

The Effect of Complex Formation between Cupric and Sulphate Ions on the Equilibrium of Cupric Trihydroxy-sulphate in Mixed Aqueous Solutions of Cupric and Potassium Sulphate

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In a recent paper by Näsänen and Tamminen¹, the solubility product of cupric trihydroxysulphate ($\text{Cu}(\text{OH})_{1.5}(\text{SO}_4)_{0.25}$) was determined in potassium sulphate solutions as a function of the ionic strength. This solubility product

$$[\text{Cu}^{++}] (\text{OH}^-)^{1.5} [\text{SO}_4^{=}]^{0.25} \quad (1)$$

where $[\text{Cu}^{++}]$ and $[\text{SO}_4^{=}]$ are molarities and (OH^-) hydroxyl ion activity, was calculated by means of the stoichiometric concentrations and the measured pH. In these calculations the complex formation between cupric and sulphate ions could not be taken into account because the complexity constants had not been determined before. Furthermore opinions diverged² regarding, whether or not cupric sulphate, is completely dissociated. The effect of potassium sulphate additions was, however, so great that complex formation seemed to be possible. Therefore a spectrophotometric investigation on the complex formation between cupric and sulphate ions was later carried out by the present author³. In this study the first complexity constant

$$k_1 = 1/K_1 = [\text{CuSO}_4] / [\text{Cu}^{++}] [\text{SO}_4^{=}] \quad (2)$$

was determined in solutions of some alkali salts. The results seemed to show that practically no higher complexes between cupric and sulphate ions exist. On the basis of these results, the effect of complex formation may be estimated.

For the determination of the solubility product, cupric sulphate, sodium hydroxide, and potassium sulphate were mixed. The total copper concentration (c_{Cu}) was relatively low ($c_{\text{Cu}} < 0.02$), and the stoichiometric concentration of sodium hydroxide (c_{B}) less than $1.5 c_{\text{Cu}}$ because cupric trihydroxysulphate is not stable when $c_{\text{B}} > 1.5 c_{\text{Cu}}$. When equilibrium was reached, the pH of the solution was measured. The concentrations of cupric and sulphate ions were calculated by means of the equations

$$[\text{Cu}^{++}] = c_{\text{Cu}} - x - [\text{CuSO}_4] \quad (3)$$

and

$$[\text{SO}_4^-] = c + c_{\text{Cu}} - 0.25 x - [\text{CuSO}_4] \quad (4)$$

where c is the molarity of the added potassium sulphate and x the decrease in concentration of cupric ion owing to precipitation. The electro-negativity equation gives

$$x = 0.667 (c_{\text{B}} + [\text{H}^+] - [\text{OH}^-]) \quad (5)$$

When $c_{\text{B}} < 1.5 c_{\text{Cu}}$, the hydroxyl ion concentration in this equation is negligible, and also, as a rule, the hydrogen ion concentration. From equations (2), (3), and (4) it follows that

$$[\text{CuSO}_4] = \frac{[\text{Cu}^{++}]_0 [\text{SO}_4^-]_0}{[\text{Cu}^{++}]_0 + [\text{SO}_4^-]_0 + K_1 - [\text{CuSO}_4]} \quad (6)$$

where

$$[\text{Cu}^{++}]_0 = c_{\text{Cu}} - x \quad (7)$$

$$[\text{SO}_4^-]_0 = c + c_{\text{Cu}} - 0.25 x \quad (8)$$

The dissociation constant of cupric sulphate was calculated with the aid of the relation

$$\text{p}K_1 = 2.099 - \frac{4.05 \sqrt{I}}{1 + 1.762 \sqrt{I}} + 0.155 I \quad (9)$$

obtained earlier³.

The results are recorded in Table 1. The relation between solubility product and ionic strength may be represented by means of the equation

$$\text{p}S = \text{p}S_0 - \frac{2.53 \sqrt{I}}{1 + \alpha \sqrt{I}} + BI \quad (10)$$

For the parameters, the values

$$\text{p}S_0 = 17.133, \alpha = 1.495 \text{ and } B = 0$$

Table 1. Solubility product of cupric trihydroxysulphate in potassium sulphate solutions at 25° C.

I	$c_{\text{Cu}} \cdot 10^2$	$c_{\text{B}} \cdot 10^2$	c	pH	pK_1	pS
0.122	1.01	0.465	—	4.99	1.695	16.903
0.117	1.01	0.555	—	5.11	1.709	16.896
0.112	1.00	0.645	—	5.38	1.722	16.855
0.191	2.04	0.374	—	4.60	1.527	16.840
0.183	2.01	0.574	—	4.70	1.544	16.786
0.177	2.00	0.733	—	4.75	1.558	16.803
0.169	1.97	0.924	—	4.84	1.575	16.810
0.159	1.95	1.178	—	5.04	1.600	16.809
0.151	1.93	1.344	—	5.36	1.620	16.790
0.332	2.02	0.555	0.0255	4.80	1.268	16.573
0.322	1.98	0.906	0.0250	4.97	1.283	16.542
0.315	1.95	1.116	0.0246	5.16	1.294	16.549
0.310	1.93	1.327	0.0244	5.41	1.302	16.575
0.636	1.98	0.906	0.125	5.09	0.949	16.340
0.628	1.95	1.161	0.123	5.28	0.952	16.342
0.624	1.93	1.327	0.122	5.55	0.957	16.333
0.894	2.01	0.574	0.255	5.09	0.817	16.149
0.881	1.97	0.924	0.249	5.21	0.822	16.190
0.874	1.95	1.178	0.246	5.43	0.824	16.157
0.869	1.93	1.340	0.244	5.73	0.828	16.164
1.19	2.01	0.574	0.458	5.21	0.763	16.044
1.17	1.97	0.924	0.449	5.34	0.765	16.067
1.16	1.95	1.178	0.443	5.55	0.764	16.046
1.16	1.93	1.344	0.438	5.85	0.764	16.051

were obtained by the method of least squares. Previously, when the complex formation was not taken into account, a value of 17.115 was obtained for pS_0 . The difference is thus of the order of magnitude of experimental errors. The parameter α is of a reasonable magnitude. In Fig. 1, where pS is plotted against \sqrt{I} , the two lower curves refer to these measurements in potassium sulphate solutions. The solid line represents the results when complex formation is taken into consideration and the dotted line when it is neglected. The effect of complex formation is thus considerable and, as expected, is greater the greater the concentration of sulphate ion.

In the paper by Näsänen and Tamminen¹, mentioned above, it was shown that the solubility of cupric hydroxyperchlorate was considerably greater than that of cupric trihydroxysulphate. Therefore in a mixed solution of cupric

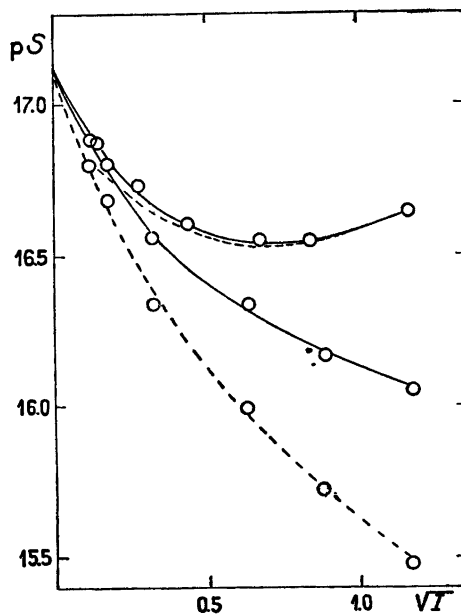


Fig. 1. Solubility product of cupric trihydroxysulphate in potassium sulphate and sodium perchlorate solutions as a function of ionic strength.

sulphate and sodium perchlorate, trihydroxysulphate is precipitated and not hydroxyperchlorate. In this way it was possible to determine the solubility product of cupric trihydroxysulphate in sodium perchlorate solutions. The results of these measurements are given in Table 2. Also in this case, the equations derived above were used in the calculations, but the dissociation constant of cupric sulphate was calculated from the equation

$$pK_1 = 2.099 - \frac{4.05 \sqrt{I}}{1 + 1.527 \sqrt{I}} + 0.161 I \quad (11)$$

The results may be represented by equation (10). For the parameters the values

$$pS_0 = 17.133, \alpha = 2.077 \text{ and } B = 0.278$$

were obtained. In Fig. 1 the two upper curves represent these results. In this case the effect of complex formation is slight, especially at higher ionic strengths.

As is seen in Fig. 1, the solubility product in sodium perchlorate solution differs considerably from that in a potassium sulphate solution with the same ionic strength. The activity coefficients, at least the activity coefficient of the

Table 2. Solubility product of cupric trihydroxysulphate in sodium perchlorate solutions at 25° C.

\sqrt{I}	$c_{\text{Cu}} \cdot 10^2$	$c_{\text{SO}_4} \cdot 10^2$	pH	pK_1	pS
0.139	1.04	0.216	4.81	1.637	16.873
0.271	1.03	0.454	5.05	1.335	16.731
0.433	1.02	0.677	5.50	1.073	16.609
0.671	1.03	0.456	5.22	0.829	16.541
0.836	1.04	0.225	4.98	0.724	16.555
1.160	1.04	0.216	4.91	0.622	16.649

cupric ion, are thus considerably greater in sodium perchlorate solutions than in potassium sulphate solutions. In this connection it may be emphasized that the above values for the solubility products and complexity constants were obtained at relatively high ionic strengths; in the former case $\sqrt{I} > 0.1$ and in the latter $\sqrt{I} > 0.2$. The equations (9), (10), and (11) are therefore valid at these ionic strengths. It is quite possible that at still lower ionic strengths, the results would agree with the expectation of the extended Debye theory, as developed by Gronwall, La Mer and Sandved. If so, the true thermodynamic constants would be somewhat smaller than the above values, which were extrapolated with the aid of the Debye-Hückel equation.

SUMMARY

The significance of complex formation in the equilibrium between cupric trihydroxysulphate and solutions of potassium sulphate or sodium perchlorate was investigated. In potassium sulphate solutions the effect was considerable, but in sodium perchlorate solutions it was very slight. The apparent and true solubility products were determined in both cases as a function of ionic strength. The true solubility product may be represented by means of the Debye-Hückel equation. The parameters were of reasonable magnitudes.

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