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Potentiometric Studies on the Equilibria of Some Copper(II)-hydroxysalts in Aqueous Salt Solutions, and Involved Complex Formation

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The solubility equilibria of copper(II)-hydroxysalts have recently been dealt with in a series of papers [1] from this laboratory. It has been shown that copper trihydroxysalts are precipitated from copper chloride, nitrate and sulphate solutions. These precipitates have a definite character and the law of mass action may be applied to their equilibria in aqueous solutions. The fact that copper hydroxyperchlorate is much more soluble than the other copper hydroxysalts, makes it possible to investigate the effect of alkali perchlorate on the solubility equilibria of the copper hydroxysalts. These studies have been continued, paying especial attention to complex formation; and in the following, results on copper hydroxybromide and some additional data concerning copper hydroxychloride and sulphate are presented.

EXPERIMENTAL

The chemicals used were of the best qualities obtainable (Kahlbaum for analysis) except the copper bromide and sodium perchlorate, which were recrystallized many times. The experiments were performed at 20° C or 25° C as indicated. For further experimental details the reader is referred to the previous papers [1].

COPPER(II)-TRIHYDROXYBROMIDE

When alkali hydroxide is added to copper bromide solution, trihydroxybromide is precipitated [2]. In Table 1 the results of experiments for the determination of the solubility product in potassium bromide solutions are recorded. The experiments were made in Pyrex flasks into which the copper bromide and potassium bromide as well as the required amount of water and sodium hydroxide solution were measured. After four — nine weeks the pH of the solutions was measured. In the calculations the following equations, derived earlier [1], were used:

$$[\mathrm{Cu}^{++}]\ (\mathrm{OH}^-)^{1.5}\ [\mathrm{Br}^-]^{0.5} = S \qquad (1)$$

$$[\mathrm{Cu}^{++}] = c_{\mathrm{Cu}} - x \qquad (2)$$

$$[\mathrm{Br}^-] = c + 2c_{\mathrm{Cu}} - 0.5x \qquad (3)$$

$$x = 0.667\ (c_{\mathrm{B}} + [\mathrm{H}^+] - [\mathrm{OH}^-]) \qquad (4)$$

Table 1. Solubility product of copper(II)-trihydroxybromide in potassium bromide solutions at 20° C.

$\sqrt{I}$	$c_{\mathrm{Cu}} \cdot 10^2$	$c_{\mathrm{B}} \cdot 10^2$	c_{KBr}	pH	pS
0.086	0.390	0.448	—	5.63	16.96
0.093	0.393	0.335	—	5.44	16.95
0.099	0.396	0.219	—	5.31	16.96
0.130	0.767	0.653	—	5.18	16.91
0.139	0.779	0.431	—	5.08	16.86
0.175	1.31	0.889	—	4.90	16.88
0.248	1.31	0.889	0.0308	4.82	16.80
0.260	1.35	0.446	0.0318	4.71	16.79
0.339	1.27	1.30	0.0896	4.94	16.72
0.350	1.31	0.889	0.0924	4.77	16.71
0.363	1.35	0.446	0.0954	4.67	16.69
0.569	1.27	1.30	0.299	4.87	16.59
0.582	1.31	0.889	0.308	4.72	16.56
0.595	1.35	0.446	0.318	4.59	16.58
0.788	1.27	1.30	0.597	4.84	16.50
0.803	1.31	0.889	0.616	4.67	16.50
0.820	1.35	0.446	0.636	4.55	16.49
0.959	1.27	1.30	0.896	4.79	16.49
0.977	1.31	0.889	0.924	4.60	16.51
0.995	1.35	0.446	0.954	4.49	16.51
1.23	1.27	1.30	1.493	4.72	16.48
1.25	1.31	0.889	1.540	4.52	16.52
1.46	1.40	1.82	2.105	4.85	16.54
1.53	1.53	0.619	2.306	4.29	16.58
1.78	1.46	1.25	3.144	4.36	16.66
1.83	1.53	0.619	3.294	4.17	16.68

where the symbols in brackets denote concentrations, (OH^-) is the activity of hydroxyl ion, c_{Cu} the total copper molarity, c_{B} that of sodium hydroxide and c that of the added alkali bromide. In Table 2 the results of a similar series in sodium perchlorate solutions are recorded. The results in both cases may be represented by the Debye-Hückel equation

$$\mathrm{p}S = \mathrm{p}S_0 - \frac{2.26\sqrt{I}}{1 + a\sqrt{I}} + BI \tag{5}$$

and the following values for the parameters at 20° were obtained:

	KBr	$NaClO_4$
$\mathrm{p}S_0$	17.145	17.145
a	1.939	2.50
B	0.128	0.380

Table 2. Solubility product of copper(II)-trihydroxybromide in sodium perchlorate solutions at 20° C.

$\sqrt{I}$	$c_{Cu} \cdot 10^2$	$c_B \cdot 10^2$	c_{NaClO_4}	pH	pS
0.217	1.40	1.82	0.0227	5.33	16.82
0.236	1.46	1.25	0.0237	4.97	16.79
0.254	1.53	0.619	0.0248	4.80	16.77
0.264	1.40	1.82	0.0453	5.35	16.78
0.282	1.46	1.25	0.0474	4.97	16.79
0.300	1.53	0.619	0.0496	4.80	16.77
0.304	1.40	1.82	0.0680	5.35	16.78
0.321	1.46	1.25	0.0710	4.98	16.78
0.339	1.53	0.619	0.0744	4.81	16.76
0.500	1.40	1.82	0.227	5.39	16.72
0.518	1.46	1.25	0.237	5.02	16.72
0.711	1.46	1.25	0.474	4.99	16.77
0.732	1.53	0.619	0.496	4.80	16.77
0.839	1.40	1.82	0.680	5.32	16.84
0.862	1.46	1.25	0.710	4.94	16.84
0.886	1.53	0.624	0.744	4.76	16.84
0.990	1.46	1.25	0.947	4.90	16.91
1.08	1.40	1.82	1.133	5.26	16.93
1.10	1.46	1.25	1.184	4.86	16.96
1.13	1.53	0.619	1.240	4.68	16.96
1.27	1.40	1.82	1.585	5.18	17.04
1.30	1.46	1.25	1.657	4.79	17.06
1.36	1.40	1.82	1.812	5.08	17.20
1.42	1.53	0.619	1.984	4.51	17.21
1.51	1.40	1.82	2.264	5.02	17.29
1.55	1.46	1.25	2.367	4.60	17.35
1.59	1.53	0.619	2.480	4.37	17.42

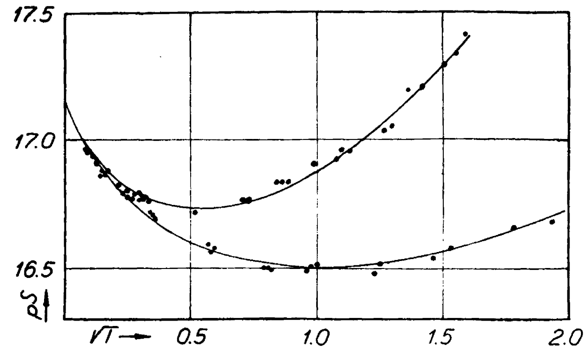

Fig. 1. Solubility product of copper(II)-trihydroxybromide in solutions of potassium bromide (lower curve) and sodium perchlorate (upper curve) at 20° C as a function of ionic strength.

In Fig. 1 the solubility product of copper hydroxybromide is represented as a function of ionic strength. The solubility product is seen to be smaller in sodium perchlorate solutions than in potassium bromide solutions. Such a difference may be interpreted in terms of complex formation between cupric and bromide ions or of the difference of the ion activity coefficients. It is, however, impossible by means of potentiometric measurements to distinguish between these two effects. But since the activity coefficients are, so far as is known, larger in perchlorate solutions than in the solutions of other electrolytes, it is possible to calculate the upper limits for the complexity constants

$$k_\nu = \frac{[\mathrm{CuBr}_\nu^{(\nu-2)-}]}{[\mathrm{Cu}^{++}][\mathrm{Br}^-]^\nu} \qquad (6)$$

For this purpose we have carried out a series of measurements in mixed solutions of sodium perchlorate and bromide at unit ionic strength. The results are presented in Table 3; each pS value is a mean value of three measurements.

Table 3. Solubility product of copper(II)-trihydroxybromide in the mixed solutions of sodium bromide and perchlorate at 25° C. I = 1.

c'_{Br}	pS	c'_{Br}	pS
0.146	16.677	0.510	16.617
0.267	16.646	0.630	16.591
0.389	16.632	0.751	16.557
		0.992	16.501

pS is seen to decrease nearly linearly with bromide concentration. From equation (6) and the stoichiometric equations

$$c'_{\mathrm{Cu}} = [\mathrm{Cu}^{++}] + [\mathrm{CuBr}^{+}] + [\mathrm{CuBr}_2] + \ldots\ldots \tag{7}$$

and

$$c'_{\mathrm{Br}} = [\mathrm{Br}^{-}] + [\mathrm{CuBr}^{+}] + 2[\mathrm{CuBr}_2] + \ldots\ldots \tag{8}$$

where

$$c'_{\mathrm{Cu}} = c_{\mathrm{Cu}} - x \text{ and } c'_{\mathrm{Br}} = c + 2c_{\mathrm{Cu}} - 0.5x$$

we obtain

$$\sum k_{\nu}[\mathrm{Br}^{-}]^{\nu-1} + (1 - S/S')/[\mathrm{Br}^{-}] = 0 \tag{9}$$

and

$$[\mathrm{Br}^{-}] = c'_{\mathrm{Br}} - (c'_{\mathrm{Cu}} \sum \nu k_{\nu}[\mathrm{Br}^{-}]^{\nu})/(1 + \sum k_{\nu}[\mathrm{Br}^{-}]^{\nu}) \tag{10}$$

where S' refers to the solution of sodium perchlorate. The solution of equation (9) by the method of least squares gives in this case

$$k_1 \leqq 0.4,\ k_2 \leqq 0.1 \text{ and } \mathrm{p}S' = 16.703$$

COPPER(II)-TRIHYDROXYCHLORIDE

The solubility product of copper(II)-trihydroxychloride in potassium chloride solutions has been determined by Näsänen and Tamminen[1]. A series of measurements was carried out by the present authors in mixed solutions of sodium perchlorate and chloride at unit ionic strength. The results are recorded in Table 4; each pS value is a mean value of three measurements. By means of equation (9) the following values for the constants were obtained:

$$k_1 \leqq 0.4,\ k_2 \leqq 1.4 \text{ and } \mathrm{p}S' = 17.163$$

Table 4. Solubility product of copper (II)-trihydroxychloride in mixed solutions of sodium chloride and perchlorate at 25° C. I = 1.

c'_{Br}	pS	c'_{Br}	pS
0.154	17.126	0.656	16.883
0.280	17.081	0.782	16.824
0.405	17.023	0.993	16.725
0.531	16.967		

COPPER(II)-TRIHYDROXYSULPHATE

The solubility equilibria of copper(II)-trihydroxysulphate has been investigated by Näsänen and Tamminen[1] in potassium sulphate solutions and by Näsänen[1] in sodium perchlorate solutions. Assuming again that the great difference between the solubility products in these solutions is due entirely to complex formation, one can calculate the upper limits for the complexity constants. In Table 5 a series of measurements in mixed solutions of sodium sulphate and perchlorate at unit ionic strength is recorded. Each value in the table is a mean value of three measurements. Equation (9) may be used in the calculation, however, for this case

$$[Cu^{++}](OH^-)^{1.5}[SO_4^{=}]^{0.25} = S \tag{11}$$

and

$$c'_{SO_4} = c + c_{Cu} - 0.25x \tag{12}$$

Table 5. Solubility product of copper(II)-trihydroxysulphate in mixed solutions of sodium sulphate and perchlorate at 20° C. I = 1-

c'_{SO_4}	pS	c'_{SO_4}	pS
0.0365	16.716	0.1982	16.207
0.0684	16.600	0.3270	15.854
0.1336	16.416		

The following values were obtained:

$$k_1 \leqq 11,\ (k_2 \sim 3),\ k_3 \leqq 150 \text{ and } pS' = 16.863$$

FORMATION OF COPPER(II)-TETRAHYDROXYSALTS

According to Weiser, Milligan and Cook[3] tetrahydroxysulphate is precipitated, in addition to the hydroxide or trihydroxysalt, when the ratio of the equivalents of copper sulphate and sodium hydroxide in a mixture is between 1 and 1.33. In corresponding conditions tetrahydroxychloride and bromide should exist according to Tobler[4]. We have investigated the precipitation curve of copper hydroxychloride and bromide and have found that, when sodium hydroxide solution is added to copper salt solution in such an amount that the ratio of moles of sodium hydroxide to copper salt exceeds 1.5, the formation of copper oxide does not begin until this ratio is about 1.6. The hydroxychloride corresponding to the value 1.6 gave, however, the same X-ray diffraction pattern as was obtained by Feitknecht[5] for trihydroxychloride

(II γ modification). The precipitate investigated was equilibriated for about one year. It is therefore obvious that trihydroxychloride and very probably also the trihydroxybromide is metastable between the values 1.5 and 1.6. Trihydroxysulphate has not been studied in this respect. This does not imply, however, that tetrahydroxychloride or bromide could not be formed in some other ways, for instance by digesting copper oxide in dilute copper chloride or bromide solutions.

DISCUSSION

The accuracy obtainable in the determination of the solubility products of hydroxysalts is not very high. On the other hand when chloride concentration is sufficiently small hydroxyperchlorate is precipitated and therefore the measurements in such conditions are impossible. As a result, the values obtained above for the complexity constants cannot be very accurate. Nevertheless the k_1 values are in satisfactory agreement with the spectrophotometric results of Näsänen[6].

For the complexity constant of the copper(II)-monochlorocomplex McConnell and Davidson[7] have recently found spectrophotometrically the value $k_1 = 1.30$. This value must, however, be considered as an upper limit, as will be shown below. The authors have measured the extinction of a solution with a small chloride concentration and much larger copper ion concentration and have used the equation

$$f(c_{\mathrm{Cu}}) = c_{\mathrm{Cu}} c_{\mathrm{HCl}}/e = c_{\mathrm{Cu}}/\varepsilon_1 + 1/\varepsilon_1 k_1 \tag{13}$$

where c_{Cu} denotes the total copper concentration, c_{HCl} that of hydrochloric acid, and e is the extinction of a 1 cm layer of the solution investigated compared to a similar solution without hydrochloric acid. The ionic strength has been kept constant by addition of perchloric acid. The authors conclude from the linear character of the curve, $f(c_{\mathrm{Cu}})$ versus c_{Cu}, that k_1 is constant in mixed solutions of copper perchlorate and perchloric acid at unit ionic strength. This is not, however, necessarily true. The linear character implies only that $1/k_1$ (or log k_1, which within the limits of the experimental error means the same in the narrow concentration range investigated), is a linear function of c_{Cu}. If we write

$$1/k_1 = 1/k_1' + b c_{\mathrm{Cu}} \tag{14}$$

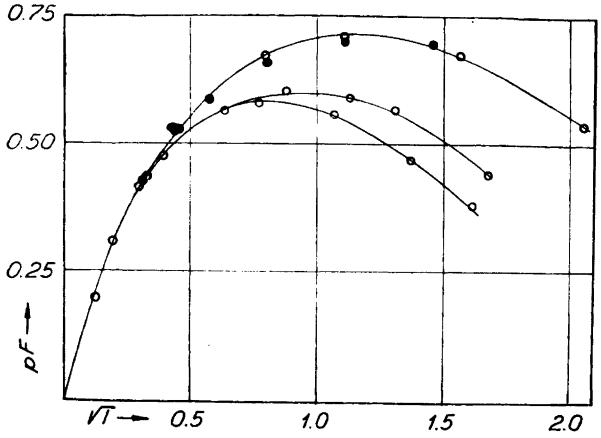

Fig. 2. Activity coefficient of the copper(II)-monochlorocomplex in perchloric acid (lower curve), sodium (middle curve), barium and calcium (upper curve) perchlorate solutions at 25° C. ●, barium perchlorate.

where k_1' is the value of k_1 in perchloric acid solution and b a parameter, we obtain from equation (13)

$$f(c_{Cu}) = c_{Cu}/\varepsilon_1 + (1/k_1' + bc_{Cu})/\varepsilon_1 \tag{15}$$

When $c_{Cu} = 0$, $f(0) = 1/\varepsilon_1 k_1'$, and the first derivative in regard to c_{Cu} is

$$f'(c_{Cu}) = (1 + b)/\varepsilon_1$$

Thus

$$k_1' = \frac{f'\ (c_{Cu})}{f(0)\ (1 + b)} \tag{16}$$

According to McConnell and Davidson

$$f'(c_{Cu})/f(0) = 1.30$$

which would be the value of k_1 if $b = 0$. When b is positive, which means that k_1 is smaller in copper perchlorate solution than in perchloric acid solution, k_1' is smaller than 1.30. Because it seems likely that k_1 is in fact smaller in copper perchlorate than in perchloric acid solution, this value must be considered as an upper limit for k_1. In fact the activity coefficient is generally different in solutions of different electrolytes. This is seen from Fig. 2, in which the activity coefficient of the copper(II)-monochlorocomplex is represented as a function of ionic strength in perchloric acid, sodium, barium and calcium perchlorate solutions. The activity coefficient

$$F = f_{Cu^{++}} f_{Cl^-} / f_{CuCl^+} \tag{17}$$

was determined by the spectrophotometric method of Näsänen[6], using the equation

$$\log \frac{e}{[Cu^{++}][Cl^-]} = \log \frac{1}{\varepsilon_1 k_{1,0}} - pF \tag{18}$$

where $k_{1,0}$ is the thermodynamic constant. For $[Cu^{++}]$ and $[Cl^-]$ the values of c_{Cu} and c_{Cl} may be used. The differences in pF at unit ionic strength are as follows:

	$HClO_4$	$NaClO_4$	$Ba(ClO_4)_2$ and $Ca(ClO_4)_2$
ΔpF	0.00	0.03	0.13

Thus the complexity constant can vary considerably with the composition of the solution. We have calculated some values for the constant k_1 in perchloric acid and copper perchlorate solution at unit ionic strength from McConnell and Davidson's data using equations (14) and (16) and adopting arbitrary values for b. We obtained

	b	k_1	ΔpF	b	k_1	ΔpF	b	k_1	ΔpF
$Cu(ClO_4)_2$		0.534			0.336			0.245	
	1		0.089	2		0.110	3		0.123
$HClO_4$		0.650			0.433			0.325	

These values, as compared to the above data obtained spectrophotometrically for ΔpF, seem to explain the discrepancy between McConnell and Davidson's results and ours. Further if barium or calcium perchlorate is used instead of perchloric acid in such experiments as those carried out by McConnell and Davidson, a value of nearly the same magnitude as our value will obviously be obtained for k_1 by means of their method of calculation.

In the copper sulphate system Fronaeus[8], by two potentiometric methods, has obtained the values:

$$k_1 = 11,\ k_2 = 10\text{—}17,\ k_3 = 200$$

and

$$k_1 = 9,\ (k_2 \sim 0),\qquad k_3 = 80$$

Our values are seen to be in satisfactory agreement with these values. On the other hand the spectrophotometric method gives lower values. Fronaeus[8] has obtained at unit ionic strength $k_1 = 5$ and Näsänen[9] $k_1 = 4$. Probably in this case also, the potentiometric values must be considered as upper limits of the constants.

SUMMARY

The solubility equilibria of copper(II)-trihydroxy chloride, bromide and sulphate have been investigated. The solubility products of these compounds were determined in solutions of some alkali chlorides, bromides, sulphates and perchlorates. The complex formation of copper(II)-ion with chloride, bromide and sulphate ions has been studied potentiometrically and upper limits for the complexity constants have been calculated. The discrepancies in the values obtained by different methods are discussed in terms of activity coefficients. The activity coefficient of the copper(II)-monochloro complex has been determined spectrophotometrically in perchloric acid, sodium, barium and calcium perchlorate solutions as a function of ionic strength.

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