

## CUPRIC OXIDE JELLIES

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Foerster<sup>1</sup> prepared a cupric oxide jelly by the hydrolysis of a solution of cupric ammonium acetate of the formula  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3$ . The latter was prepared in a very pure crystalline state by addition of excess alcoholic ammonia to an alcoholic solution of cupric acetate and distilling off the excess alcohol. A solution of this highly soluble salt was prepared either by the addition of a very small amount of water or by allowing the salt to deliquesce. On diluting this concentrated solution a jelly was formed which changed in time to a fine powder.

Finch<sup>2</sup> working in Bancroft's laboratory has repeated and extended the investigations of Foerster. He found that a jelly could be obtained simply by adding an excess of water directly to the crystals of cupric ammonium acetate and shaking to ensure rapid solution. Like Foerster, Finch observed that the jelly was not permanent and that quite as good a suspension was obtained which approached a jelly in properties simply by adding ammonia in suitable amount to saturated  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; but this method was unsatisfactory as a gelatinous precipitate formed in a short time. It was found that a good jelly could be obtained by the addition of 0.5 gm. of  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$  to 50 cc. of saturated  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  and precipitating with 3 cc of diluted ammonia (1:1). Since no jelly was obtained by the addition of  $\text{NH}_4\text{OH}$  to a solution of  $\text{CuSO}_4$  it was thought that the manganese radical was the effective one. This proved incorrect since no jellies could be obtained in the presence of manganese salts other than the sulphate. To reconcile the good effect of a small amount of manganous sulphate with the fact that  $\text{CuSO}_4$  gave no jelly it was concluded that a small amount of sulphate was the

<sup>1</sup> Ber. deutsch. chem. Ges., 25, 3416 (1892).

<sup>2</sup> Jour. Phys Chem., 18, 26 (1914).

important thing. This was proven to be true. A good jelly resulted by using 50 cc saturated  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 4 drops of concentrated  $\text{H}_2\text{SO}_4$  and 3-4 cc diluted ammonia (1:1).  $\text{K}_2\text{SO}_4$  in small amount could be substituted for  $\text{H}_2\text{SO}_4$  but a permanent jelly was not obtained using a small amount of  $\text{CuSO}_4$ . Finch's experiments led to the conclusion that permanent cupric oxide jellies can be formed only by the addition of a suitable amount of ammonia to cupric acetate solution in the presence of a small amount of sulphate ion. No explanation is suggested to account for the facts: first, that a limiting concentration of ammonia is necessary; second, that copper acetate is effective but not copper sulphate, chloride, or nitrate; and third, that the presence of a small amount of sulphate ion in conjunction with copper acetate is necessary for the formation of a permanent jelly.

I have pointed out that in general a jelly will be formed if a suitable amount of a hydrous substance is gotten into colloidal solution and allowed to precipitate at a suitable rate.<sup>1</sup> The presence of salts influence the formation of jellies in so far as the precipitating and stabilizing action of the ions affect the rate of precipitation. Since cupric oxide adsorbs water strongly it possesses the necessary property for forming a jelly providing it is allowed to precipitate at a suitable rate. It seemed probable therefore that the specific conditions for the formation of a cupric oxide jelly as found by Finch, could be explained in the light of the general theory. Some experiments were undertaken with this end in view.

#### Experimental

*The precipitation of cupric acetate with ammonia.* A saturated solution of cupric acetate was prepared and found by analysis to be 0.77 N. 25 cc portions were precipitated with 3, 4, 5 and 6 cc respectively of 3 N ammonia. The precipitate which was obtained in each case apparently enclosed all the water and from this point of view might be considered a jelly. The fact that it settled quickly giving a slight super-

<sup>1</sup> Jour. Phys. Chem., 26, 429, 681 (1922).

natant liquid proved that it was merely a bulky gelatinous precipitate and not a jelly. A similar precipitate was obtained with the sulphate, chloride and nitrate of copper.

The results were what might be expected. Von Weimarn<sup>1</sup> has shown that jelly-like masses of insoluble salts are formed by mixing concentrated solutions of soluble salts containing the desired ions. With the hydrous oxides the concentration of the solutions mixed need not be so great as for a salt that normally precipitates in a very slightly hydrous, crystalline form like  $\text{BaSO}_4$ . Still the general conditions are the same and it has been our experience that the bulky gelatinous precipitates obtained by rapid precipitation cannot be classed true jellies as they are quite different in appearance and in character from the firm uniform jellies obtained by slow precipitation from colloidal solutions. The failure to obtain jellies by direct precipitation led to a quantitative study of Finch's method.

*Experiments with cupric acetate and ammonium hydroxide in the presence of potassium sulphate.* A mixing apparatus was prepared consisting of a glass tube 20 cm long and 4 cm in diameter supplied with rubber stoppers. Through a hole in the center of one stopper was placed a glass rod on the end of which was sealed a 10 cc glass cup. 25 cc portions of cupric acetate were first placed in the tube together with 1, 2, 3 or 4 cc portions of potassium sulphate. In the cup were placed varying amounts of 3 N ammonium hydroxide. The tube was stoppered and inverted with a quick jerk; this ensures rapid uniform mixing. The contents of the mixer was then poured into a large test tube and allowed to stand. Observations were made each hour until a gelatinous precipitate formed, for the first 6 hours and daily thereafter for two weeks. A part of these observations are recorded in Table XIV. Where the term "precipitate" is used, is meant a gelatinous precipitate with considerable supernatant liquid, as distinct from a jelly. It will be noted that in most cases the jellies are not permanent but break down after a few hours.

<sup>1</sup> Grundzüge der Dispersoidchemie, 67 (1914).

The results recorded in Table I show the best conditions for obtaining a firm jelly while closer observations of these experiments indicate the explanation of the results. It was noted at the outset that the addition of less than the equivalent amount of  $\text{NH}_4\text{OH}$  did not produce a precipitate but a perfectly clear solution which starts to precipitate spontaneously after intervals that vary from a few seconds to several minutes depending on the amounts of  $\text{K}_2\text{SO}_4$  and  $\text{NH}_4\text{OH}$

TABLE I

Solutions added to 25 cc 0.75 N $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$		Observations after			
N $\text{K}_2\text{SO}_4$ cc	3N $\text{NH}_4\text{OH}$ cc	4 hours	1 day	7 days	14 days
1	3	Precipitate	_____	_____	_____
2	3	Soft jelly	Precipitate	_____	_____
3	3	Precipitate	_____	_____	_____
4	3	Precipitate	_____	_____	_____
1	4	Good jelly	Soft jelly	Precipitate	_____
2	4	Good jelly	Good jelly	Precipitate	_____
3	4	Good jelly	Fair jelly	Precipitate	_____
4	4	Good jelly	Precipitate	_____	_____
1	5	Good jelly	Good jelly	Fair jelly	Precipitate
2	5	Good jelly	Good jelly	Good jelly	Good jelly
3	5	Good jelly	Good jelly	Fair jelly	Precipitate
4	5	Precipitate	_____	_____	_____
1	6	Fair jelly	Precipitate	_____	_____
2	6	Fair jelly	Precipitate	_____	_____
3	6	Fair jelly	Precipitate	_____	_____
4	6	Precipitate	_____	_____	_____

added. We have seen that a comparatively slow precipitation from colloidal solution favors the formation of a firm jelly so that the problem resolved itself into finding the most favorable conditions of precipitation. A firm jelly that remained unbroken for more than 3 months was obtained by adding 5 cc of 3 N  $\text{NH}_4\text{OH}$  to 25 cc of 0.75 N  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  containing 2 cc of  $\text{K}_2\text{SO}_4$ . With too little  $\text{K}_2\text{SO}_4$  a gelatinous precipitate formed at once on adding the equivalent amount

of  $\text{NH}_4\text{OH}$ ; the same is true with an excess of  $\text{K}_2\text{SO}_4$ . With a suitable amount of sulphate and too little  $\text{NH}_4\text{OH}$  not enough precipitation takes place to form a firm jelly. This was observed with 3 cc, which is one-half the equivalent of the copper present. With too much  $\text{NH}_4\text{OH}$  not only does precipitation take place too rapidly but a portion of the copper goes to the deep blue copper ammonium complex. This was observed with 6 cc of  $\text{NH}_4\text{OH}$ , an amount equivalent to the copper. The conditions that we have found most favorable are similar to those of Finch<sup>1</sup> who obtained the best results by adding

TABLE II

Solutions added to 25 cc 0.77 N $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$		Observations after			
N $\text{CuSO}_4$ cc	3N $\text{NH}_4\text{OH}$ cc	4 hours	24 hours	7 days	14 days
1	5	Good jelly	Good jelly	Fair jelly	Precipitate
2	5	Good jelly	Good jelly	Good jelly	Fair jelly
3	5	Good jelly	Fair jelly	Precipitate	_____
$(\text{NH}_4)_2\text{SO}_4$					
	1	Soft jelly	Fair jelly	Precipitate	_____
	2	Good jelly	Good jelly	Good jelly	Good jelly
	3	Good jelly	Good jelly	Good jelly	Precipitate

3-4 cc of  $\text{NH}_4\text{OH}$  (1:1) to 50 cc of saturated  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  containing 0.5 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ . This sulphate is equivalent to 2.24 cc of N salt in 25 cc as compared with 2 cc which we have found most satisfactory.

Since  $\text{K}_2\text{SO}_4$  and  $\text{MnSO}_4$  seem equally satisfactory there seemed no reason why other sulphates including  $\text{CuSO}_4$  might not be used. The results with  $\text{CuSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  recorded in Table II confirm this view.

A close observation of the formation of the jellies showed that in every case the presence of sulphate prevented immediate precipitation; but with too little sulphate the precipitation

<sup>1</sup> Loc. cit.

was too slow and with too much sulphate, the precipitation was too rapid to form a firm permanent jelly. This action of sulphate was investigated further as described in the next paragraph.

*Action of  $\text{NH}_4\text{OH}$  on copper acetate solution in the presence of ammonium sulphate.* The amount of ammonia necessary to cause a slight permanent precipitate at once when added to copper acetate in the presence and absence of sulphate was determined as follows: 25 cc of 0.75 N copper acetate with or without  $(\text{NH}_4)_2\text{SO}_4$  was placed in the mixing apparatus and a known amount of 3 N  $\text{NH}_4\text{OH}$  in the cup. The mixer

TABLE III

Solutions mixed			Observations
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ 0.75 N	$(\text{NH}_4)_2\text{SO}_4$ N	$\text{NH}_4\text{OH}$ 3 N	
25	0.0	1.75	No precipitate
25	0.0	2.00	Very slight precipitate
25	0.2	2.75	No precipitate
25	0.2	3.00	Slight precipitate
25	0.2	3.25	Large precipitate
25	0.4	3.25	No precipitate
25	0.4	3.50	Slight precipitate
25	0.8	4-8	No precipitate. Goes over directly to the blue copper ammonium complex

was shaken and the solution observed promptly to determine whether or not a precipitate formed at once. By repeated trials the conditions for the formation of a slight permanent precipitate were found with considerable accuracy. The results are given in Table III.

It will be noted that 2 cc of 3 N  $\text{NH}_4\text{OH}$  must be added rapidly to 25 cc of 0.75 N  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  in order to get a slight permanent precipitate at once. A similar precipitate was obtained on adding but 0.10 cc of 3 N  $\text{NH}_4\text{OH}$  to 25 cc of 0.75 N solutions of  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{CuCl}_2$ . Thus the acetate is the only one of the four salts which gives colloidal

hydrous cupric oxide of appreciable concentration on adding  $\text{NH}_4\text{OH}$  to the 0.75 N solution. A much higher concentration of the colloid may be obtained by adding to the acetate solution a very small amount of sulphate ion. It is altogether likely that small amounts of multivalent ions other than  $\text{SO}_4^{--}$  would be equally effective but none of the common ions can be employed on account of the insolubility of their copper salts. The colloids obtained in this way of whatever concentration are so instable that spontaneous precipitation takes place on standing. It is this combination of circumstances that enables one to prepare a stable cupric oxide jelly by regulating the conditions so that a suitable concentration of colloid precipitates at a suitable rate.

### Summary

The results of this investigation may be summarized as follows:

1. Hydrous cupric oxide jellies are formed when a suitable concentration of colloidal oxide is precipitated at a suitable rate. The desired conditions may be realized by adding ammonia to cupric acetate in the presence of a small amount of sulphate and allowing the colloidal solution to precipitate spontaneously.

2. Jellies are not formed by adding ammonia to sulphate, chloride or nitrate since no colloid forms but immediate precipitation results with the formation of a gelatinous precipitate. Jellies are not formed by adding ammonia to cupric acetate alone since a colloid of suitable concentration cannot be prepared in this way.

3. The results of the experiments on the formation of cupric oxide jellies are in accord with the author's general theory.

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