

within limits, does not affect the amount of platinum remaining on the cathode after solution of the copper deposit.

3. The effects of certain elements on the use of diethyl dithiocarbamate as an indicator for copper have been shown.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

SOLUTIONS OF SALTS IN PURE ACETIC ACID. IV. CUPRIC ACETATE AND AMMONIUM CUPRIC ACETATE

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RECEIVED FEBRUARY 6, 1931

PUBLISHED APRIL 6, 1931

Introduction

In the first article of this series,¹ it was mentioned that cupric acetate is but slightly soluble in pure acetic acid, and that its solubility is markedly increased upon the addition of ammonium acetate; it was suggested that in this respect the cupric and ammonium acetates might be regarded as analogous to the corresponding hydroxides, whose interaction in aqueous solution is so familiar a phenomenon. No quantitative solubility data for cupric acetate in anhydrous acetic acid have been reported previously. Sandved,² however, determined the isotherm for the ternary system cupric acetate-acetic acid-water at 25°, and a short extrapolation from his data indicates the solubility in the pure acid to be about 0.24 mole per cent. of cupric acetate, the solid phase being the acid salt $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$. In the present investigation the solubility of cupric acetate over a range of temperatures has been measured, both in pure acetic acid and in the presence of ammonium acetate in varying concentration. The effect of potassium acetate, at one concentration, was determined also. Consideration of the results obtained has led to certain new ideas, which will be developed below, with respect to the analogy between these solvent effects and the corresponding phenomena in aqueous solution.

Method

Preparation of Materials.—The acetic acid, ammonium acetate and potassium acetate employed were all prepared as described in the second paper of this series.³ The anhydrous cupric acetate used was prepared by recrystallizing the hydrate from solution in dilute acetic acid, and dehydrating at 90° until analysis showed no water to be present. Samples of the product, which was dark bluish-green, were analyzed for copper by the electrolytic and by the iodimetric method, and gave closely concordant results, averaging 34.99% of copper (calcd. for $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, 35.00%).

Binary System.—The solubility of cupric acetate in pure acetic acid was determined

¹ Davidson, *THIS JOURNAL*, 50, 1890 (1928).

² Sandved, *J. Chem. Soc.*, 2967 (1927).

³ Davidson and McAllister, *THIS JOURNAL*, 52, 507 (1930).

by the freezing point method previously described,³ large stoppered test-tubes provided with thermometer and stirrer being used for the freezing point determinations. Short-range calibrated thermometers were employed, and each freezing point was determined at least twice. The equilibrium temperatures reported are believed to be correct to within 0.2°.

Ternary System.—In the study of the solvent effect of ammonium acetate, the method described in the preceding paper of this series⁴ was employed. Acetic acid solutions were prepared containing 7.9, 11.6, 15.1, 20.7, 22.1 and 23.7 mole per cent., respectively, of ammonium acetate. Known amounts of cupric acetate were dissolved in these solvents, and the equilibrium temperatures were determined just as in the binary systems. In these cases, however, due to the greater viscosity and deeper color of the solutions, the same degree of accuracy could not be attained; most of the temperatures reported, however, are believed to be correct to within 1°. By plotting these temperatures as ordinates against the mole percentages of cupric acetate as abscissas, a series of curves was obtained, each representing the variation with temperature of the solubility of cupric acetate in a solution having a fixed value of the ratio, number of moles of ammonium acetate/number of moles of (ammonium acetate + acetic acid), which ratio will hereafter be referred to as *R*.

Analysis of Solid Phases.—Samples of the solid phases present at equilibrium were obtained by crystallization from the solution under suitable conditions, followed by filtration and rapid drying between porous tiles. When the compound contained only cupric acetate and acetic acid, determination of copper by the electrolytic or iodimetric method sufficed to fix its composition. When a qualitative test showed ammonia to be present in the solid phase, however, a portion of the sample was analyzed for copper as above, and another portion for ammonia by addition of sodium hydroxide solution, followed by distillation into standard hydrochloric acid.

The data obtained are tabulated below, and are represented also in the accompanying diagrams. The concentration of cupric acetate in the solution is expressed throughout in mole percentage, and the equilibrium temperature is denoted by *T*.

Results

I. Binary System $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{--HC}_2\text{H}_3\text{O}_2$.—The solutions were bluish-green, and showed no change in color on heating.

(a) Solid phase $\text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.0	0.0307	0.0471	0.0831	0.0904
<i>T</i>	16.65	16.63	16.50	16.43	16.57
(b) Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.169	0.236	0.266	0.305	0.408
<i>T</i>	25.3	30.1	32.4	35.0	41.5
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.487	0.584	0.768	0.773	0.976
<i>T</i>	45.8	48.7	56.0	55.7	61.0
(c) Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ (?)					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.844	0.912	0.976		
<i>T</i>	91.3	95.5	99.0		

The curve for this system is given in Fig. 1. The solubility of cupric acetate in pure acetic acid at 25° is found to be 0.166 mole per cent., a figure

⁴ Davidson and McAllister, *THIS JOURNAL*, 52, 519 (1930).

somewhat smaller than that obtained by extrapolation from the data of Sandved.²

The solid phase (b) was light blue-green in color, and was quite unstable, rapidly losing acetic acid vapor on exposure to the atmosphere. Because of this instability, a high degree of accuracy was not to be expected in its analysis; the percentage of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ would tend to be too high. Five analyses for copper, in which the samples were handled as rapidly as possible before weighing, gave the following results (calculated to mole per cent. of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$): 51.14, 54.41, 56.02, 52.73, 50.28; average 52.93%. It is believed that these figures establish satisfactorily that the compound is the solvate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$, previously reported by Sandved. In the neighborhood of 50° this compound undergoes transition to a dark bluish-green substance (c) which could not be obtained in sufficient quantity for analysis, but which appears to be unsolvated $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.

II. Ternary System $\text{NH}_4\text{-C}_2\text{H}_3\text{O}_2\text{-Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-HC}_2\text{H}_3\text{O}_2$.—These solutions were greenish-blue at ordinary temperatures. On heating, a

marked deepening in color took place, together with a change toward the violet. At temperatures in the neighborhood of 120° for small values of R , or lower for the larger values, they attained a deep violet-blue color strongly reminiscent of aqueous cupric ammonia solutions; on cooling, they resumed their original greenish-blue color. This color change will be discussed later.

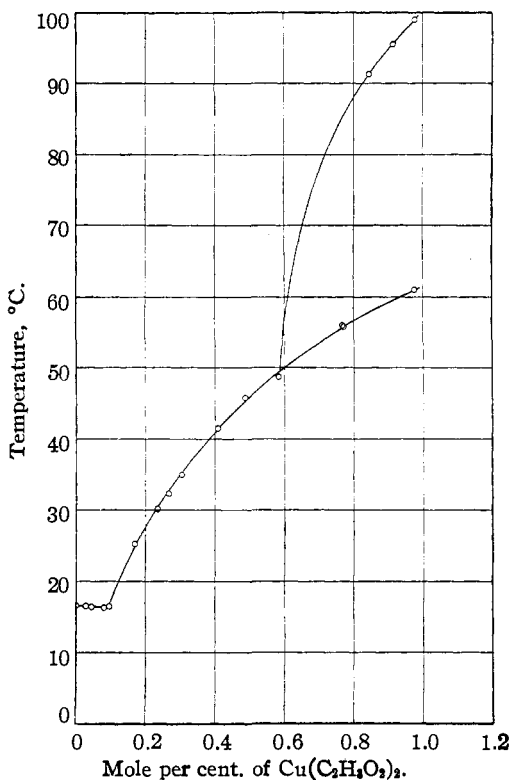


Fig. 1.—Solubility curve of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ in pure $\text{HC}_2\text{H}_3\text{O}_2$.

A. Mole ratio $R = 0.079$. Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$

$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %	0.624	0.693	0.800	0.929
T	33.8	37.3	40.7	45.2

B. Mole ratio $R = 0.116$. Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.816	1.026	1.179		
T	32.5	38.5	42.7		
C. Mole ratio $R = 0.151$. Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	1.005	1.072	1.273	1.488	1.746
T	28.0	31.8	36.8	41.2	42.7
D. Mole ratio $R = 0.207$. (a) Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.796	1.188	1.584		
T	31.5	32.5	33.5		
(b) Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	1.708	1.766	1.890		
T	37.0	40.7	41.8		
E. Mole ratio $R = 0.221$. Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.777	1.125	1.399		
T	31.0	34.0	34.0		
F. Mole ratio $R = 0.237$. Solid phase $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$					
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, %.....	0.448	0.532	0.765		
T	48.0	50.5	54.0		

The curves for this system are given in Fig. 2; for purposes of comparison, part of the curve for the binary system is reproduced here also. In

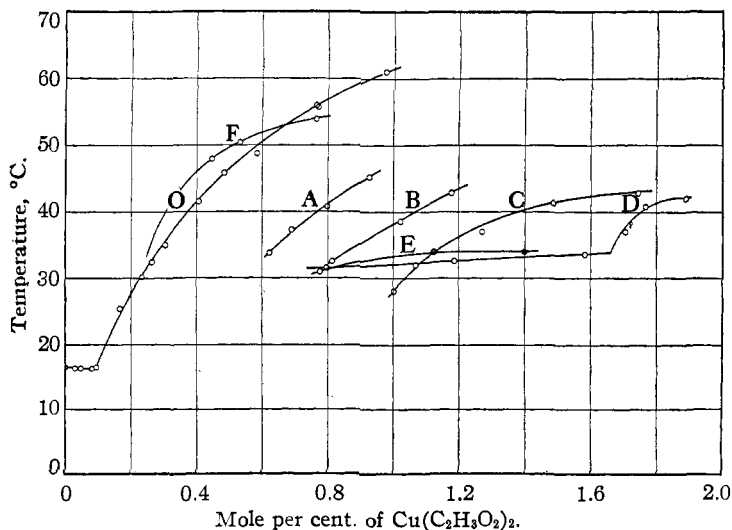


Fig. 2.—Solubility curves of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ in $\text{HC}_2\text{H}_3\text{O}_2$ containing various concentrations of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$: O, $R = 0$ (pure $\text{HC}_2\text{H}_3\text{O}_2$); A, $R = 0.079$; B, $R = 0.116$; C, $R = 0.151$; D, $R = 0.207$; E, $R = 0.221$; F, $R = 0.237$.

series A, B, C and D (b), the solid phase was light blue-green in color, as in (b) of the binary system; qualitative tests showed it to contain no am-

monia. No quantitative analysis of this compound was made, since its close resemblance in appearance and behavior to the solid phase which had been isolated, under similar conditions, from the binary system, was deemed sufficient to identify it as the same substance, namely, the solvated cupric acetate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$. Further evidence of the correctness of this conclusion is to be found in the solubility isotherm of Fig. 3 (to be discussed in detail later); it will be seen that the solubility values for cupric acetate in pure acetic acid and at the lower concentrations of ammonium acetate fall upon a perfectly smooth curve, which could hardly be the case unless they referred to the same solid phase throughout this range.

In series D(a), E and F, the solid phase was quite evidently a different compound from that just discussed. It was deep blue in color, fairly stable on exposure to the atmosphere, and evolved ammonia on treatment with sodium hydroxide. In this case, the high viscosity of the mother liquor made its complete removal difficult; three quantitative analyses, however, gave the following results

	Mole. % $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	Mole. % $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	Mole. % $\text{HC}_2\text{H}_3\text{O}_2$ (by difference)
	10.85	46.18	42.97
	9.49	43.49	47.02
	10.17	44.16	45.67
Average	10.17	44.61	45.22
Calcd. for $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$	11.11	44.44	44.44

These figures leave little room for doubt that the deep blue substance is a ternary compound, or solvated ammonium cupric acetate, of the composition given. No such compound has been reported previously, although an ammoniated cupric acetate of the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_3$ is well known,⁵ a hydrated ammonium cupric acetate, $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$, is to be found in the literature,⁶ and there is also some evidence for the existence of a hydrate of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, although this compound has not been isolated in a pure state.⁷

It appears from these data that the solubility of cupric acetate in acetic acid at any fixed temperature between 30 and 45° increases with increasing concentration of ammonium acetate, so long as solvated cupric acetate is the stable solid phase. Upon the appearance of the ternary compound, however, the mole percentage of cupric acetate in the saturated solution begins to decrease with increasing ammonium acetate concentration. This is more clearly brought out in Fig. 3, which represents an isotherm for 33.7°, plotted from data obtained from Fig. 2. It will be seen that the

⁵ Horn, *Am. Chem. J.*, 39, 184 (1908); see also Ephraim and Bolle, *Ber.*, 48, 638 (1915).

⁶ Richards and Oenslager, *Am. Chem. J.*, 17, 297 (1895).

⁷ Foerster, *Ber.*, 25, 3416 (1892).

solubility of cupric acetate, which is 0.280 mole per cent. in pure acetic acid at this temperature, increases upon the addition of ammonium acetate until R is 0.207, when the solubility reaches a maximum of 1.66 mole per cent., and a new solid phase appears. Beyond this point the concentration of cupric acetate in the saturated solution diminishes very rapidly with further addition of ammonium acetate, falling to a value of no more than 0.25 mole per cent. (somewhat less than the solubility in acetic acid alone) at the highest concentration of ammonium acetate investigated ($R = 0.237$). Shortly beyond this point, when $R = 0.258$, the compound $\text{NH}_4\text{-C}_2\text{H}_3\text{O}_2\cdot\text{HC}_2\text{H}_3\text{O}_2$ appears as solid phase.

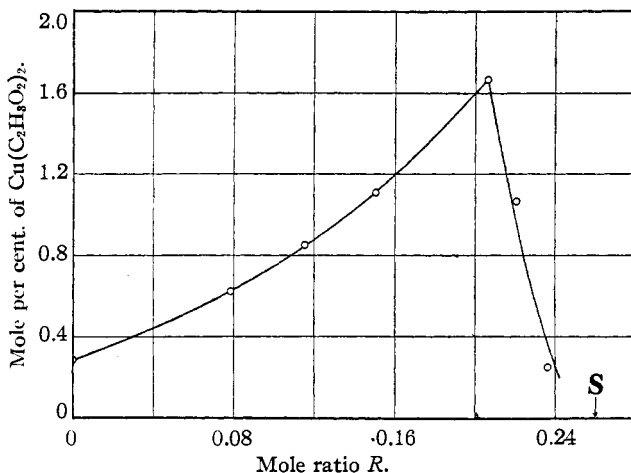
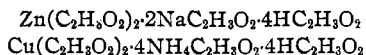


Fig. 3.—Effect of varying concentration of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ upon the solubility of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ in $\text{HC}_2\text{H}_3\text{O}_2$ at a fixed temperature: isotherm at 33.7° . S indicates saturated solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

In order to determine whether or not the solvent action upon cupric acetate, which has just been discussed, is due solely to the presence of ammonia, one further experiment was carried out, in which *potassium* acetate was employed as solvent. An acetic acid solution of the latter salt, in which R was 0.083, was found to dissolve 0.476 mole per cent. of cupric acetate at 33.7° . This is evidently of the same order as the solubility of the cupric salt in ammonium acetate solution under similar conditions. One marked difference between the two cases, however, is worthy of mention. Although the potassium acetate–cupric acetate solution was very similar in color, at ordinary temperatures, to a corresponding solution containing the ammonium salt, yet in the former case no perceptible color change took place on heating; at 100° the colors of the two solutions were quite unlike. The possible significance of this fact will be considered in the following section.

Discussion

As was stated in the introduction to this article, when it was first discovered that cupric acetate readily dissolved in an acetic acid solution of ammonium acetate, we were disposed to regard this phenomenon as quite analogous to the solubility of cupric hydroxide in aqueous ammonium hydroxide. Superficially, indeed, besides the purely formal resemblance, there is a fairly close parallel between the observed facts in the two cases. The solubility of cupric hydroxide increases with increasing concentration of ammonium hydroxide,⁸ and although there is no satisfactory evidence as to the solid phase in equilibrium with concentrated solutions, the compound $\text{Cu}(\text{OH})_2 \cdot 4\text{NH}_3$ is commonly supposed to be present in the solution.^{8b,9} The ternary compound obtained in the present investigation might, correspondingly, be regarded as a solvated $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_3$. Further, as stated above, the violet-blue color which appears at high temperatures in the ternary solutions herein described, is strikingly similar to that of the aqueous solutions under discussion. But there are a number of considerations which tend to cast doubt upon the validity of this analogy. Foremost among these is the fact that solutions of ammonium acetate in acetic acid, unlike ammonium hydroxide in water, have no appreciable vapor pressure of ammonia at ordinary temperatures; the ammonium acetate is quite stable and gives every indication of being as strong a base as the corresponding potassium compound, which, indeed, it closely resembles. Not only are the freezing-point curves of potassium and of ammonium acetates in acetic acid very similar,¹⁰ but it has been found that the two bases behave in exactly the same manner upon electrometric titration with strong acids.¹¹ It has just been shown, too, that the solvent action upon cupric acetate is not peculiar to the ammonium salt but is exhibited by potassium acetate to a similar degree. Furthermore, the isotherm obtained in this investigation is quite similar to that previously found⁴ for the system sodium acetate–zinc acetate–acetic acid, and the ternary addition compounds obtained in the two cases are of the same nature, as may be seen by comparing the two formulas



All of these facts point toward the conclusion that the solvent effect of ammonium acetate upon cupric acetate, at least at low temperatures, is due to the strongly basic nature of the ammonium compound, rather than to any specific effect of the ammonia which it contains, and that the analogous

⁸ (a) Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904); (b) Dawson, *Z. physik. Chem.*, **69**, 110 (1909).

⁹ De Wijs, *Rec. trav. chim.*, **44**, 663 (1925).

¹⁰ Ref. 3, p. 510.

¹¹ Hall, private communication.

phenomenon in aqueous solutions should be sought in the effect of strong alkalis, rather than of ammonium hydroxide, upon cupric hydroxide.

It is true that cupric hydroxide is not ordinarily regarded as amphoteric; but, as has frequently been pointed out,¹² the difference among the various metals in this respect must be regarded merely as one of degree. Cupric hydroxide is, indeed, appreciably soluble in concentrated aqueous solutions of sodium or potassium hydroxide, giving a deep blue solution. The most reliable quantitative data that have been obtained on this point appear to be those of Müller¹³ for the system sodium hydroxide–cupric hydroxide–water. He found that the solubility of cupric hydroxide¹⁴ in sodium hydroxide solutions at 18° increases, at first, with increasing concentration of alkali, reaching a maximum of about 0.3 mole per liter in approximately 12.5 molar sodium hydroxide solution. Here, however, a new solid phase appears, which is referred to as sodium cuprite, and is apparently of the formula $\text{Na}_2\text{CuO}_2 \cdot 2\text{H}_2\text{O}$, or $\text{Cu}(\text{OH})_2 \cdot 2\text{NaOH}$, and from this point on the concentration of cupric hydroxide in the saturated solution decreases sharply with increasing concentration of alkali. The relationships in the ternary system studied in the present investigation are obviously quite similar to those just discussed, with the ternary addition compound, whose formula might alternatively be written $(\text{NH}_4)_4\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_6 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$, playing the same part as the sodium cuprite in the aqueous system.¹⁵ However, as in the case of the sodium zinc acetate discussed previously,⁴ we are hardly prepared, as yet, definitely to characterize this compound; further study of its properties will be required before it can be determined whether or not it should be considered as a cuprite.¹⁶

In supposing the effect of ammonium acetate upon cupric acetate to be of the same nature as that of potassium acetate, and in drawing an analogy between these effects, on the one hand, and that of strong alkalis upon cupric hydroxide in aqueous solution, on the other, we have apparently disregarded the marked reversible deepening of color which occurs in the ammonium acetate–cupric acetate solutions, and in these alone, on heating. We suggest the following hypothesis¹⁷ to account for this color change.

¹² See, for instance, Goudriaan, *Rec. trav. chim.*, 39, 505 (1920); Kraus, *Trans. Am. Electrochem. Soc.*, 45, 175 (1924); Franklin, *THIS JOURNAL*, 46, 2144 (1924).

¹³ Müller, *Z. physik. Chem.*, 105, 73 (1924).

¹⁴ Cupric hydroxide was found to be metastable with respect to cupric oxide under these conditions; nevertheless its solubility could be determined.

¹⁵ Just as the sodium cuprite is unstable in contact with pure water, and can exist only in the presence of concentrated sodium hydroxide solutions, so the ternary compound of this article is unstable in the presence of pure acetic acid.

¹⁶ In the ammonia system, a compound of a somewhat analogous nature, having the formula $\text{CuNK}_2 \cdot 3\text{NH}_3$, or $\text{CuNH}_2 \cdot 2\text{KNH}_2 \cdot \text{NH}_3$, was described by Franklin, *THIS JOURNAL*, 34, 1501 (1912), and was called by him potassium ammonocuprite. In this compound, however, the copper is in the cuprous, not the cupric, state.

¹⁷ Cf. Ref. 1, p. 1894.

An ammonium acetate solution in acetic acid may, of course, be regarded, with equal validity, as a solution of *ammonia* in this solvent. At ordinary temperatures, as has been mentioned above, there is every reason to believe that the ammonia is completely combined with the solvent. As the temperature is raised, however, an increasing dissociation into ammonia and solvent doubtless occurs, just as in the case of aqueous ammonium hydroxide. It has, in fact, been shown¹⁸ that the vapor pressure of ammonia from a concentrated solution of ammonium acetate in acetic acid at the boiling point must be appreciable, since the distillate from such a solution contains a perceptible quantity of ammonia. It therefore seems reasonable to suppose that while ammonium acetate in acetic acid at room temperature is comparable to potassium hydroxide rather than to ammonium hydroxide in aqueous solution, yet at temperatures above 100° it begins to exhibit properties analogous to those of aqueous ammonia at ordinary temperatures. The ammonia, then, being but loosely held by the solvent under these conditions, may be available for the formation of other ammonia complexes. If this hypothesis is correct, the violet-blue color which appears in the cupric acetate-ammonium acetate solutions at elevated temperatures may be due to a complex ion, $\text{Cu}(\text{NH}_3)_n^{++}$, of the same nature as that which gives rise to a similar color in the aqueous cupric ammonia solutions.

Summary

1. The solubility of cupric acetate in pure acetic acid and in the presence of ammonium acetate in concentrations up to 23.7 mole per cent. has been determined at various temperatures.
2. The concentration of cupric acetate in the saturated solutions at a fixed temperature has been found to increase with increasing concentration of ammonium acetate as long as a solvated cupric acetate is the stable solid phase, but to decrease with further addition of ammonium acetate after the appearance of a ternary addition compound as solid phase.
3. A solvated ammonium cupric acetate of the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ has been isolated and analyzed.
4. The ternary system here studied has been compared with solutions of cupric hydroxide in concentrated aqueous alkali solutions, and certain resemblances have been pointed out.
5. An hypothesis has been advanced to account for the violet-blue color which appears at elevated temperatures in ammonium acetate-cupric acetate-acetic acid solutions.

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¹⁸ Davidson, *Trans. Kans. Acad. Sci.*, **31**, 60 (1928).