured in an actual experiment. Several series of electrical calibrations were carried out to test the reproducibility of the calorimetric system; the standard deviation of the ε mean was always better than 0.1%. In order to check the accuracy of the calorimeter, a THAM buffer solution was titrated with HCl standard solution; the found enthalpy change value of 11.33 ± 0.05 kcal mol^{-1}, was in good agreement with the value obtained by Grenthe et al.[13] under the same experimental conditions. The accuracy of the calorimeter was checked also by measuring the neutralization heat between $HClO_4$ and NaOH standard solution at an ionic strength of 0.1 M. The enthalpy change value was -13.47 ± 0.02 kcal mol^{-1} in good agreement with that (−13.49) calculated from −13.34 kcal mol^{-1} at infinite dilution[13–15]. The enthalpies of hydrolysis of Cu^{2+} were obtained from calorimetric titrations of $Cu(ClO_4)_2$ solutions 1–6 mM containing $HClO_4$ 2–4 mM with $NaClO_4$ added to maintain an ionic strength of 0.1 M, and thermostated until stabilization of the calorimetric system. The titrant, NaOH 0.1 M contained in a teflon spiral immersed into the same thermostatic bath (LKB Model 7603 A) as the titration vessel, was delivered from a Radiometer motorized burette Model ABU 12B at 0.25 ml min^{-1}, with a 2.5 μl accuracy. Successive reagent additions and electrical calibrations were continued and the temperature of the contents of the calorimeter were restored to that of the thermostat blowing a stream of cold nitrogen gas through a tube inserted in a glass well contained in the titration vessel. Parallel experiments were made of the heat of mixing of the NaOH solutions with 0.1 M $NaClO_4$ and the corrections were used in the calculations.

Calculations

The hydrolysis constants of cupric ion were calculated by two computer programs, SCOGSB[16,3] and MINIQUAD[17]. Both refine the formation constants by Gauss least squares method, the first by minimizing the error squares sum:

$$U = \sum_i (v_{calc,i} - v_{exp,i})^2$$

where v_i is the titre, the second by minimizing the error squares sum:

$$U = \sum_i (C_{calc,i} - C_{obs,i})^2$$

where C_i are the analytical concentrations of Cu^{2+} and H^+. Simultaneous refinement of the $E°$ value and the analytical concentration of the hydrogen ion were obtained by computer program ACBA[18]. This program allows the refinement, by the Gauss least squares method, of all the parameters of an acid–base titration by minimizing the error squares sum in titre, as in the SCOGSB computer program.

The enthalpy change values were calculated by computer program DOEC[19] that minimizes the error squares sum:

$$U = \sum_i (Q_{corr,calc,i} - Q_{corr,exp,i})^2 .$$

The standard deviations in titre, by the SCOGSB and ACBA programs, were 10^{-2}; the standard deviations in the analytical concentrations, by the MINIQUAD program, were <0.1%. In the refined value of $[H^+]_T$ and $E°$ the standard deviations were about 0.05% and 0.1 mV, respectively; in Q_{corr} values, by DOEC program, they were about 0.01 cal.

The uncertainties in the β and ΔH values were also calculated in terms of standard deviations and are reported in Tables 1–5.

RESULTS AND DISCUSSION

Our investigations were carried out in the range of 1–6 mM cupric ion concentration because this range is frequently used for the determination of thermodynamic parameters in aqueous solution. The ionic strength was maintained at 0.1 M ± 5%. This uncertainty allows a precision of about ±0.002 logarithmic unities in the activity coefficients.

In Table 1 hydrolysis constant values are reported. They were calculated by considering various hypotheses and by two computer programs.

TABLE 1

HYDROLYSIS CONSTANTS OF COPPER(II) OBTAINED USING DIFFERENT HYPOTHESES AND TWO COMPUTER PROGRAMS, AT 25°C AND $I = 0.1$M ($NaClO_4$)

Program	$-\log \beta_{11}$	$-\log \beta_{22}$	$-\log \beta_{34}$	R^a	R_i/R_0
SCOGSB	7.72	10.75	21.38	0.0023	—
	—	10.65	21.59	0.0029	1.26
	—	10.61	—	0.0036	1.57
	8.49	10.62	—	0.0037	1.61
MINIQUAD	7.70	10.75	21.36		

[a] $R = (\Sigma r_i^2 / \Sigma v_i^2)^{1/2}$; $r_i = v_{exp} - v_{calc}$

The hydrolysis constants refer to the reactions

$$pCu^{2+} + qH_2O = Cu_p(OH)_q^{2p-q} + qH^+$$

$$\beta_{pq} = [Cu_p(OH)_q^{2p-q}][H^+]^q/[Cu^{2+}]^p$$

It is well known that only the fit of experimental data is not sufficient to establish the species in the solution as a consequence of hydrolysis of a metal ion. Thus we used Hamilton test[20] as proposed by Vacca et al.[21]. As $\mathfrak{R}_{3,111,0.05} = 1.05 R_i/R_0$ (see Table 1 and ref. 20), we can affirm, at the 5% significance level, that the hydrolytic species are Cu(OH), $Cu_2(OH)_2$ and $Cu_3(OH)_4$. Moreover, the values of the hydrolysis constants, obtained by the two different programs SCOGSB and MINIQUAD, coincide accurately and might indicate the absence of systematic errors which might effect, in a different way, the hydrolysis constants.

In Table 2 the values of our hydrolysis constants together with those taken from the literature are reported. Our values agree with the other ones, considering the

TABLE 2

COMPARISON OF THE HYDROLYSIS CONSTANTS OF COPPER(II) DETERMINED BY DIFFERENT WORKERS

Medium (M)	*Temp.*	$-\log \beta_{11}$	$-\log \beta_{22}$	$-\log \beta_{34}$	*Ref.*
0	20°C	—	10.53	21.17	7
0	T (K)	—	$3833/T - 2.497$	—	7
I	18°C	—	$10.674 \times 1.58\, I^{1/2}$	—	7
0	25°C	7.34	10.57	—	8
0.1 $NaClO_4$	20°C	—	10.78	—	9
3 (Na)ClO_4	25°C	—	10.6	—	6
0.1 ($NaClO_4$)	25°C	7.71±0.05	10.75±0.01	21.37±0.04	this work

different experimental conditions and that in any case the monomeric or trimeric species is not accounted for. It must be noted, particularly, that the monomeric species is negligible only for cupric ion concentrations greater than 6 mM because already at this analytical concentration the percentage of Cu(OH), at pH 6.0, is 1.56 (8% of hydrolysed cupric ion) and becomes, at $[Cu]_T$ 1 mM and pH 6.5, 4.36 (16% of hydrolysed cupric ion). In Table 3 the percentages of formation of the species Cu(OH), $Cu_2(OH)_2$ and $Cu_3(OH)_4$ against the analytical concentration of the cupric ion are reported. This table allows the evaluation of the actual weight of the reported species at pH 6.0 and 6.5. In Fig. 1 the distribution diagram of the hydrolytic species versus pH is reported. It was obtained by the computer program DISDI[22].

TABLE 3

COMPUTED EQUILIBRIUM CONCENTRATIONS FOR COPPER(II)-HYDROXYL SPECIES AT 25°C AND $I = 0.1M$ ($NaClO_4$)

	pH	*10^3 $[Cu]_T$ M*						
		6.00	*4.50*	*3.00*	*1.50*	*1.00*	*0.90*	*0.45*
% Cu as CuOH	6.0	1.56	1.62	1.70	1.78	1.81	1.81	1.84
	6.5					4.36	4.46	4.98
% Cu as $Cu_2(OH)_2$	6.0	14.26	11.62	8.46	4.64	3.20	2.90	1.50
	6.5					18.60	17.50	10.94
% Cu as $Cu_3(OH)_4$	6.0	2.46	1.56	0.78	0.24	0.12	0.09	0.03
	6.5					4.74	4.11	1.44
% Cu hydrolysed	6.0	18.27	14.80	10.95	6.66	5.13	4.80	3.37
	6.5					27.70	26.07	17.36

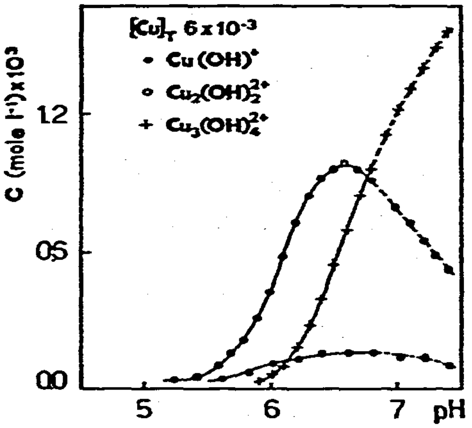

Fig. 1. Distribution diagram for copper (II)-hydroxyl species at 25°C and $I = 0.1M$ $NaClO_4$.

In Table 4 the cupric ion ΔH hydrolysis values together with some data taken from the literature are reported. The agreement of ΔH_{22} values is good, considering the different experimental conditions; ΔH_{11} and ΔH_{34} values were not found in the literature. Hamilton's test on calorimetric data confirmed the hydrolytic species found by potentiometric measurements.

TABLE 4

HEATS OF FORMATION OF COPPER(II) HYDROXOCOMPLEXES

T (°C)	*I* (*M*)	*Method*[a]	ΔH_{11}	ΔH_{22}	ΔH_{34}	*Ref.*
25	3 (Na)ClO_4	cal	(11-12)[b]	15.8	—	10
—	—	td	—	17.5	—	7
25	0.1 ($NaClO_4$)	cal	8.5±0.7	18.4±0.4	26±1	this work

[a] cal = direct calorimetry; td = temperature dependence of potentiometric data. [b] Calculated assuming $\Delta S = 0$.

In Table 5 all the thermodynamic parameters referring to the hydrolysis of the cupric ion and calculated by potentiometric and calorimetric data are reported.

TABLE 5

log EQUILIBRIUM CONSTANT, ΔG, ΔH, AND ΔS VALUES FOR THE HYDROLYSIS OF COPPER(II) AT 25°C AND $I = 0.1$M ($NaClO_4$)

Reaction		*log β*	ΔG	ΔH	ΔS
$Cu^{2+} + H_2O = Cu(OH)^+ + H^+$	(1)	−7.72	10.52	8.5	−7
$2Cu^{2+} + 2H_2O = Cu_2(OH)_2^{2+} + 2H^+$	(2)	−10.75	14.65	18.4	−13
$3Cu^{2+} + 4H_2O = Cu_3(OH)_4^{2+} + 4H^+$	(3)	−21.38	29.14	26	−11
$Cu^{2+} + OH^- = Cu(OH)^+$	(4)	6.00	−8.18	−5.0	11
$2Cu^{2+} + 2OH^- = Cu_2(OH)_2^{2+}$	(5)	16.69	−22.75	−8.5	48
$3Cu^{2+} + 4OH^- = Cu_3(OH)_4^{2+}$	(6)	33.50	−45.66	−28	59
$2Cu(OH)^+ = Cu_2(OH)_2^{2+}$	(7)	4.69	−6.39	1.5	28

Perrin[7] put forward some hypothesis about the structure of the dimeric and trimeric species in agreement with what Martell[23] also proposed for the hydrolytic species of cupric ion complexes.

Such a suggestion can be reconfirmed by the ΔH and ΔS values found by us which are reported here; in particular the high ΔS values referring to the equilibria (refs. 5–7, Table 5) could be explained by the formation of chelate rings.

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