ACTA CHEMICA SCANDINAVICA 16 (1962) 2384–2388

Stability of the Mixed Copper Complex of 1,2-Diaminopropane and 5-Sulphosalicylic Acid in Aqueous Sodium Perchlorate Solutions

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The stability constant of the mixed copper complex ($CuXY^-$) of 1,2-diaminopropane (Y) and 5-sulphosalicylic acid (H_3X) was determined by the potentiometric pH method. The measurements were carried out at seven different ionic strengths adjusted with sodium perchlorate. As expected, the stability of the mixed complex was highly dependent on ionic strength. The gross stability constant of the mixed complex at 25°C is $10^{20.39}$, $10^{19.09}$, $10^{18.49}$ and $10^{18.74}$ at ionic strengths 0, 0.1, 1, and 2, respectively. At the same ionic strengths and temperature the equilibrium constant of the disproportionation $2\,MXY^- \rightleftharpoons MX_2^{4-} + MY_2^{2+}$ was found to be $10^{-3.94}$, $10^{-1.83}$, $10^{-0.09}$ and $10^{+0.25}$, respectively.

In a recent study [1] the formation of mixed copper complexes of 1,2-diaminopropane and 5-sulphosalicylic acid was dealt with. It was shown that one mixed complex was formed. These measurements were made without any additional neutral salt present. This investigation has since been continued by paying attention especially to the effect of sodium perchlorate.

The method used consisted of a potentiometric pH titration of a mixed solution of copper perchlorate, sulphosalicylic acid (H_3X) and diprotonated 1,2-diaminopropane added as its perchlorate ($H_2Y(ClO_4)_2$) with sodium hydroxide solution. The experimental details have been described recently [1,2].

It is possible to calculate the concentration of the mixed complex MXY^- at each point of the titration curve since the stability constants of all the other complexes are known [2]. The following equations can be written:

$$c_x = [H_2X] + [HX] + [MX] + 2\,[MX_2] + [MXY] \qquad (1)$$

$$c_y = [H_2Y] + [HY] + [MY] + 2\,[MY_2] + [MXY] \qquad (2)$$

$$c_M = [M] + [MX] + [MX_2] + [MY] + [MY_2] + [MXY] \qquad (3)$$

$$3c_x + 2c_y + c_A - c_B = [H] + [HX] + 2\,[H_2X] + [HY] + 2\,[H_2Y] \qquad (4)$$

where c_x, c_y, c_A, c_M, and c_B are the respective total concentrations of H_3X, $H_2Y(ClO_4)_2$, free perchloric acid, copper ion, and sodium hydroxide. In addition, the following equilibrium constants are known:

$$[H]\,[HX]/[H_2X] = K_2^{(x)};\ [H]\,[HY]/[H_2Y] = K_1^{(y)} \tag{5}$$

$$[MX]\,[H]/[M]\,[HX] = K_I^{(x)};\ [MX_2]\,[H]/[MX]\,[HX] = K_{II}^{(x)} \tag{6}$$

$$[MY]\,[H]^2/[M]\,[H_2Y] = K_I^{(y)};\ [MY_2]\,[H]^2/[MY]\,[H_2Y] = K_{II}^{(y)} \tag{7}$$

Combination of eqns. (4) and (5) gives

$$[HX] = a-b\,[H_2Y] \tag{8}$$

where

$$a = \frac{3c_x+2c_y+c_A-c_B-[H]}{1+2[H]/K_2^{(x)}}\ ;\ b = \frac{2+K_1^{(y)}/[H]}{1+2[H]/K_2^{(x)}} \tag{9}$$

All measurements were made with $c_M = c_y$. On this condition eqns. (1)—(8) give

$$A_1[H_2Y]^3 + A_2[H_2Y]^2 + A_3[H_2Y] + A_4 = 0 \tag{10}$$

The coefficients A_1, A_2, A_3, and A_4 can be calculated from

$$A_1 = b^2hm-hk + bdk-b^3dm \tag{11}$$

$$A_2 = -2\,abhm + b^2cm + b^2dl + 3\,ab^2dm-hn-ck-adk \tag{12}$$

$$A_3 = a^2hm-bcl-2\,abcm-bd-2\,abdl-3\,a^2bdm-h \tag{13}$$

$$A_4 = c + acl + acm + ad + a^2dl + a^3dm \tag{14}$$

where

$$\begin{array}{llll} c & = c_y-c_x; & d & = 1 + [H]/K_2^{(x)} \\ h & = 1 + K_1^{(y)}[H]; & k & = K_I^{(y)}\,K_{II}^{(y)}[H]^4 \\ l & = K_I^{(x)}/[H]; & m & = K_I^{(x)}\,K_{II}^{(x)}/[H]^2 \\ n & = K_I^{(y)}/[H]^2 & & \end{array} \tag{15}$$

The calculation of $[H_2Y]$ was carried out with an IBM 1620 computer by Dr. Heikki Varho in the Computing Centre of the University of Helsinki.

After $[H_2Y]$ had been obtained, $[HX]$ was calculated from eqn. (8) and the concentration of copper ion from

$$[M] = (c + d[HX])/(1-m[HX]^2 + n[H_2Y] + k[H_2Y]^2) \tag{16}$$

The concentrations of all the other species except the mixed complex could then be calculated from eqns. (6) and (7) and the concentration of the mixed complex from one of eqns. (1)—(3).

The equilibrium constants defined by eqns. (5), (6) and (7) have been determined earlier in our laboratory [2]. The results for sodium perchlorate solutions are

$$pK_2^{(x)} = 2.84-\frac{2.04\,\sqrt{I}}{1+2.1\,\sqrt{I}}+0.17\,I \tag{17}$$

$$\mathrm{p}K_{\mathrm{I}}^{(\mathrm{x})} = 1.77 + \frac{3.054\sqrt{I}}{1+3.3\sqrt{I}} + 0.013\,I \tag{18}$$

$$\mathrm{p}K_{\mathrm{II}}^{(\mathrm{x})} = 6.09 - \frac{6.11\sqrt{I}}{1+2.4\sqrt{I}} + 0.064\,I \tag{19}$$

$$\mathrm{p}K_{1}^{(\mathrm{y})} = 6.607 + \frac{1.018\sqrt{I}}{1+1.42\sqrt{I}} + 0.180\,I \tag{20}$$

$$\mathrm{p}K_{2}^{(\mathrm{y})} = 9.817 - \frac{0.509\sqrt{I}}{1+2.2\sqrt{I}} + \frac{0.509\sqrt{I}}{1+\sqrt{I}} + 0.214\,I \tag{21}$$

$$\log\beta_1^{(\mathrm{y})} = 10.56 + 0.89\,I - 0.52\,I^{3/2} + 0.13\,I^2 \tag{22}$$

$$\log\beta_2^{(\mathrm{y})} = 19.64 + 2.11\,I - 1.24\,I^{3/2} + 0.28\,I^2 \tag{23}$$

$$\mathrm{p}K_{\mathrm{I}}^{(\mathrm{y})} = \mathrm{p}K_1^{(\mathrm{y})} + \mathrm{p}K_2^{(\mathrm{y})} - \log\beta_1^{(\mathrm{y})} \tag{24}$$

$$\mathrm{p}K_{\mathrm{II}}^{(\mathrm{y})} = \mathrm{p}K_{\mathrm{I}}^{(\mathrm{y})} + 2\log\beta_1^{(\mathrm{y})} - \log\beta_2^{(\mathrm{y})} \tag{25}$$

Table 1. The calculation of the concentration of the mixed complex from the data of a titration of an aqueous solution of copper ion, 5-sulphosalicylic acid and diprotonated 1,2-diaminopropane with sodium hydroxide. Ionic strength adjusted by addition of sodium perchlorate to the value one. $c_M = c_y$. 25°C.

$c_x \times 10^3$	$c_y \times 10^3$	$c_A \times 10^3$	$c_B \times 10^3$	$[H] \times 10^6$	$[H_2Y] \times 10^3$	$[HX] \times 10^3$	$[MXY] \times 10^3$	$K_A \times 10^3$
23.619	5.905	0.655	61.106	5.00	0.722	20.712	0.612	0.080
23.529	5.882	0.652	61.254	4.25	0.590	20.518	0.728	0.088
23.440	5.860	0.650	61.401	3.52	0.466	20.313	0.836	0.093
23.351	5.838	0.647	61.547	2.87	0.358	20.077	0.963	0.098
23.264	5.816	0.645	61.692	2.30	0.268	19.812	1.110	0.104
23.176	5.794	0.642	61.836	1.75	0.187	19.523	1.222	0.103
23.090	5.772	0.640	61.978	1.31	0.1286	19.200	1.205	0.087
23.004	5.751	0.638	62.120	0.921	0.0816	18.855	1.457	0.100
22.918	5.730	0.635	62.261	0.596	0.0473	18.483	1.453	0.086
							Mean	0.093

Titrations were carried out at seven different ionic strengths. The ionic strengths were calculated from $I = \frac{1}{2}\,\Sigma\, c_i z_i^2$. Data from a typical titration are recorded in Table 1. In this table the values of the equilibrium constant K_A of the reaction

$$\mathrm{MY}^{2+} + \mathrm{HX}^{2-} \rightleftharpoons \mathrm{MXY}^{-} + \mathrm{H}^{+} \tag{26}$$

are given as calculated from different points on the titration curve. This reaction was chosen for scrutiny since the species MY^{2+}, HX^{2-}, and MXY^- predominate in the experimental conditions in question and the hydrogen ion concentration could be directly determined. The results are summarised in Table 2. The respective values of the equilibrium constant K_B of the reaction

$$\mathrm{MX}^{-} + \mathrm{Y} \rightleftharpoons \mathrm{MXY}^{-} \tag{27}$$

Table 2. Effect of ionic strength on the stability of the mixed copper complex of 1,2-diaminopropane and 5-sulphosalicylic acid at 25°C. No sodium perchlorate was added in the three first experiments.

I	pK_A	log K_B	pK_D
0	2.70	—	3.94
0.017	3.07	9.55	2.87
0.045	3.20	9.54	2.44
0.100	3.41	9.46	1.83
0.550	3.87	9.44	0.57
1.000	4.03	9.51	0.09
2.000	4.19	9.76	−0.25

calculated from

$$\log K_B = \log\beta_1^{(y)} + pK_I^{(x)} - pK_A \tag{28}$$

are also given in Table 2. The exceptional variation of constant K_B at low ionic strengths may be due to systematic errors. In fact, this constant is presented by the equation

$$\log K_B = 9.48 + 0.109\ I \tag{29}$$

with an average deviation of ± 0.07. Also the values of the constant K_D of the disproportionation

$$2\,MXY^- \rightleftharpoons MX_2^{4-} + MY_2^{2+} \tag{30}$$

calculated from

$$pK_D = pK_{II}^{(x)} - pK_I^{(x)} - \log\beta_2^{(y)} + 2\log K_B \tag{31}$$

are given in Table 2. As expected, the variation of this constant with ionic strength is very great.

The constant K_A can be presented by the equation

$$pK_A = 2.70 + \frac{3.054\sqrt{I}}{1+1.25\sqrt{I}} - 0.035\ I \tag{32}$$

within ± 0.02. Using eqns. (32) and (17)—(25), it is possible to calculate the values of all the equilibrium constants at an arbitrary ionic strength.

The values of the gross stability constants $\beta_2^{(x)}$, $\beta_2^{(y)}$, and $\beta_2^{(xy)}$, the last defined by

$$[MXY]/[M][X][Y] = \beta_2^{(xy)} \tag{33}$$

Table 3. Stability constant $\beta_2^{(xy)}$ of the mixed complex and the constants $\beta_2^{(x)}$ and $\beta_2^{(y)}$ in sodium perchlorate solutions at 25°C.

I	$\log\beta_2^{(x)}$	$\log\beta_2^{(y)}$	$\log\beta_2^{(xy)}$
0	17.20	19.64	20.39
0.017	16.85	19.67	19.70
0.045	16.70	19.72	19.43
0.100	16.50	19.82	19.09
0.550	16.14	20.37	18.54
1.000	16.10	20.79	18.49
2.000	16.27	21.47	18.74

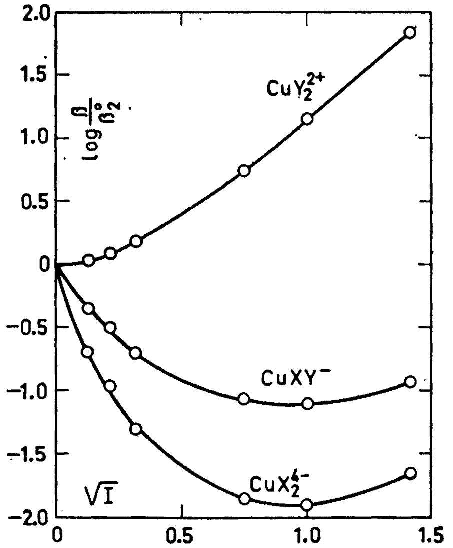

Fig. 1. The gross stability constants of CuX_2^{4-}, $CuXY^-$ and CuY_2^{2+} as functions of ionic strength in sodium perchlorate solutions at 25°C.

at the above ionic strengths are shown in Table 3. The stability constant of the mixed complex was calculated from

$$\log\beta_2^{(xy)} = pK_3^{(x)} + \log\beta_1^{(y)} - pK_A \tag{34}$$

and that of MX_2^{4-} from

$$\log\beta_2^{(x)} = 2\,pK_3^{(x)} - pK_I^{(x)} - pK_{II}^{(x)}. \tag{35}$$

In the calculation of $\beta_2^{(x)}$ and $\beta_2^{(xy)}$ also the values of the third acid dissociation constant of 5-sulphosalicylic acid were needed. The result of Näsänen and Paakkola[3]

$$pK_3^{(x)} = 12.53 - \frac{3.054\sqrt{I}}{1+1.31\sqrt{I}} + 0.262\,I \tag{36}$$

referring to sodium perchlorate solutions was used. The variation of the gross stability constants $\beta_2^{(x)}$, $\beta_2^{(y)}$ and $\beta_2^{(xy)}$ of complexes MX_2^{4-}, MY_2^{2+}, and MXY^- with ionic strength is seen in Fig. 1. The marked dependence of the stability of the mixed complex on ionic strength appears from this figures as well as from the values of the disproportination constant K_D given in Table 2.

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Received June 21, 1962.