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Spectrophotometric Study on Complex Formation between Cupric and Sulphate Ions

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Recently[1] methods have been developed for the determination of all complexity constants of a complex system. The primary assumption in these methods is the possibility of carrying out the investigation at a constant concentration of a highly dissociated neutral salt and at a low concentrations of the complex forming substances. Thus the activity coefficients remain constant and the classical law of mass action can be applied. In systems of slight complexity, this condition cannot be fullfilled because of a high and greatly varying ligand concentration. In such cases the variation of the activity coefficients must be taken into consideration. An attempt in this direction has been made by J. Bjerrum[2] who made some approximate assumptions in regard to activity coefficients, which are reasonable at high ligand concentrations. Thus this method cannot be used for determinations at lower ionic strengths, which were carried out in this study. Therefore a new method was developed which permits the determination of the first complexity constant from the light absorption measurements over wide limits of ionic strength. The method is applied in regard to the cupric sulphate system.

CALCULATION OF THE FIRST COMPLEXITY CONSTANT

The first complexity constant of cupric sulphate is defined by

$$k_1 = [\mathrm{CuSO_4}]/[\mathrm{Cu^{++}}][\mathrm{SO_4^{=}}] \tag{1}$$

If the first complex is the only one in the system the following stoichiometric equations are valid:

$$c_{\mathrm{Cu}} = [\mathrm{CuSO_4}] + [\mathrm{Cu^{++}}] \tag{2}$$

and

$$c_{SO_4} = [SO_4^{=}] + [CuSO_4] \tag{3}$$

where c_{Cu} and c_{SO_4} are the stoichiometric molarities of the cupric and sulphate ions. From equations (1), (2) and (3) the familiar expression follows:

$$y/c_{Cu} = x/(x + K_1) \tag{4}$$

where $x = [SO_4^{=}]$, $y = [CuSO_4]$ and $K_1 = 1/k_1$. On the other hand according to Beer's law

$$\varepsilon = e/c_{Cu} = (E - \varepsilon_{Cu}[Cu^{++}] - \varepsilon_{SO_4}[SO_4^{=}])/c_{Cu} = \varepsilon_{CuSO_4} y/c_{Cu} \tag{5}$$

where E is the extinction (d = 1 cm), and ε_{Cu}, ε_{SO_4}, ε_{CuSO_4} are molar extinction coefficients. The elimination of y/c_{Cu} from equations (4) and (5) leads to the expression

$$\varepsilon = \frac{\varepsilon_{CuSO_4}\, x}{x + K_1} \tag{6}$$

or

$$\log\varepsilon = \log\varepsilon_{CuSO_4} + \log\frac{x}{x + K_1} \tag{7}$$

The differentiation of equation (7) gives

$$\varphi = \frac{\mathrm{dlog}\,\varepsilon}{\mathrm{dlog}\,x} = \frac{K_1 - x(\mathrm{d}K_1/\mathrm{d}x)}{x + K_1} \tag{8}$$

This equation can be put into the form

$$\varphi = \frac{K_1(1 - \psi_1)}{x + K_1} \tag{9}$$

where $\psi_1 = \mathrm{dlog}\,K_1/\mathrm{dlog}\,x$. The solution of equation (9) for K_1 gives

$$K_1 = \frac{\varphi\, x}{1 - \varphi - \psi_1} \tag{10}$$

The first complexity constant can be calculated by means of this equation. When the composition of the solution can be held nearly constant during the measurement K_1 is constant and we can put $\psi_1 = 0$. Thus in this case K_1 can be calculated very simply from the experimental φ-values. When, however, this condition is not fulfilled the computation is much more difficult. Differentiation of the Debye-Hückel equation

$$\mathrm{p}K_1 = \mathrm{p}K_{1.0} - \frac{4.05\sqrt{I}}{1 + \alpha\sqrt{I}} + B\,I \tag{11}$$

used as the interpolation equation, gives

$$\frac{\mathrm{dp}K_1}{\mathrm{dp}x} = 6.909\,x\left(1 - \frac{1}{3}\,\frac{\mathrm{d}y}{\mathrm{d}x}\right)\left(\frac{2.03}{\sqrt{I}\,(1 + \alpha\sqrt{I}\,)^2} - B\right) \tag{12}$$

where

$$I = 3c_{\mathrm{Cu}} + 3x - y \tag{13}$$

and

$$\frac{\mathrm{d}y}{\mathrm{d}x} = c_{\mathrm{Cu}}K_1\,(1 - \psi_1)/(x + K_1) \tag{14}$$

From equation (10) and (11) we obtain

$$F = \mathrm{p}K_{1.0} - \frac{4.05\sqrt{I}}{1 + \alpha\sqrt{I}} + BI - p\varphi - px + p(1 - \varphi - \psi_1) = 0 \tag{15}$$

For every x-value we get an equation (15) with tree unknowns $\mathrm{p}K_{1.0}$, α and B. When rough values for the unknowns have been found the final solution can be obtained by successive approximations using the method of least squares.

In a system with only a complex the derived equations are valid at all ligand concentrations. In systems with more than a complex the equations are very nearly correct in low ligand concentrations but incorrect at high ligand concentrations. The above equations can, however, easily be extended to systems with higher, additive nonabsorbing complexes. Instead of equation (10) we obtain in this case

$$K_1 = \frac{\varphi\,x}{1 - \varphi - \psi_1 - \sum\limits_{2} (\nu - 1 + \varphi + \psi_1 - \psi_\nu)x^\nu/K_\nu} \tag{16}$$

where the constants K_ν are defined by

$$1/K_\nu = k_\nu = \frac{[\mathrm{Cu(SO_4)}_\nu^{(2\nu-2)-}]}{[\mathrm{Cu^{++}}][\mathrm{SO_4^=}]^\nu} \qquad (17)$$

and $\psi_\nu = \mathrm{dp}K_\nu/\mathrm{dp}x$.

Equation (16) can further be generalized to a system with an absorbing complex $\mathrm{Cu(SO_4)}_\nu^{(2\nu-2)-}$.

EXPERIMENTAL

Cupric perchlorate was prepared by dissolving cupric oxide, Kahlbaum for analysis, in perchloric acid and recrystallizing several times.

Lithium sulphate, B. D. H. laboratory reagent, was recrystallized many times. The other chemicals were the best qualities obtainable and were used without purification.

The light absorption measurements were made with a Beckman Quartz Spectrophotometer Model DU. The slit width at ultraviolet wavelengths was 0.20—0.24 mm (272—320 mμ) corresponding to a spectral band width 0.8—1.1 mμ. The increase or decrease of the slit width by 50 per cent did not affect the results. The temperature of the room where the measurements were made was maintained at 25° C. Because the photometer lamp increases the temperature in the cell compartment the extinction measurements were made so rapid that the temperature of the solution measured did not find time to change. Later the »mounting block» was equipped with a refrigerator coil soldered into the block. The block was held at constant temperature with the aid of a »contact thermometer» which was put into a hole bored in the block.

RESULTS

A typical measurements series is represented in Fig. 1. In this series the cupric perchlorate concentration was constant ($c_{\mathrm{Cu}} = 0{,}01003$) and the wavelength 272 mμ. In the figure log ε is plotted against the logarithm of the sulphate ion concentration x. Several similar series were made at wavelengths 272—320 mμ. The curves obtained proved to be parallel within experimental errors if the cupric perchlorate concentration was not raised so high that the composition of the salt medium changed considerably. The own absorption of cupric ions is at these wavelengths negligible. It is interesting that the slope of the curves seems to be the same also at the red and the beginning of the infrared wavelengths within experimental errors which, admittedly, are considerable because of the great own absorption of cupric ions. These results seem to prove that this system has only a complex which absorbs light and still more they make it probable that the system has only this complex. The complex in question is obviously the first one, $\mathrm{CuSO_4}$.

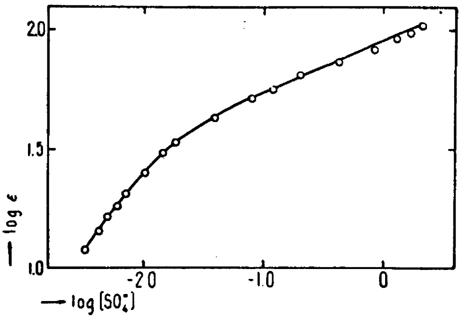

Fig. 1. The effect of lithium sulphate additions on light absorption of cupric perchlorate solutions. $c_{Cu} = 0.01003$, $\lambda = 272$ *mμ*, $\varepsilon_{Cu} \approx 0$.

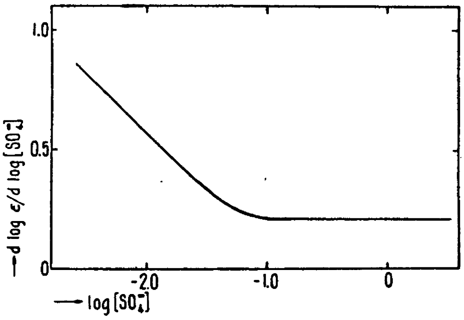

Fig. 2. The dependence of dlogε/dlogx on the sulphate ion concentration.

For the calculation of the first complexity constant, the quantity $\varphi = $ dlogε/dlog x must first be determined. With this intention the experimental data of logε were fitted at high ligand concentrations to a polynomial of the first order and at lower ligand concentrations to two polynomials of the second order. These polynomials were then differentiated. The results were checked by graphical means. The mean value of the quantity φ obtained from the data at different wavelengths is plotted in Fig. 2 against log x.

In Table 1 the calculations of the constant K_1 are represented at some ionic strengths. In this table pK_1 means the values calculated by means of equation (18), p$\bar{K}_1$ the values obtained with the aid of equation (10) and ΔpK_I is their difference. The calculations carried out by the method of least squares in the manner described above gave the result

Table 1. Calculation of the first complexity constant of cupric sulphate system.

$\sqrt{I}$	x	φ	ψ_1	pK_1	p$\bar{K}_1$	ΔpK
0.205	0.004	0.765	0.142	1.466	1.482	− 0.016
0.274	0.015	0.486	0.354	1.323	1.341	− 0.018
0.387	0.040	0.280	0.528	1.133	1.234	− 0.101
0.574	0.100	0.212	0.616	0.901	0.910	− 0.009
0.693	0.150	0.212	0.616	0.792	0.734	+ 0.058
0.883	0.250	0.212	0.581	0.659	0.592	+ 0.067
1.110	0.400	0.212	0.497	0.549	0.536	+ 0.013
1.560	0.800	0.212	0.282	0.428	0.475	− 0.047
1.940	1.245	0.212	0.0688	0.393	0.436	− 0.043
2.300	1.750	0.212	− 0.162	0.400	0.409	− 0.009
2.600	2.240	0.212	− 0.373	0.428	0.389	+ 0.039

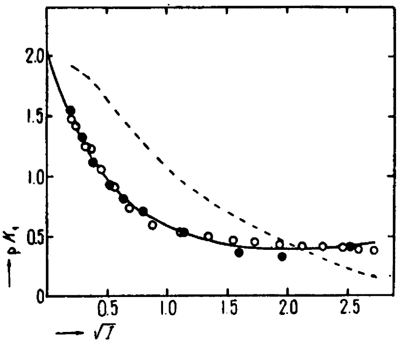

Fig. 3. The first complexity constant of cupric sulphate in lithium sulphate solutions.

$$\log k_1 = \mathrm{p}K_1 = 2.099 - \frac{4.05\sqrt{I}}{1 + 1.618\sqrt{I}} + 0.0520\, I \qquad (18)$$

In Fig. 3 $\mathrm{p}K_1$ is plotted against $\sqrt{I}$. The hollow circles in the figure mean the values calculated with the aid of equation (10) and the full circles the values calculated by means of equation (25). The dotted line represents the values obtained by means of equation (10) assuming that the activity coefficients do not vary and thus $\psi_1 = 0$. In the final calculations twenty points were used.

Some experiments were carried out concerning the effect of added perchloric acid on the extinction of cupric sulphate solution. The results are represented in Fig. 4. The shapes of the curves come obviously from the formation of bisulphate ions. When sulphuric acid instead of perchloric acid was added the extinction of cupric sulphate solution remains nearly constant until relatively high sulphuric acid concentrations. It is therefore obvious that cupric and bisulphate ions form nonabsorbing complexes as $\mathrm{CuHSO_4^+}$.

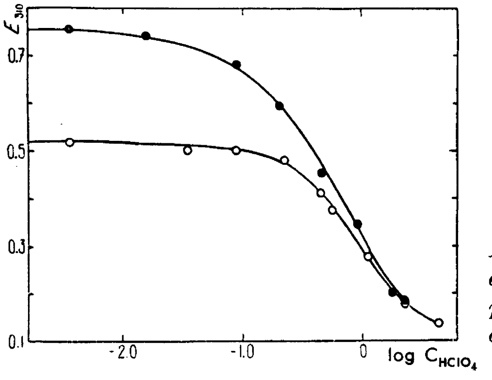

Fig. 4. The effect of perchloric acid on the extinction of cupric sulphate solutions. Upper curve: $c_{CuSO_4} = 0.487$, *Lower curve:* $c_{CuSO_4} = 0.243$, $c_{Li_2SO_4} = 0.619$; $\lambda = 31$ *mμ.0*

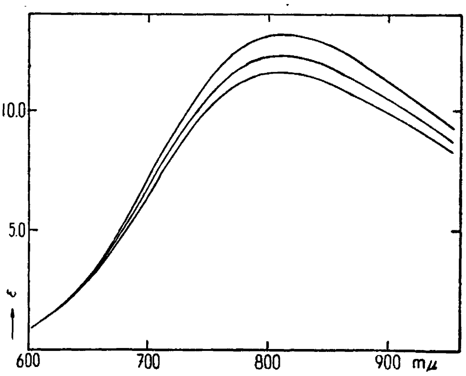

Fig. 5. Absorption spectra of some cupric salt solutions. Upper curve: $c_{Cu(ClO_4)_2} = 0.0823$, $c_{Li_2SO_4} = 2.13$, *Middle curve:* $c_{CuSO_4} = 0.0605$, *Lower curve:* $c_{Cu(ClO_4)_2} = 0.0600$.

The formation of these complexes takes place of course also on addition of perchloric acid.

As is known cupric perchlorate solution has two absorption maxima, the one at extreme ultraviolet wavelengths, the other at about 820 mμ. It is interesting that by adding sulphate ions to cupric perchlorate solution the extinction also increases at longer wavelengths. Also the extinction of cupric sulphate solution is greater than that of a cupric perchlorate solution at equal concentrations. In Fig. 5 absorption spectra of some cupric perchlorate and sulphate solutions are represented.

It is noteworthy that the extinction of cupric sulphate solution seems to increase linearly with the concentration at longer wavelengths. This fact has sometimes been presented as evidence of the complete dissociation of cupric sulphate. This linear relation can, however, be comprehended even if complex formation occurs. According to Beer's law the extinction of cupric sulphate solution is

$$E = \varepsilon_1 [Cu^{++}] + \varepsilon_2 [CuSO_4] \qquad (19)$$

or

$$E = \varepsilon_1 c_{Cu} + (\varepsilon_2 - \varepsilon_1)[CuSO_4] \qquad (20)$$

When $\varepsilon_2 - \varepsilon_1 > 0$ the extinction is greater than that of an equally concentrated perchlorate solution. If $\varepsilon_2 - \varepsilon_1$ is relatively low compared to ε_1 the latter term in (20) is small compared with the former and the non-linear relation between $[CuSO_4]$ and c_{Cu} has only a slight effect on the extinction. Moreover the relation between $[CuSO_4]$ and c_{Cu} is also roughly linear as seen from the equation

$$[CuSO_4] = c_{Cu}^2 / (K_1 + 2c_{Cu} - [CuSO_4]) \qquad (21)$$

which follows from equations (1) and (2). It is therefore very difficult to ascertain experimentally the non-linear character of this relation. At ultraviolet wavelengths from about 250 mμ towards longer wavelenths, ε_1 is very small and therefore the relation between the extinction and the concentration is more distinctly non-linear and this can also be verified experimentally.

DISCUSSION

The fact that the slopes of the curves representing log ε as a function of log x do not depend on the wavelength between 272 and 320 mμ within experimental errors seems to prove that in the cupric sulphate system only a complex exists. The numerical values of the slopes indicate that the dominating complex is the first one. We can also study this question by means of the extended equation (16). Putting $\nu = 2$ we obtain from this equation

$$K_1 = \varphi x / \{1 - \varphi - \psi_1 - (1 + \varphi + \psi_1 - \psi_2)\, x^2 / K_2\} \qquad (22)$$

We can further assume that $\psi_1 = \psi_2$. When $K_2 = \infty$ we have equation (10). It is now obvious that the effect of the second complex appears more at high ligand concentrations. Therefore we can assume that p$K_{1,0}$ and a in equation (18) have correct values. The only unknown is B. For each value K_2 the corresponding value of B can now be calculated by means of equations (22), (18) and (12). The solution can be performed by graphical means. Now tree possibilities exist as represented in Fig. 6 where the difference of the pK_1 values calculated by means of equation (11) and (22) is plotted against B. The upper curve represents the case when no solution exists with positive K_2 values. In this case higher absorbing complexes obviously belong to the system. The lower curve represents the case when solutions with positive K_2 values can be found. The middle curve represents the case when no higher complex can exist in the system. A solution can be found in this case only when $K_2 = \infty$. Experimental data gave so slight departures from the case 2 that we can say the system has no higher complexes. A rough estimation gave for the second complexity constant the upper limit $k_2 < 0.05$.

That the first complex $CuSO_4$ is the absorbing one in the system appears from the numerical values of the quantity φ. Supposing that the complex $Cu(SO_4)_i^{(2i-2)-}$ is the only one, we obtain instead of equation (10)

$$K_i = 1/k_i = \varphi x^i / (i - \varphi - \psi_i) \qquad (23)$$

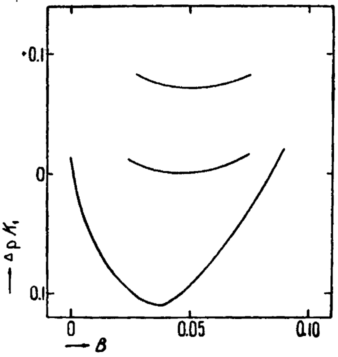

Fig. 6. Calculation of the coefficient B by graphical means.

Using this equation with $i > 1$ we obtain from the experimental data an unreasonably steep curve representing the relation between pK_i and $\sqrt{I}$.

The accuracy of the values obtained for the first complexity constant appears from Fig. 3 where the hollow circles mean the values calculated with the aid of equation (10). Another way of estimating the accuracy is as follows. We calculate first the values of the constant K_1 by means of equation (18) with the experimental values of c_{Cu} and $c_{\mathrm{SO_4}}$. The corresponding values of $[\mathrm{CuSO_4}]$ can then be calculated with the aid of equation

$$[\mathrm{CuSO_4}] = c_{\mathrm{Cu}}c_{\mathrm{SO_4}}/(K_1 + c_{\mathrm{Cu}} + c_{\mathrm{SO_4}} - [\mathrm{CuSO_4}]) \tag{24}$$

which follows from equations (1), (2) and (3). Now values for the molar extinction coefficient of the complex $\mathrm{CuSO_4}$ can be calculated by means of equation (5). The values obtained should be equal but are not because of errors made in determining the quantity φ. Now the values of constant K_1 can be calculated by means of equation

$$K_1 = \frac{(c_{\mathrm{Cu}} - e/\varepsilon_{\mathrm{CuSO_4}})\ (c_{\mathrm{SO_4}} - e/\varepsilon_{\mathrm{CuSO_4}})}{e/\varepsilon_{\mathrm{CuSO_4}}} \tag{25}$$

The calculations were carried out with such a value $\varepsilon_{\mathrm{CuSO_4}} = 120$ ($\lambda = 272$ mμ) that the values of K_1 obtained fit as well as possible with the K_1 values from equation (18). These values are represented in Fig. 3 with full circles. As seen in Fig. 3 the values calculated by means of equation (25) do not deviate more from the values calculated by means of equation (18) than the values calculated by means of equation (10).

The dissociation and light absorption of cupric sulphate solution have often been investigated. Mecke and Ley[3] as well as Ley and Heidbrink[4] have proved that cupric sulphate solutions »obey Beer's law» at the red but not at ultraviolet wavelengths. They consider complex formation as possible. Several authors have investigated this system with methods which are based upon the more or less arbitrary selection of some relations to represent the behaviour of the hypothetical completely dissociated electrolyte [5]. Therefore the results obtained cannot be very reliable. In this way Davies [6] as well as Owen and Curry [7] have obtained for K_1 the value 0.005 and 0.0043 respectively from conductance measurements. For all that these values do not deviate very much from the value obtained in this paper for the thermodynamic constant $K_{1,0} = 0.008$. Recently Fronaeus [8] has studied the cupric sulphate system by means of potentiometric and spectrophotometric methods using sodium sulphate — sodium perchlorate solutions with ionic strength 1 and assuming that the activity coefficients do not change with the composition. The values obtained for the first complexity constant, spectrophotometrically $k_1 = 5$ and potentiometrically $k_1 = 10$, are not very much different from the present value at this ionic strength $k_1 = 4$. On the contrary the values obtained for higher complexity constants, $k_2 = 10$—17 and $k_3 = 200$, seem to be too high. This can be understood because the variation of activity coefficients has not been taken into account. A clear view of the importance of considering the change of activity coefficients is given in Fig. 3 where the dotted line represents the results without considering the change of activity coefficients.

SUMMARY

A method for the study of complex formation in systems with slight complexity, taking into account the change of activity coefficients, is described.

The first complexity constant of cupric sulphate has been determined in lithium sulphate solutions as the function of ionic strength by means of light absorption measurements.

The possibility of the existence of other complexes in the system is discussed. Their effect can appear only at high ionic strengths and is obviously slight.

It is proved that the light absorption of a cupric sulphate solution is greater than that of a equimolar cupric perchlorate solution even at red wavelengths. This, as well as the fact that cupric sulphate solutions »obey Beer's law» at these wavelengths is proved to be in agreement with complex formation.

The effect of perchloric and sulphuric acid on the light absorption of cupric sulphate solutions has been investigated. It is obvious that complex formation between cupric and bisulphate ions occurs.

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