

## The Effect of Some Alkali Salts on the Light Absorption of the Aqueous Solutions of Cupric Sulphate and on the Dissociation of Cupric Sulphate

REINO NÄSÄNEN

*Propaedeutic-chemical Laboratory, University of Helsinki, Helsinki, Finland*

In a previous paper<sup>1</sup> it has been shown that the light absorption of cupric sulphate solution can be interpreted by means of one complex,  $\text{CuSO}_4$ . In this paper a calculation method which permits the determination of the dissociation constant of this complex, within wide limits of ionic strength, was derived on the basis of Beer's law. With the aid of the dissociation constant values determined in this way and the corresponding extinction values, the molar extinction coefficients can be calculated at different wavelengths. The values of the molar extinction coefficients permit, on the one hand, the comparison of the results obtained at different wavelengths. On the other hand the dissociation constant can be calculated by means of the molar extinction coefficient values also in such cases where the original method cannot be used. This method has since been used by the present author for determination of the dissociation constant of cupric sulphate in the solutions of some alkali salts. The results of these measurements are reported below.

The equations used in the calculations are

$$e = E/d - \epsilon_{\text{Cu}^{++}} [\text{Cu}^{++}] = \epsilon_{\text{CuSO}_4} [\text{CuSO}_4] \quad (1)$$

and

$$K = \frac{(c_{\text{Cu}} - e/\epsilon_{\text{CuSO}_4}) (c_{\text{SO}_4} - e/\epsilon_{\text{CuSO}_4})}{e/\epsilon_{\text{CuSO}_4}} \quad (2)$$

where  $E$  is the extinction,  $d$  the thickness of the absorbing layer in cm,  $\epsilon_{\text{Cu}^{++}}$  and  $\epsilon_{\text{CuSO}_4}$  molar extinction coefficients,  $c_{\text{Cu}}$  the total copper and  $c_{\text{SO}_4}$  the total sulphate concentration.

The measurements were carried out by means of a Beckman Quartz Spectrophotometer Model DU. The spectral band width was about  $1\text{ m}\mu$ . The temperature of the room, where the measurements were carried out, and that of the cell compartment was kept constant at  $25^\circ$ . The chemicals used when not pro analysis grade were prepared and purified as described earlier<sup>1</sup>.

Most of the measurements were carried out at  $272\text{ m}\mu$  because the light absorption of the complex is relatively high at this wavelength but the light absorption of cupric ion is very low, even if not quite negligible, at the concentrations used. At longer wavelengths the absorption of cupric ion is still less but the absorption of the complex in question is also much smaller and therefore much higher copper concentrations must be used. Hence the measurements could not be done in as low ionic strength as required.

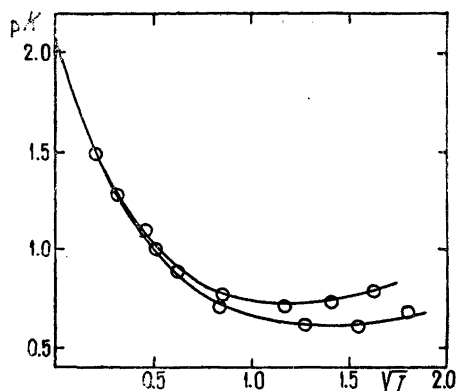
Table 1 shows some results of the measurements in lithium and sodium perchlorate solutions. These measurements were carried out at  $272\text{ m}\mu$ . At this wavelength the molar extinction coefficient of cupric sulphate has, according to earlier determinations<sup>1</sup>, the value 120, which was used in the calculations. The molar extinction coefficient of cupric ion can be determined from the light absorption measurements in cupric perchlorate solutions as cupric perchlorate is obviously practically completely dissociated. The light absorption of cupric perchlorate solution seems, however, to be to some extent dependent on the pH of the solution, evidently because of the hydrolyse. Therefore the pH of the solutions was measured as well. For the molar extinction coefficient of cupric ion in the solutions investigated the value 0.8 was obtained at this wavelength. The correction of  $pK$  due to the light absorption of cupric ion amounts in these measurements at the most to 0.02 at low ionic

*Table 1. Determination of the dissociation constant of cupric sulphate in lithium and sodium perchlorate solutions.*

$$\lambda = 272\text{ m}\mu, \epsilon_{\text{CuSO}_4} = 120, \epsilon_{\text{Cu}^{++}} = 0.8.$$

| Salt             | $c_{\text{Cu}} \cdot 10^3$ | $I$   | $e \cdot 10^3$ | $[\text{CuSO}_4] \cdot 10^3$ | $[\text{Cu}^{++}] \cdot 10^3$ | $pK$  |
|------------------|----------------------------|-------|----------------|------------------------------|-------------------------------|-------|
| $\text{LiClO}_4$ | 15.32                      | 0.705 | 141.0          | 1.175                        | 14.14                         | 0.770 |
| »                | »                          | 1.35  | 122.6          | 1.022                        | 14.30                         | 0.699 |
| »                | »                          | 2.00  | 132.0          | 1.100                        | 14.21                         | 0.735 |
| »                | »                          | 2.65  | 145.0          | 1.208                        | 14.11                         | 0.783 |
| $\text{NaClO}_4$ | 15.10                      | 0.209 | 247.6          | 2.063                        | 13.04                         | 1.084 |
| »                | »                          | 0.369 | 172.0          | 1.433                        | 13.67                         | 0.886 |
| »                | »                          | 0.684 | 120.7          | 1.006                        | 14.09                         | 0.706 |
| »                | »                          | 1.62  | 100.6          | 0.838                        | 14.26                         | 0.613 |
| »                | »                          | 2.40  | 100.2          | 0.835                        | 14.26                         | 0.613 |
| »                | »                          | 3.20  | 115.7          | 0.964                        | 14.13                         | 0.684 |

Fig. 1. Dissociation constant of cupric sulphate in lithium perchlorate (upper curve) and sodium perchlorate (lower curve) solutions.



strengths and to 0.05 at higher ionic strengths. The results can be represented by means of the Debye-Hückel equation

$$pK = pK_0 - \frac{4.05 \sqrt{I}}{1 + \alpha \sqrt{I}} + BI \quad (3)$$

For  $pK_0$  the value obtained in the previous paper with a different method was adopted. The values of  $\alpha$  and  $B$  were calculated using the method of least squares. The following values were obtained

|                    | $pK_0$ | $\alpha$ | $B$   |
|--------------------|--------|----------|-------|
| LiClO <sub>4</sub> | 2.099  | 1.550    | 0.211 |
| NaClO <sub>4</sub> | 2.099  | 1.527    | 0.161 |

In Fig. 1 the dissociation constant is represented in relation to ionic strength. As seen  $pK$  is higher in lithium than in sodium perchlorate solutions. The differences in  $pK$  values are, however, of a magnitude common in equilibrium constants of electrolytes. The values obtained for  $\alpha$  and  $B$  are of reasonable magnitude.

In lithium sulphate solutions numerous measurements were performed. The results of some measurements are given in Table 2. In this case the correction due to the light absorption of cupric ion is smaller than in perchlorate solutions, amounting at most to 0.02 in  $pK$  at lower ionic strengths, and it is still smaller at higher ionic strength.

Table 2. Determination of the dissociation constant of cupric sulphate in lithium sulphate solutions.  $\lambda = 272 \text{ m}\mu$ .  $\epsilon_{\text{CuSO}_4} = 120$ ,  $\epsilon_{\text{Cu}} = 0.8$ .  $c_{\text{Cu}} = 0.01003$ .

| $c_{\text{SO}_4}$ | $I$    | $e \cdot 10^3$ | $[\text{CuSO}_4] \cdot 10^3$ | $[\text{Cu}^{++}] \cdot 10^3$ | $[\text{SO}_4^{--}]$ | $pK$  |
|-------------------|--------|----------------|------------------------------|-------------------------------|----------------------|-------|
| 0.00412           | 0.0386 | 116            | 0.967                        | 9.06                          | 0.00315              | 1.529 |
| 0.00515           | 0.0409 | 138            | 1.150                        | 8.88                          | 0.00400              | 1.510 |
| 0.00618           | 0.0433 | 160            | 1.333                        | 8.70                          | 0.00485              | 1.500 |
| 0.00712           | 0.0455 | 178            | 1.483                        | 8.55                          | 0.00564              | 1.488 |
| 0.00823           | 0.0481 | 199            | 1.658                        | 8.37                          | 0.00657              | 1.479 |
| 0.00852           | 0.0491 | 198            | 1.650                        | 8.38                          | 0.00687              | 1.457 |
| 0.0103            | 0.0533 | 225            | 1.875                        | 8.15                          | 0.00843              | 1.437 |
| 0.0123            | 0.0587 | 250            | 2.08                         | 7.95                          | 0.01022              | 1.408 |
| 0.0128            | 0.0600 | 256            | 2.13                         | 7.90                          | 0.01067              | 1.403 |
| 0.0170            | 0.0711 | 299            | 2.49                         | 7.54                          | 0.01451              | 1.357 |
| 0.0213            | 0.0829 | 333            | 2.78                         | 7.25                          | 0.0182               | 1.316 |
| 0.0426            | 0.144  | 407            | 3.39                         | 6.64                          | 0.0392               | 1.115 |
| 0.0852            | 0.269  | 487            | 4.06                         | 5.97                          | 0.0811               | 0.924 |
| 0.128             | 0.397  | 534            | 4.45                         | 5.58                          | 0.124                | 0.808 |
| 0.213             | 0.649  | 621            | 5.18                         | 4.85                          | 0.208                | 0.711 |
| 0.426             | 1.284  | 705            | 5.86                         | 4.15                          | 0.420                | 0.528 |
| 0.852             | 2.559  | 794            | 6.62                         | 3.41                          | 0.845                | 0.361 |
| 1.28              | 3.841  | 883            | 7.36                         | 2.67                          | 1.273                | 0.335 |
| 1.70              | 5.099  | 933            | 7.78                         | 2.25                          | 1.692                | 0.310 |
| 2.13              | 6.387  | 1019           | 8.49                         | 1.54                          | 2.122                | 0.415 |

In Tables 3 and 4 some of the results in sodium and potassium sulphate solutions are recorded. The measurements in lithium sulphate solutions gave for the parameter  $pK_0$  in the Debye-Hückel equation the value 2.122, calculated by method of least squares. The value 2.099, obtained in the previous paper, differs so little from this value that it was used in the calculations. For the parameters of the Debye-Hückel equation in sulphate solutions the following values were obtained:

Table 3. Determination of the dissociation constant of cupric sulphate in sodium sulphate solutions.  $\lambda = 272 \text{ m}\mu$ .  $\epsilon_{\text{CuSO}_4} = 120$ .  $\epsilon_{\text{Cu}^{++}} = 0.8$ .  $c_{\text{Cu}} = 0.01150$ .

| $c_{\text{SO}_4}$ | $I$   | $e \cdot 10^3$ | $[\text{CuSO}_4] \cdot 10^3$ | $[\text{Cu}^{++}] \cdot 10^3$ | $pK$  |
|-------------------|-------|----------------|------------------------------|-------------------------------|-------|
| 0.1316            | 0.384 | 667            | 5.55                         | 5.95                          | 0.869 |
| 0.232             | 0.702 | 764            | 6.36                         | 5.14                          | 0.737 |
| 0.493             | 1.464 | 887            | 7.39                         | 4.11                          | 0.568 |
| 0.733             | 2.190 | 955            | 7.96                         | 3.54                          | 0.491 |
| 0.976             | 2.924 | 1018           | 8.48                         | 3.02                          | 0.462 |

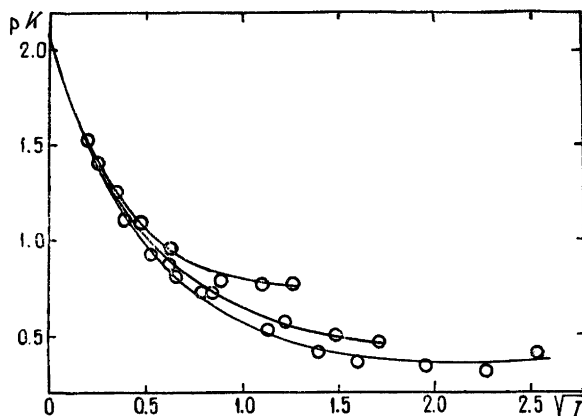


Fig. 2. Dissociation constant of cupric sulphate in lithium (lower curve), sodium (middle curve) and potassium (upper curve) sulphate solutions.

Table 4. Determination of the dissociation constant of cupric sulphate in potassium sulphate solutions.  $\lambda = 272 \text{ m}\mu$ .  $\epsilon_{\text{CuSO}_4} = 120$ .  $\epsilon_{\text{Cu}^{++}} = 0.8$ .  $c_{\text{Cu}} = 0.01150$ .

| $c_{\text{SO}_4}$ | $I$                      | $e \cdot 10^3$ | $[\text{CuSO}_4] \cdot 10^3$ | $[\text{Cu}^{++}] \cdot 10^3$ | $pK$  |
|-------------------|--------------------------|----------------|------------------------------|-------------------------------|-------|
| 0.0766            | 0.218                    | 666            | 5.55                         | 5.95                          | 1.080 |
| 0.1415            | 0.393                    | 792            | 6.60                         | 4.90                          | 0.970 |
| 0.271             | 0.795                    | 857            | 7.14                         | 4.36                          | 0.793 |
| 0.402             | 1.202                    | 960            | 8.00                         | 3.50                          | 0.763 |
| 0.531             | 1.580                    | 1038           | 8.65                         | 2.85                          | 0.765 |
|                   |                          | $pK_0$         | $a$                          | $B$                           |       |
|                   | $\text{K}_2\text{SO}_4$  | 2.099          | 1.762                        | 0.155                         |       |
|                   | $\text{Na}_2\text{SO}_4$ | 2.099          | 1.676                        | 0.0534                        |       |
|                   | $\text{Li}_2\text{SO}_4$ | 2.099          | 1.536                        | 0.0576                        |       |

Fig. 2 shows the variation of the dissociation constant of cupric sulphate with ionic strength in alkali sulphate solutions. It is seen that  $pK$  is highest in potassium sulphate and lowest in lithium sulphate solutions. Thus at a given ionic strength

$$pK(\text{LiClO}_4) > pK(\text{NaClO}_4)$$

but

$$pK(\text{Li}_2\text{SO}_4) < pK(\text{Na}_2\text{SO}_4) < pK(\text{K}_2\text{SO}_4)$$

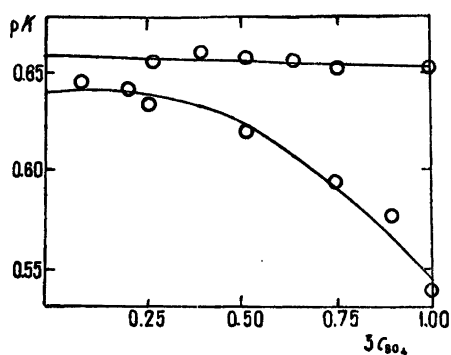
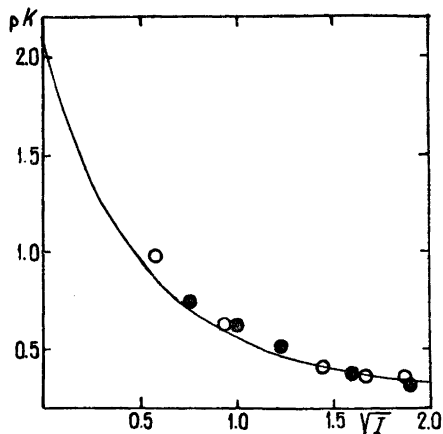


Fig. 3. Dissociation constant of cupric sulphate in mixed solutions. Upper curve: sodium perchlorate - sodium sulphate ( $I = 1.0$ ). Lower curve: sodium perchlorate - lithium sulphate ( $I = 1.2$ ).

The order in perchlorate solutions is obviously the «normal» one. The reverse order in sulphate solutions may perhaps be attributed to a further complex formation or ionic association. The possibility of the existence of higher complexes between cupric and sulphate ions is discussed in the previous paper<sup>1</sup>. It seems, however, improbable that these complexes would exist to any appreciable extent. According to Onsager's<sup>2</sup> as well as to Righellato and Davies'<sup>3</sup> interpretation of conductance data such ions as  $\text{LiSO}_4^-$ ,  $\text{NaSO}_4^-$  and  $\text{KSO}_4^-$  are present in alkali sulphate solutions. The estimated dissociation constants were 0.23, 0.20 and 0.15 respectively. Accordingly the effect of these ions would be appreciable but the reverse order of the salt effect in sulphate solutions cannot be explained by means of them. But, by means of such ions as  $\text{LiCuSO}_4^+$ ,  $\text{NaCuSO}_4^+$  and  $\text{KCuSO}_4^+$  the mentioned effect may be explained. The effect of these ions depends on their dissociation constant values as well as on the values of the molar extinction coefficients. The correction of  $pK$  is positive when the molar extinction coefficient of such an ion is small, and negative when the molar extinction coefficient is great. It may thus be possible that the calculated value of  $pK$  is too high in potassium sulphate solutions but too low in sodium and lithium sulphate solutions. This correction would change the results also in perchlorate solutions but in a still less degree.

Some measurements were carried out in mixed solutions of sodium perchlorate and sodium sulphate at constant ionic strength ( $I = 1.0$ ). The results represented in Fig. 3 show that the  $pK$  values in these solutions vary linearly with the quantity  $3c_{\text{SO}_4}/I$ , as expected. The fact that the activity coefficients in sodium perchlorate and sodium sulphate solutions are nearly equal, permits determination of the dissociation constant and of the molar extinction coefficient of cupric sulphate at a constant ionic strength, by the use of equations (1) and (2), where  $K$  and  $\epsilon_{\text{CuSO}_4}$  are the only unknowns.

Fig. 4. Effect of wavelength and total copper concentration on the results. Solid line:  $c_{\text{Cu}} = 0.01003$ ,  $\lambda = 272 \text{ m}\mu$ . The empty circles:  $c_{\text{Cu}} = 0.1511$ ,  $\lambda = 310 \text{ m}\mu$ . The filled circles:  $c_{\text{Cu}} = 0.259$ ,  $\lambda = 310 \text{ m}\mu$ . At  $310 \text{ m}\mu$   $\epsilon_{\text{CuSO}_4} = 3.80$ ,  $\epsilon_{\text{Cu}^{++}} = 0.08$ .



Similar series was carried out in mixed solutions of sodium perchlorate and lithium sulphate at constant ionic strength ( $I = 1.2$ ). The results of these measurements are also given in Fig. 3. The relation between  $pK$  and  $3c_{\text{SO}_4}/I$  is not linear in this case as expected on the basis of the above results, because, by adding lithium sulphate to sodium perchlorate solution the ion combination  $\text{Li}^+ - \text{SO}_4^-$  obviously cause a lowering in  $pK$  values as  $pK$  is smaller in lithium sulphate solutions than in sodium perchlorate solutions, but simultaneously the combination  $\text{Li}^+ - \text{ClO}_4^-$  causes a change in the opposite direction as  $pK$  is higher in lithium perchlorate than in sodium perchlorate solutions. This relation can be represented by means of the equation

$$pK = a + bx + dx(1 - x) \quad (4)$$

where  $a$ ,  $b$ ,  $d$  are parameters and  $x = 3c_{\text{SO}_4}/I$ . The calculation by the method of least squares gave

$$pK = 0.640 - 0.095 x + 0.125 x(1 - x)$$

Some measurements were carried out also at  $310 \text{ m}\mu$ . The results of these measurements which were made in lithium sulphate solutions are given in Fig. 4. The solid line refers to measurements at  $272 \text{ m}\mu$  at which the cupric sulphate concentration was  $0.01003$ . The empty circles refer to measurements at  $310 \text{ m}\mu$ ,  $c_{\text{Cu}} = 0.1511$  and the filled circles to measurements at the same wavelength,  $c_{\text{Cu}} = 0.259$ . The results at  $310 \text{ m}\mu$  agree thus relatively well with results at  $272 \text{ m}\mu$ . The two first points at low ionic strength refer to pure cupric sulphate. The dissociation constant of cupric sulphate in cupric

sulphate solutions is thus nearly equal to that in lithium or still better to that in sodium sulphate solutions. These measurements support the earlier results which seemed to prove that the first complex is the only between cupric and sulphate ions.

The accuracy of the results of this study depends chiefly on the reliability of the molar extinction coefficient values. This question was discussed in the previous paper<sup>1</sup>. It may be mentioned here that the results in perchlorate and diluted sulphate solutions are relatively insensitive to the error in the molar extinction coefficient. The concentrated sulphate solutions are in this respect more unfavourable.

#### SUMMARY

The dissociation constant of cupric sulphate has been determined in lithium and sodium perchlorate as well as in lithium, sodium and potassium sulphate solutions over a wide range of ionic strength from the light absorption measurements. The order of the salt effect is in alkali perchlorate solutions the opposite to that in alkali sulphate solutions.

The measurements in mixed solutions of sodium perchlorate and sulphate gave a linear relation between  $pK$  and the composition. Similar measurements in mixed solutions of lithium sulphate and sodium perchlorate proved that the relation between  $pK$  and the composition is not linear.

The possibility of existence of other complexes than  $\text{CuSO}_4$  in the solutions investigated is discussed. The measurements at different wavelengths and total copper concentrations support the result of the previous paper<sup>1</sup> that the first complex  $\text{CuSO}_4$  is practically the only between cupric and sulphate ions.

#### REFERENCES

1. Näsänen, R. *Acta Chem. Scand.* 3 (1949) 179.
2. Onsager, L. *Physik. Z.* 28 (1927) 277.
3. Righellato, R. C., and Davies, C. W. *Trans. Faraday Soc.* 23 (1930) 592.

Received June 8, 1949.