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Studies on Copper(II) Periodates

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The first and second ionization constants of periodic acid in aqueous solutions at 25° C were determined. By mixing copper perchlorate, sodium periodate and sodium hydroxide solutions the compounds Cu_2HIO_6, $Cu_5(IO_6)_2$ and Cu_2NaIO_6 were precipitated as indicated by the results of chemical analysis and the form of the potentiometric precipitation curve. The solubility products and the limits of existence of these compounds were determined. The hydrates of these compounds were preliminarily investigated and the existence of the mono-, di-, and trihydrates of Cu_2HIO_6 and the pentahydrate of $Cu_5(IO_6)_2$ was confirmed. Dehydrated Cu_2NaIO_6 was also obtained.

The aim of the present investigation was to check the compositions of the copper periodates reported in the literature [1] and particularly to determine the limits of existence for these compounds. With this purpose in view varying amounts of sodium periodate, copper perchlorate and sodium hydroxide solutions were mixed and after equilibrium was reached the precipitates formed and the solutions were analyzed and their pH's determined.

EXPERIMENTAL

The stock solution of sodium periodate was prepared from commercial $NaIO_4$ and that of copper perchlorate from copper oxide and perchloric acid. The sodium hydroxide, carbonate free, was prepared and stored in the usual way. All chemicals were of analytical grade (Merck, Darmstadt).

The pH was measured with a glass electrode using a Radiometer PHM 3 pH meter.

For determination of copper the precipitates were treated with hydrochloric acid and thereafter the copper of the copper chloride so formed was titrated iodometrically. The sum of the copper and periodate was determined iodometrically.

Copper sodium periodate was converted to chlorides by means of hydrochloric acid and then analyzed iodometrically (copper) and using Dowex 2 ion exchanger (sodium) [2].

RESULTS

For the quantitative treatment of the equilibrium the ionization constants of periodic acid were necessary. The first ionization

$$H_5IO_6 + H_2O = H_3O^+ + H_4IO_6^- \qquad (1)$$

has been many times investigated [3]. Our results for the constant

$$\frac{(H^+)[H_4IO_6^-]}{[H_5IO_6]} = K_1' \tag{2}$$

are presented in Table 1. In equation (2) the denotation $[H_4IO_6^-]$ and $[H_5IO_6]$ may be considered as total concentrations of the negatively univalent ions and the neutral constituents respectively. Besides the ion $H_4IO_6^-$, at least IO_4^- should exist corresponding to the equilibrium[3]

$$H_4IO_6^- = IO_4^- + 2\ H_2O \tag{3}$$

For our purposes the single hydration can be neglected. In Table 1, c_{IO_4} denotes

Table 1. Determination of the first ionization constant of periodic acid at 25° C.

$\sqrt{I}$	$c_{IO_4} \cdot 10^3$	$c_A \cdot 10^3$	pH	pK_1'
0.080	4.72	1.895	2.821	1.58
0.082	4.70	2.36	2.719	1.54
0.085	4.69	2.82	2.635	1.47
0.087	4.68	3.28	2.567	1.46

Mean $pK_1' = 1.51 \pm 0.03$, $\sqrt{I} = 0.084$
Thermod. constant $pK_{1,0} = 1.55 \pm 0.03$

the total concentration of $NaIO_4$ and c_A that of the perchloric acid added. The equation

$$pK_1' = pH + \log\{(c_A - [H^+])/(c_{IO_4} - c_A + [H^+])\} \tag{4}$$

was used in the calculation. The hydrogen ion concentration was obtained from the pH values using the activity coefficient values of Näsänen, Lumme and Mukula [4]. The thermodynamic constant was calculated in the usual way using the Debye-Hückel equation.

The second ionization

$$H_4IO_6^- + H_2O = H_3IO_6^{=} + H_3O^+ \tag{5}$$

has been studied recently by Crouthamel *et al.*[3] They seem to be the only ones who have determined the second ionization constant

$$\frac{(H^+)[H_3IO_6^{=}]}{[H_4IO_6^-]} = K_2' \tag{6}$$

The possible single hydration is neglected in this case also. The spectrophotometric investigation of Crouthamel *et al.*[3] seems to show the absence of polyacids such as $H_4I_2O_9$ at least in dilute solutions. Our results are presented

Table 2. Determination of the second ionization constant of periodic acid at 25° C.

$\sqrt{I}$	$c_{IO_4} \cdot 10^3$	$c_B \cdot 10^3$	pH	pK_2'
0.078	4.74	0.679	7.376	8.153
0.086	4.71	1.344	7.760	8.160
0.093	4.69	2.007	8.017	8.144
0.100	4.67	2.666	8.264	8.139

Mean $pK_2' = 8.149 \pm 0.005$; $\sqrt{I} = 0.089$
$pK_{2,0} = 8.269$

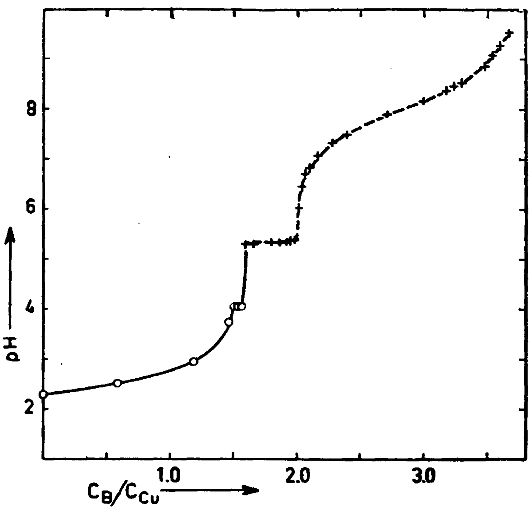

Fig. 1. Titration of a mixed solution of sodium metaperiodate and copper perchlorate with sodium hydroxide. ○ *5 ml 0.1* M *$NaIO_4$, 10 ml 0.0475* M *$Cu(ClO_4)_2$, 50 ml H_2O.* + *10 ml 0.1* M *$NaIO_4$, 10 ml 0.0475* M *$Cu(ClO_4)_2$, 50 ml H_2O.*

in Table 2. In the calculation the equation

$$pK_2' = pH + \log\{(c_{IO_4}—c_B)/c_B\}$$

was used. Here c_B is the stoichiometric concentration of sodium hydroxide in solution.

The results on copper periodate are presented in Fig. 1 and in Tables 3, 4 and 5. In Fig. 1 the pH of the equilibrium solutions as a function of c_B/c_{Cu} is presented. Here c_{Cu} is the stoichiometric concentration of the copper perchlorate added. Between 0 and 1.5 for c_B/c_{Cu} the composition of the precipitate corresponds to the formula $Cu_2HIO_6 \cdot x\ H_2O$. This was confirmed by analysis of the copper and the sum of the copper and periodate in the precipitate. Also the jump near $c_B/c_{Cu} = 1.5$ is in agreement with the reaction

$$2\ Cu^{++} + H_4IO_6^- = Cu_2HIO_6\ (s) + 3\ H^+ \quad (7)$$

From 1.5 to 1.6 $Cu_5(IO_6)_2 \cdot x\ H_2O$ exist simultaneously with $Cu_2HIO_6 \cdot x\ H_2O$. When $c_B/c_{Cu} = 1.6$ the analysis showed that only $Cu_5(IO_6)_2 \cdot x\ H_2O$ exists. The sudden increase of pH at $c_B/c_{Cu} = 1.6$ is in agreement with the reaction

$$5\ Cu^{++} + 2\ H_4IO_6^- = Cu_5(IO_6)_2(s) + 8\ H^+ \quad (8)$$

Between 1.6 and 2 a mixture of $Cu_5(IO_6)_2 \cdot x\ H_2O$ and $Cu_2NaIO_6 \cdot x\ H_2O$ exists. The jump of pH at $c_B/c_{Cu} = 2$ is in agreement with the reaction

$$2\ Cu^{++} + H_4IO_6^- + Na^+ = Cu_2NaIO_6(s) + 4\ H^+ \quad (9)$$

When $c_B/c_{Cu} > 2$ only Cu_2NaIO_6 exists, as was confirmed by analysis of the precipitate and by powder diagrams. That between 1.5 and 1.6 a mixture of

Cu_2HIO_6 and $Cu_5(IO_6)_2$ exists and between 1.6 and 2 a mixture of $Cu_5(IO_6)_2$ and Cu_2NaIO_6, seems to be confirmed by the powder diagrams.

Some preliminary determinations of water of crystallization were also made. After drying in a desiccator for one night $Cu_2HIO_6 \cdot 2\ H_2O$ was obtained. This seems to absorb water at high vapor pressures so that $Cu_2HIO_6 \cdot 3\ H_2O$ is formed. When heated at 150° C in air $Cu_2HIO_6 \cdot H_2O$ was obtained. When heated at 100° C in vacuum $Cu_5(IO_6)_2 \cdot x\ H_2O$ gave $Cu_5(IO_6)_2 \cdot 5\ H_2O$. At higher temperatures in vacuum it began to decompose. Possibly higher hydrates exist in this case too. When heated at 150° C in air dehydrated Cu_2NaIO_6 was obtained.

The quantitative treatment of this equilibrium may be based on the reactions (3), (5), (7), (8) and (9). The case is, however, formally analogous with the equilibrium of metal hydroxy salts[5]. Therefore instead of reactions (7), (8) and (9) the following reactions may be used:

$$Cu^{++} + 1.5\ OH^- + 0.5\ H_4IO_6^- = Cu(OH)_{1.5}(H_4IO_6)_{0.5}(s) \tag{10}$$

$$Cu^{++} + 1.6\ OH^- + 0.4\ H_4IO_6^- = Cu(OH)_{1.6}(H_4IO_6)_{0.4}(s) \tag{11}$$

$$Cu^{++} + 2\ OH^- + 0.5\ Na^+ + 0.5\ H_4IO_6^- = CuNa_{0.5}(OH)_2(H_4IO_6)_{0.5}(s) \tag{12}$$

We obtain therefore

$$[Cu^{++}](OH^-)^{1.5}[H_4IO_6^-]^{0.5} = S_{1.5} \tag{13}$$

$$[Cu^{++}](OH^-)^{1.6}[H_4IO_6^-]^{0.4} = S_{1.6} \tag{14}$$

$$[Cu^{++}][Na^+]^{0.5}(OH^-)^2[H_4IO_6^-]^{0.5} = S_2 \tag{15}$$

where bracketed symbols designate respective concentrations and (OH^-) hydroxyl ion activity. When $c_B/c_{Cu} < 1.5$ we have in addition to equation (13)

$$[H_4IO_6^-] = \frac{c_{IO_4} - 0.333\ (c_B + [H^+])}{1 + 1.333(H^+)/K_1'} \tag{16}$$

where c_{IO_4} is the stoichiometric concentration of sodium periodate. Further

$$[Cu^{++}] = c_{Cu} - 2\ c_{IO_4} + 2[H_4IO_6^-]\{1 + (H^+)/K_1'\} \tag{17}$$

With the aid of (16) and (17) the solubility product S_1 may be calculated using the pH values measured, the stoichiometric concentrations and the value of K_1' known. These results are presented in Table 3.

Table 3. Determination of the solubility product of Cu_2HIO_6 $(Cu(OH)_{1.5}(H_4IO_6)_{0.5})$ *at 25° C.*

pH	$c_{IO_4} \cdot 10^3$	$c_B \cdot 10^3$	$c_{Cu} \cdot 10^3$	$[Cu^{++}] \cdot 10^3$	$[H_4IO_6^-] \cdot 10^3$	$pS_{1.5}$	$\sqrt{I}$
2.314	8.33	0.00	8.03	3.81	5.41	21.07	0.146
2.536	8.07	4.60	7.77	2.23	4.86	21.00	0.144
2.939	7.81	8.89	7.52	0.64	4.22	20.97	0.137
					mean value	21.02	0.142

When c_B/c_{Cu} is between 1.5 and 1.6, reactions (13) and (14) are simultaneously valid. Consequently

$$pS_{1.6} = pS_{1.5} + 0.1\ pOH - 0.1\ pH_4IO_6 \tag{18}$$

From electroneutrality we obtain

$$[H_4IO_6^-] = c_B + c_{IO_4} - 2\ c_{Cu} + [H^+] + 2\ S_{1.5}/(OH^-)^{1.5}[H_4IO_6^-]^{0.5} \quad (19)$$

with sufficient accuracy. In equation (19) the two last terms may generally be neglected. By means of (18) and (19) it is thus possible to calculate the solubility product $S_{1.6}$. These results are summarised in Table 4.

Table 4. Determination of the solubility product of $Cu_5(IO_6)_2$ $(Cu(OH)_{1.6}(H_4IO_6)_{0.4})$ *at 25° C.*

pH	$c_B \cdot 10^3$	$c_{IO_4} \cdot 10^3$	$c_{Cu} \cdot 10^3$	$\sqrt{I}$	$pS_{1.5}$	$pS_{1.6}$
4.072	11.17	7.69	7.39	0.184	20.95	21.71
4.139	11.17	7.69	7.39	0.184	20.95	21.71
4.173	11.37	7.67	7.38	0.184	20.95	21.71
4.224	11.37	7.67	7.38	0.184	20.95	21.70
4.207	11.57	7.66	7.37	0.184	20.95	21.70
4.325	11.57	7.66	7.37	0.184	20.95	21.69
4.241	10.03	13.33	6.33	0.189	20.96	21.74

When c_B/c_{Cu} is between 1.6 and 2.0 equations (14) and (15) are simultaneously valid and we obtain

$$pS_2 = pS_{1.6} + 0.4\ pOH + 0.5\ pNa + 0.1\ pHI_4O_6 \quad (20)$$

From the electroneutrality and stoichiometric relations we further obtain

$$[Na^+] = c_{IO_4} + 2\ c_{Cu} - 0.25\ c_B - 2\ S_{1.6}/(OH^-)^{1.6}[H_4IO_6^-]^{0.4} \quad (21)$$

and

$$[H_4IO_6^-] = c_{IO_4} - 0.25\ c_B \quad (22)$$

Here only the constituent $H_4IO_6^-$ has been taken into consideration, the other terms being negligible. With the aid of equations (20), (21) and (22) we obtain the solubility products S_2. These results are summarized in Table 5.

Table 5. Determination of the solubility product of Cu_2NaIO_6 $(CuNa_{0.5}(OH)_2(H_4IO_6)_{0.5})$ *at 25° C.*

pH	$c_B \cdot 10^3$	$c_{IO_4} \cdot 10^3$	$c_{Cu} \cdot 10^3$	$\sqrt{I}$	$pS_{1.6}$	pS_2
5.289	10.04	13.28	6.31	0.153	21.77	26.27
5.289	10.39	13.24	6.29	0.152	21.77	26.27
5.356	11.26	13.17	6.25	0.151	21.77	26.25
5.322	11.60	13.12	6.23	0.151	21.77	26.26
5.339	11.95	13.08	6.22	0.150	21.77	26.26
5.356	12.12	13.07	6.21	0.150	21.77	26.25
5.356	12.28	13.06	6.20	0.150	21.77	26.25
				0.151	mean value	26.26

From the values obtained for the solubility product the thermodynamic values were estimated by means of the Debye-Hückel equation

$$p(S/S^\circ) = \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (23)$$

where A has the values 2.29 ($S_{1.5}$), 2.24 ($S_{1.6}$) and 2.54 (S_2). Hence we obtain for the thermodynamic constants:

$$pS^{\circ}_{1.5} = 21.29, \; pS^{\circ}_{1.6} = 22.02, \text{ and } pS^{\circ}_2 = 26.57. \quad (25^{\circ}\text{ C})$$

Besides the measurements reported in Tables 3, 4 and 5 some additional measurements were performed under other conditions. Their results were generally in good agreement with the above results. However for S_2 a series with a considerably smaller value for c_{IO_4} did not give very good results and the values for pS_2 were somewhat smaller than the values reported above. A series with a high sodium perchlorate concentration gave reasonable results and the pH between 1.6 and 2 (*cf.* Fig. 1) was lower to the extent expected.

DISCUSSION

The value obtained here for the first ionization constant ($pK_{1,0} = 1.55$) is in relatively good agreement with the value of Crouthamel *et al.*[3] ($pK_{1,0} = 1.6$). The agreement between the values for the second constant is still better. Here $pK_{2,0} = 8.27$, Crouthamel *et al.*[3] have obtained potentiometrically $pK_{2,0} = 8.25$.

The existence of Cu_2HIO_6 and $Cu_5(IO_6)_2$ was reported long ago[1], but Cu_2NaIO_6 seems not have been reported before. The limits of existence and the solubility products of these compounds seem not have been determined before. The hydrates found in the present investigation $Cu_2HIO_6 \cdot 3\ H_2O$ and $Cu_5(IO_6)_2 \cdot 5\ H_2O$ have been reported long ago by Rammelsberg[1] but $Cu_2HIO_6 \cdot 2\ H_2O$ and $Cu_2HIO_6 \cdot H_2O$ seem not to have been reported before. Further removal of water from $Cu_2HIO_6 \cdot H_2O$ and $Cu_5(IO_6)_2 \cdot 5\ H_2O$ seems not to be possible by heating in air or vacuum because of the decomposition.

REFERENCES

1. Langlois, *Ann. chim. et phys.* [3] **34** (1852) 273; Rammelsberg, C. *Pogg. Ann. Physik* **210** (1868) 519; Kimmins, C. W. *J. Chem. Soc.* **55** (1889) 150.
2. Samuelson, O. *Ion exchangers in analytical chemistry*, Stockholm 1952, p. 156.
3. *Cf.* Crouthamel, C. E., Meek, H. V., Martin, P. S. and Banks, C. V. *J. Am. Chem. Soc.* **71** (1949) 3031; Crouthamel, C. E., Hayes, A. M. and Martin, D. S. *Ibid.* **73** (1951) 82; Hessaby, A. and Souchay, P. *Bull. soc. chim. France* **1953** (606).
4. Näsänen, R., Lumme, P. and Mukula, A-L. *Acta Chem. Scand.* **5** (1951) 1199.
5. *Cf.* Näsänen, R. *Ann. Acad. Sci. Fennicae* **A 59** (1942) 7; Näsänen, R. and Tamminen, V. *J. Am. Chem. Soc.* **71** (1949) 1994; Feitknecht, W. *Helv. Chim. Acta* **16** (1933) 1302; Geloso, M. and Deschamps, P. *Anal. Chim. Acta* **7** (1952) 127; Faucherre, J. *Bull. soc. chim. France* **1954** 128.

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