XVIII.—*The Colour of Cupric Salts in Aqueous Solution.*

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THE question of the influence of electrolytic dissociation on colour has recently been the subject of much discussion. It is held by one school, following Ostwald, that dissociation alone is sufficient to account for a change of colour; whilst other chemists, such as Hantzsch, maintain that the colour of an undissociated molecule in solution is identical with that of the ions which it produces, and that the observed changes of colour are due to changes of constitution. It was with the view of obtaining some information on this question that the following experiments were carried out; and although the results are as yet inconclusive, they seem of sufficient interest to be worth recording.

The changes of colour shown by solutions of cupric salts have long been known, and have been the subject of many investigations. These have, however, been directed mainly to two points: either to showing that in very dilute solution the light-absorption of all cupric salts is the same, being that of the cupric ion, or to discovering the conditions which determine the fairly sharp change from blue to green or brown, exhibited by most cupric salts at high concentrations.

The first point may be taken as satisfactorily established for coloured ions in general, by the work of Ostwald (*Zeitsch. physikal. Chem.*, 1892, **9**, 579), Pfüger (*Ann. Physik*, 1903, [iv], **12**, 430), and others; the colour of an ion in a completely dissociated solution is unaffected by the other (colourless) ion by which it is accompanied. The second point is still somewhat obscure, but the researches of Donnan and Bassett (*Trans.*, 1902, **81**, 939) make it probable that the change of tint in concentrated solution is due to the formation of complex ions or complex undissociated molecules.

Much less attention has been directed to the region lying between these two extremes, where the solution is sufficiently dilute to be blue, and yet is not wholly dissociated. Such work as has been done has all been spectroscopic, consisting either in the measurement of the absorption bands, or in the determination of the intensity of the absorption for light of certain definite wave-lengths. The former method is open to various objections; as Ewan says (*Phil. Mag.*, 1892, [v], 33, 317): "It is quite possible that general absorption may exist in a spectrum which, not being sufficiently large altogether to extinguish the light at any place, may pass unnoticed." In the latter method (compare B. E. Moore, *Zeitsch. physikal. Chem.*, 1906, 55, 641), the very abundance of data obtainable has so far prevented any definite quantitative relations being deduced, although various observers have noticed, for example, the great depth of colour of the acetate solution, and that this diminishes on dilution.

It seemed possible that a clearer view would be obtained by the direct quantitative determination of the depth of colour of the blue solutions of various cupric salts at varying dilutions. This we have endeavoured to carry out. The apparatus used was the Donnan tintometer (*Zeitsch. physikal. Chem.*, 1896, 19, 465); the method of working is that of Donnan, slightly modified, as described by T. S. Moore and one of us (*Zeitsch. physikal. Chem.*, 1907, 58, 385). The principle is simple. Two graduated glass tubes with plane glass bottoms are equally illuminated by an incandescent gas burner; one is filled with the liquid to be examined, the other with a standard solution the height of which can be altered at will. The upper surface of the liquid in both tubes is free. By a suitable arrangement of mirrors the lights transmitted by the two tubes are brought into immediate contiguity, and the level of the standard liquid adjusted until the two tints appear identical. The depth of colour of the liquid in the first tube is then directly proportional to the height of the standard liquid in the second. This apparatus will only compare two colours the tint of which is the same. Even a small difference in the nature of the colour makes it impossible to find a point of equality, and hence our measurements were necessarily limited by the concentration at which the green colour makes its appearance.

The standard used was an approximately fifth-(molecular)-normal copper sulphate solution, slightly acidified with sulphuric acid in order to eliminate any influence of alkali dissolved from the glass. It was not necessary to know the exact strength of this standard, as its value was determined each day by comparison with a solution of known strength and depth of colour. The experimental tubes were found by calibration to be of equal diameter throughout. Hence, if a known volume of a copper solution is placed in the tube, and successive

quantities of water are added, the optical thickness (concentration of copper multiplied by thickness of layer) remains unaltered, the concentration itself being measured by the height of the liquid in the tube.

The simplest hypothesis is that the changes which accompany dilution, whether they consist in the breaking down of complexes, in ionic dissociation, or in changes in the state of hydration, do not involve any alteration in the absorption. If this is the case, the colour will be proportional to the optical thickness; moreover, the (colourless) anion, since it does not affect the colour at infinite dilution, will not affect it at any other dilution either. This, however, is not the case; the colour depends both on the concentration and on the nature of the anion. This dependence is most easily expressed by determining at various dilutions and for various salts what may be called the molecular depth of colour; that is to say, the amount of colour of a gram-molecule of the salt, dissolved in various quantities of water, and contained in a tube of uniform diameter, the colour of a gram-molecule of copper sulphate in 5 litres of water being taken as 1. This magnitude we denote by C_v .

The following example will make the method of calculation clear.

Each solution was measured by both of us separately, the mean of at least four concordant values for each observer being taken. If these means were not themselves concordant (within 0.5 mm. on a total height of from 4 to 12 cm.) the measurements were repeated. The temperature of observation was 18°.

Thus with cupric acetate the following values were obtained. Ten c.c. of a $N/5$ solution were taken and diluted to a height of 5.22 cm. (volume = 30 c.c. V , the volume of solution in litres containing 1 gram-molecule of the salt = 15). The readings of the standard were:

N. V. S.*	3.80 cm.	H. T. T.*	3.79 cm.
	3.80 "		3.80 "
	3.82 "		3.81 "
	3.79 "		3.80 "
	<hr/>		<hr/>
	3.80 "		3.80 "
Mean,	3.80 cm.		

Water was then added until the liquid stood at 6.09 cm. (Volume = 35 c.c. $V = 17.5$.) Readings:

N. V. S.	3.75 cm.	H. T. T.	3.70 cm.
	3.71 "		3.72 "
	3.71 "		3.70 "
	3.72 "		3.70 "
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	3.72 "		3.70 "
Mean,	3.71 cm.		

Author's initials.

The tube was then filled with the $N/5$ -copper sulphate solution to a height of 8.70 cm. (= 50 c.c.), and read again :

N. V. S.	3.70 cm.	H. T. T.	3.70 cm.
	3.67 "		3.68 "
	3.67 "		3.65 "
	3.71 "		3.68 "
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	3.69 "		3.68 "
Mean,	3.69 cm.		

Now, since 50 c.c. of the $N/5$ sulphate solution balance 3.69 cm. of the standard, 5,000 c.c. (containing 1 gram-molecule) in a tube of this diameter would balance 369 cm. This therefore is the unit of colour.

In the first case quoted, 30 c.c. of $N/15$ copper acetate balance 3.80 cm. Hence 15,000 c.c. (one gram-mol.) would balance 3.80×500 cm. Thus the value of C_v for the acetate at $V=15$ is $\frac{3.80 \times 500}{369} = 5.15$. Similarly in the second case, where the optical

thickness is the same, $C_v = \frac{3.72 \times 500}{369} = 5.02$.

The salts examined fall into two classes, which gave very different results : (1) those of weak acids (propionate, acetate, formate, monochloroacetate), and (2) those of strong acids (sulphate, chloride, bromide, and nitrate). The salts of the second class are very difficult to measure accurately. Their colour is very much paler than that of the weak acid salts, even in the strongest solutions, and the change of colour with dilution, which is always an increase, is very small ; but we give the results for what they are worth.

The weak acid salts, on the other hand, have a much deeper colour, which is deeper the weaker the acid, and the effect of dilution is much greater, and in the opposite direction, the colour diminishing with the concentration.

In the following tables, V represents the number of litres containing a gram-molecule, h the mean height of the balancing column of standard, and C_v the molecular depth of colour. The measurements of copper sulphate give the height of standard required to balance 8.70 cm. (50 c.c.) of the $N/5$ sulphate solution on each occasion. The temperature was in all cases 18° .

1. *Cupric Propionate*.—Three series of observations were made. The first two, (a) and (b), were not compared with the sulphate, but were referred through the values for $V = 20$ to (c), which was directly compared with the sulphate. In (c) the liquid was diluted up to a height of 15.66 cm. ($V=22.5$) and then a portion was poured

away. The remainder, which measured 10.04 cm., was then further diluted, the necessary correction being applied in calculating C_v :

(a). 10 c.c. $N/5$ solution taken.

V .	h in cm.	C_v .
5	6.25	8.01
10	4.77	6.12
15	4.24	5.44
20	3.90	(5.00)

(b). 10 c.c. $N/5$ solution taken.

V .	h in cm.	C_v .
10	4.68	6.16
20	3.80	(5.00)
25	3.50	4.60
30	3.39	4.46
35	3.31	4.35
45	3.16	4.16

(c). 20 c.c. $N/5$ solution.

V .	h in cm.	C_v .
13	8.32	5.62
15	8.03	5.43
17.5	7.73	5.22
20	7.40	5.00
22.5	7.19	4.86
22.5	4.65	4.86
25	4.50	4.70

V .	h in cm.	C_v .
27.5	4.43	4.63
30	4.28	4.47
32.5	4.20	4.40

Copper sulphate : 50 c.c. $N/5$ solution.

5	3.70	1
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2. *Cupric Acetate* : 10 c.c. $N/5$ solution.

V .	h in cm.	C_v .
5	4.86	6.59
7.5	4.39	5.95
10	4.13	5.59
12.5	3.99	5.41
15	3.80	5.15
17.5	3.71	5.03
20	3.61	4.89

V .	h in cm.	C_v .
25	3.49	4.73
30	3.38	4.58
40	3.22	4.36

Copper sulphate : 50 c.c. $N/5$ solution.

5	3.69	1
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3. *Cupric Formate*.

(a). 10 c.c. $N/3$ solution.

V .	h in cm.	C_v .
3	4.84	3.90
9	4.03	3.25
12	3.89	3.14
15	3.88	3.13
18	3.83	3.09

Sulphate : 50 c.c. $N/5$ solution.

5	3.73	1
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(b). 10 c.c. $N/3$ solution.

V .	h in cm.	C_v .
3	4.89	3.88
6	4.32	3.43
9	4.10	3.24

Sulphate : 50 c.c. $N/5$ solution.

5	3.78	1
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4. *Cupric Monochloroacetate* : 10 c.c. normal solution.

V .	h in cm.	C_v .
1	13.97	3.74
2	11.82	3.17
3	10.92	2.92
4	10.38	2.78
5	10.08	2.70
6	9.85	2.64

V .	h in cm.	C_v .
7	9.44	2.53
8	9.30	2.50
9.6	8.89	2.38

Sulphate : 50 c.c. $N/5$ solution.

5	3.73	1
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5. *Cupric Sulphate* : 10 c.c. normal solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>	<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
1	3.44	0.91	5	3.80	1.00
2	3.62	0.95	6	3.83	1.01
3	3.75	0.98	7	3.94	1.04
4	3.72	0.98			

6. *Cupric Chloride*.

(a). 10 c.c. normal solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
3	3.45	0.96
4	3.58	0.98
5	3.63	1.01
6.5	3.64	1.01
7	3.61	1.00

Sulphate : 50 c.c. *N*/5 solution.

5	3.61	1
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(b). 10 c.c. normal solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
2	3.69	0.95
4	3.82	0.98
6	3.83	0.98
9	3.98	1.02

Sulphate : 50 c.c. *N*/5 solution.

5	3.90	1
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7. *Cupric Bromide* : 20 c.c. 2*N*/3 solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
3	4.60	0.94 (still green)
4.5	4.71	0.96
5	4.70	0.96
7	4.71	0.96

Sulphate : 50 c.c. *N*/5 solution.

5	3.66	1
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8. *Cupric Nitrate*.

(a). 10 c.c. normal solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
1	3.91	1.08
2	3.84	1.06
3	3.89	1.07
4	3.90	1.07
5	3.91	1.08
7	3.97	1.10
9	4.06	1.12

(b). 10 c.c. 2*N* solution.

<i>V.</i>	<i>h</i> in cm.	<i>C_v</i>
0.5	8.24	1.14
1	7.70	1.07
1.5	7.65	1.06
2	7.64	1.06

Sulphate : 50 c.c. *N*/5 solution.

5	3.61	1
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The curves given in Fig. 1 represent the relation between colour and concentration for the salts of weak acids. The curve for copper sulphate is added for comparison. It is not a straight line, but would appear practically straight on the scale employed.

In the case of the strong acids, the concentrations which could be investigated were limited on the one hand by that at which the solution assumes a green tint (or in the case of the sulphate by the solubility), and on the other by that at which the colour (even with a

layer of 17 cm.) becomes too pale for measurement. This gives practically the limits of $V=1$ to $V=9$. The variations of colour

FIG. 1.

within these limits are very small. They are represented in Fig. 2, the colour-scale being very large, but they cannot be regarded as having more than a qualitative value.

FIG. 2.

Discussion of Results.

1. *Weak Acid Salts.*—We may assume that at extreme dilution equivalent solutions of all cupric salts with colourless anions have the same tint and depth of colour. The value for infinite dilution cannot be determined by our method; but from the course of the curves for strong acid salts, where the change of colour with dilution is small, and the dissociation even at $V=9$ is already very large, it is probable that the limiting value of C_v is less than 1.5.

At the highest dilutions examined the salts of weak acids have a value of C_v considerably higher than this, rising from about two for the chloroacetate to four for the acetate and propionate. As the concentration increases, C_v increases also, and the more rapidly the weaker the acid,* until at about $V=4$, where it has reached for the acetate a value of 7, and for the propionate of more than 8, the solution begins to show a distinct greenish tinge, and further measurements become impossible.

It is therefore evident that these cupric solutions contain at least two substances of the same blue tint, but differing in depth of colour. The identity of tint is especially to be noticed, as it is not at all what we should expect. As it appears that the depth of colour of cupric solutions depends, except at extreme dilution, on the nature of the anion, it is clear that this is due at least to the recombination of the anion with the cupric cation, and hence the view that ionisation has no effect on colour is incorrect. But it would seem that, at least in these cases, it is only the depth of colour that is affected by the anion, and not the tint. As has been explained, all the solutions we examined, whether of strong or weak acids, were compared with the same standard, a $N/5$ copper sulphate solution; and up to a concentration of $N/4$ (in some instances much higher than this) no change of tint was observed, although the depth varied with the anion and the dilution in the proportion of 1 to 8. It follows that the cupric ion is capable of forming compounds in the solution of a different depth of colour, but of practically the same absorption in the visible part of the spectrum. These compounds may be of four kinds: either the univalent ions CuA^+ (where A represents a univalent anion) and the undissociated molecules CuA_2 , or complex ions such as CuA_4^{2-} , or the products of hydrolytic dissociation, or hydrates of any of these molecular species. The last of these possibilities may be left out of account, as practically nothing is known as to the constitution of these hydrates or their

* The dissociation constants of these acids are:—

Propionic, $K \times 10^4$	= 0.134	Formic.....	= 2.14
Acetic	0.180	Monochloroacetic ...	15.00

influence on colour (compare Donnan, *Zeitsch. physikal. Chem.*, 1905, **53**, 317). The recent work of Jones and Uhler (*Amer. Chem. J.*, 1907, **37**, 126, 207) is open to the general objections which apply to the spectrometric method, and, moreover, their plan of adding to the solution a colourless salt with the same anion must produce a disturbance of the ionic equilibrium the amount of which can scarcely be determined, and which they altogether fail to consider. The question of hydrolysis is one on which it is difficult to come to a definite conclusion, and there are no determinations of the amount of hydrolysis of salts of the type MX_2 . But there are several reasons for thinking that its influence is small, and may be, at least provisionally, neglected. In the first place, if hydrolysis were the determining factor in the change of colour, we should expect this change to be much more rapid with the salts of the weakest acids (acetate and propionate) than with those of the much stronger formic and chloroacetic acids: whereas the reverse is the case. Again, it is not to be supposed that anything like complete hydrolysis has taken place at a dilution of $N/40$, at which the hydrolysis of sodium acetate is only 0.02 per cent., and even that of potassium cyanide is less than 3 per cent.; so that the colour-curves should still be tending downwards at this point, whereas they have become nearly horizontal. Finally, a rough idea of the influence of hydrolysis can be arrived at by observing the effect on the colour of adding free acetic acid to a copper acetate solution. The amount of hydrogen ions in the solution due to hydrolysis will be small compared with the total quantity of acetate ions, and hence the addition of free acid will greatly diminish the hydrolysis without much affecting the degree of ionic dissociation of the salt. Experiment showed that the colour of a solution of $N/6$ copper acetate was increased less than 1 per cent. by the presence of $N/2$ acetic acid. We therefore conclude that while hydrolysis must be regarded as a possible disturbing factor, it is not probable that it has an appreciable effect on our results.

As regards complex ions, it is probable, as Donnan has shown, that it is to the presence of complex anions containing copper that the green or brown colour of concentrated solutions is due.

We are therefore inclined to suggest that the point where the solution changes from green to blue is that at which these complex ions become negligible in quantity, and the solution contains no molecules other than CuA_2 and the ions CuA' , Cu'' , and A' . Of these, the last, as we know, will have no influence on the absorption, and may be neglected. The absorption will therefore be due to the three species CuA_2 , CuA' , and Cu'' (or some of them); identical in tint, but differing in depth of colour; and the change of colour on dilution will be caused by the production of the latter species at the expense of

the former. On extreme dilution only Cu^{++} ions remain, whatever the nature of the anion, and here therefore all copper salts give the same absorption: the value of C_v for this, as we have shown, is probably between 1 and 1.5. If it were possible in any way to determine the amounts of CuA_2 , CuA' , and Cu^{++} present in a solution, their colour-values could be calculated, and our hypothesis checked. But at present this does not appear to be possible. There is no means of measuring the amount of dissociation of a ternary salt, such as CuA_2 . The conductivity is no guide, since we cannot determine the velocity of the ion CuA' , and the indirect methods which have been suggested, such as the measurement of the concentration of the ion A' by the solubility-product, are not sufficiently accurate.

If there are appreciable quantities of all the three coloured substances CuA_2 , CuA' , and Cu^{++} present in the solution, both the changes $\text{CuA}_2 \rightarrow \text{CuA}'$ and $\text{CuA}' \rightarrow \text{Cu}^{++}$ must occur on dilution. If the second of these occurs to an appreciable extent within the dilutions investigated, we should expect all the curves to tend to the same point, the colour of the Cu^{++} ion, $C_v = 1.5$. We should also expect a change in the nature of the curve at the point where the second dissociation began to make itself felt. But neither of these conditions is fulfilled. There is no change in the nature of the curves, and they each tend to a different limit, which is always greater than 1.5. From these results, and especially from the second, we infer that only one dissociation is taking place, and that this is the first one, $\text{CuA}_2 \rightarrow \text{CuA}'$. This leads to a somewhat remarkable conclusion. It will be seen from the shape of the curves that whatever change has been going on during the dilution has very nearly reached its end at the highest dilutions observed, since at this point all the curves become very nearly horizontal. If, therefore, our view is correct, the second dissociation of a copper salt of a weak acid cannot begin to take place appreciably until the first has proceeded very far; whereas in the analogous case of the dibasic organic acids Ostwald has shown that the second dissociation takes place appreciably when the first is only half completed. In other words, in the copper salts of weak monobasic acids the second dissociation constant is very much smaller compared to the first than it is in the case of the organic dibasic acids themselves. And the reason for this is not far to seek. Ostwald has pointed out for the latter that in analogous series the larger the first ionisation-constant, the smaller the second. This he explains by the fact that the proximity of the two carboxyl groups, which increases the first ionisation-constant, at the same time diminishes the second, as the negative charge produced by the loss of the first hydrogen ion resists the appearance of a second negative charge, which must occur if a second hydrogen ion were split off; and does so

If this view is correct, which seems at least possible, we have an explanation of the fact which appears very clearly from our curves, that the dissociation proceeds very far within the limits of dilution examined, and yet does not give any sign of the production of Cu^{++} ions, which would lead to a value of C_p below 1.5.

$$C_p = a(1 - x) + bx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$
[illegible]
$$kV\left(-V\frac{dC_v}{dV}\right)\left(a-C_v+V\frac{dC_v}{dV}\right)=\left(a-C_v+2V\frac{dC_v}{dV}\right)^2. \quad (3).$$

The results we arrived at by applying this method to the weak acid curves confirm our hypothesis, as constant values of b are obtained in each case, while x , the degree of dissociation, rises to over 90 per cent. But as the numbers cannot, for the reasons we have given, be regarded as absolutely correct, but only relatively so, we propose to reserve their publication until we have obtained more trustworthy data.

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to increase rapidly. This indicates that in this case the complex ions have the same tint as the $\text{Cu}(\text{NO}_3)_2$ molecule, but are deeper in colour.

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