

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

THE EFFECT OF AMMONIUM FORMATE UPON THE SOLUBILITY OF CUPRIC FORMATE IN FORMIC ACID

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Introduction

In a previous article,¹ it was shown that the solubility of cupric acetate in anhydrous acetic acid is markedly increased in the presence of ammonium acetate, and comparisons were drawn between this phenomenon, on the one hand, and the analogous effects of alkalis and of ammonium hydroxide upon cupric hydroxide in aqueous solution, on the other. It seemed desirable to study the corresponding system in another solvent, in order to determine whether acetic acid were unique among non-aqueous media, in this respect, or whether the behavior referred to might be regarded as a more or less general effect of ammonia in systems of the type $\text{CuX}_2\text{-HX}$. For this investigation, formic acid was chosen as solvent; this substance is a liquid over a wide temperature range (8.5 to 100.5°), is readily prepared in a pure state, and is known to be a good solvent for numerous salts.

The solubility of cupric formate in anhydrous formic acid was found by Kendall and Adler² to be very small, the saturated solution at 140° containing less than 0.1 mole per cent. of solute; no further data are given. In the present work the solubility of cupric formate over a range of temperatures has been measured, both in pure formic acid and in the presence of ammonium formate in varying concentration. The effect of potassium formate, at one concentration, was determined also. The results were similar to, though not identical with, those obtained in acetic acid solution, as will be shown below.

Method

Preparation of Materials.—The formic acid employed was prepared from a good grade of 90% acid by dehydration with boric anhydride, B_2O_3 , as suggested by Schlesinger and Martin.³ The acid was allowed to remain for a week in contact with a slight excess over the theoretical quantity of boric anhydride; it was then distilled off, treated with a small amount of fresh dehydrating agent, and again allowed to stand for several days. Finally the liquid was decanted and distilled under reduced pressure. The product had a freezing point of 8.3 to 8.5°, and was practically 100% formic acid.

Ammonium formate was prepared by passing dry ammonia into 100% formic acid until complete solidification had occurred. The product was desiccated over 99% sulfuric acid, and was then found to have a melting point of 117–118°, agreeing with that reported by Kendall and Adler. Potassium formate was obtained by dissolving pure potassium carbonate in an excess of 90% formic acid, heating to expel carbon dioxide

¹ Davidson and Griswold, *THIS JOURNAL*, **53**, 1341 (1931).

² Kendall and Adler, *ibid.*, **43**, 1470 (1921).

³ Schlesinger and Martin, *ibid.*, **36**, 1589 (1914).

evaporating off most of the excess acid, and then heating to 150° for several days and finally to 190° for about an hour. The product had a melting point of 168°, agreeing with that reported by Kendall and Adler.

In the preparation of pure anhydrous cupric formate, some difficulty was encountered. An aqueous solution of the salt was readily obtained by dissolving basic cupric carbonate in 50% formic acid and heating to expel carbon dioxide. On cooling to room temperature, crystals of the tetrahydrate separated out. The first attempt to dehydrate this compound by heating to constant weight at 80°, as recommended by Kendall and Adler, was entirely successful, yielding a bright blue product which showed, upon analysis by the electrolytic method, 41.35% of copper (calcd. for $\text{Cu}(\text{CHO}_2)_2$, 41.39%). Strangely enough, however, several attempts to obtain further quantities of the salt by this method failed, because the cupric formate was partially changed, on heating, to a dark brown substance of unknown chemical nature, before the dehydration was complete. A somewhat different procedure was therefore adopted. Instead of being allowed to cool to room temperature, the solution was maintained at 80°; the crystals separating out under these conditions consisted of the anhydrous salt.⁴ These crystals were pressed between porous tiles and then dried at 75° for ten hours. The resulting product showed no discoloration, and analysis proved it to be pure anhydrous cupric formate.

Binary System.—The solubility of cupric formate in formic acid was determined by the freezing point method previously described.⁵ Large test-tubes, each fitted with a thermometer and a stirrer in such a manner as to exclude moisture, were used for the freezing point determinations. Four calibrated thermometers were employed, and each freezing point was determined at least twice. Because of the very low solubility, in this case, and the very minute amounts of solid phase which could be made to separate, the accurate determination of freezing points was a matter of some difficulty. However, the temperatures reported are believed to be correct to within 0.5°.

Ternary System.—In the study of the solvent effect of ammonium formate, the method described in previous articles^{1,6} dealing with similar ternary systems was again employed. Preliminary experiments having shown that the solubility of the copper salt, at any given concentration of ammonium salt, was much smaller in this case than in the acetic acid system, rather high concentrations of ammonium formate were used. Formic acid solutions were prepared containing 10.00, 19.73, 29.75, 33.54 and 43.75 mole per cent., respectively, of ammonium formate. Known amounts of cupric formate were dissolved in these solvents,⁷ and the equilibrium temperatures were determined just as in the binary systems. Thus a series of curves was obtained, each of which represented the solubility of cupric formate, at various temperatures, in a solvent having a fixed value of the ratio, number of moles of ammonium formate/number of moles of (ammonium formate + formic acid); this ratio will subsequently be referred to as *R*.

Analysis of Solid Phases.—When the solid phase in equilibrium with the solution was obtainable in sufficient quantity to make it possible, samples were prepared for analysis by crystallization from the solution under appropriate conditions, filtration and drying between porous tiles as rapidly as possible, to minimize loss of formic acid. Qualitative tests showed no ammonia to be present in any of the solid phases. Cupric formate and formic acid being the only components, a quantitative determination of copper by the electrolytic method was sufficient to fix the composition of the compound.

⁴ Lossen and Voss, *Ann.*, 266, 33 (1891).

⁵ See, for instance, Davidson and McAllister, *This Journal*, 52, 507 (1930).

⁶ Davidson and McAllister, *ibid.*, 52, 519 (1930).

⁷ The color of the solutions, at room temperature, was a blue resembling that of the cupric ion in aqueous solution; on heating, however, it changed to a deep violet-blue. This color change will be discussed later.

The data obtained are tabulated below, and are also presented graphically in the accompanying diagrams. The concentration of cupric formate in the solution is expressed throughout in mole percentage; T denotes the equilibrium temperature.

Results

I. Binary System $\text{Cu}(\text{CHO}_2)_2\text{-HCHO}_2$

$\text{Cu}(\text{CHO}_2)_2$, %.....	0.0045	0.0048	0.0066	0.0075
T	35	42	49	52

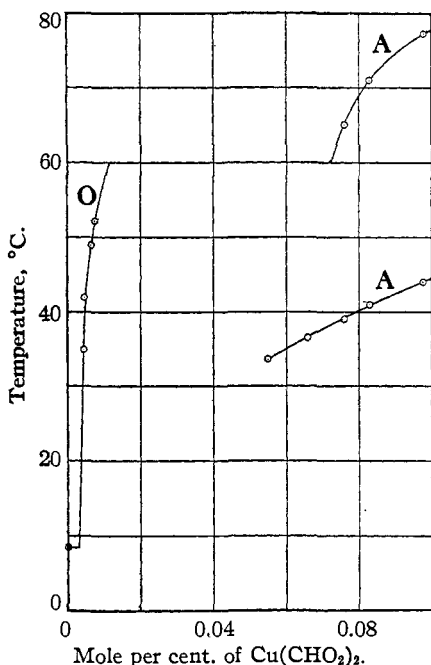


Fig. 1.—Solubility curves of $\text{Cu}(\text{CHO}_2)_2$ in pure HCHO_2 (Curve O) and in 10% NH_4CHO_2 (Curve A).

were obtained in this series, one corresponding to a stable, the other to a metastable equilibrium.

$\text{Cu}(\text{CHO}_2)_2$, %.....	0.055	0.066	0.076	0.083	0.098
T (unstable modification).....	33.5	36.5	39	41	44
T (stable modification).....	65	71	77

B. Mole ratio $R = 0.1973$

$\text{Cu}(\text{CHO}_2)_2$, %.....	0.319	0.399	0.465
T	60.0	70.5	77.2

C. Mole ratio $R = 0.2975$. Solid phase $2\text{Cu}(\text{CHO}_2)_2\cdot 3\text{HCHO}_2$

$\text{Cu}(\text{CHO}_2)_2$, %.....	1.016	1.286	1.365
T	51.5	68.5	74.0

The curve for this system is given in Fig. 1. It is evident that the solubility of cupric formate at ordinary temperatures is extremely small, far below the maximum value of 0.1% that was given for 140° by Kendall and Adler. It was found impossible to determine equilibrium temperatures below 35°; however, the curvature was so slight as to make it possible to continue the curve to the eutectic point by extrapolation. The solubility at 25° is 0.0040 mole per cent., about one-fortieth of the value obtained for cupric acetate in acetic acid.¹ The solid phase appeared to be bright blue in color, but could not be obtained in sufficient quantity for analysis.

II. Ternary System $\text{NH}_4\text{CHO}_2\text{-Cu}(\text{CHO}_2)_2\text{-HCHO}_2$

A. Mole Ratio $R = 0.10$

Two sets of equilibrium temperatures

D. Mole ratio $R = 0.3354$. Solid phase $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$						
$\text{Cu}(\text{CHO}_2)_2$, %.....	1.179	1.308	1.501	1.680	1.950	2.004
T	29.0	31.0	33.0	38.5	43.0	44.0
E. Mole ratio $R = 0.4375$. Solid phase $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$						
$\text{Cu}(\text{CHO}_2)_2$, %.....	1.990	2.470	2.816	3.131		
T	37.0	43.5	48.5	51.5		

The curves for this system are given in Fig. 2; the one for the lowest concentration of ammonium formate is shown also in Fig. 1, on the same scale as that used in the binary system, for purposes of comparison with the solubility curve of cupric formate in formic acid alone. In series A and B the solid phases were bright blue in color and similar in appearance to that obtained in the binary system; they contained no ammonia, and therefore consisted of cupric formate, presumably solvated. They could not be obtained in sufficient quantity for a reliable quantitative analysis, however.

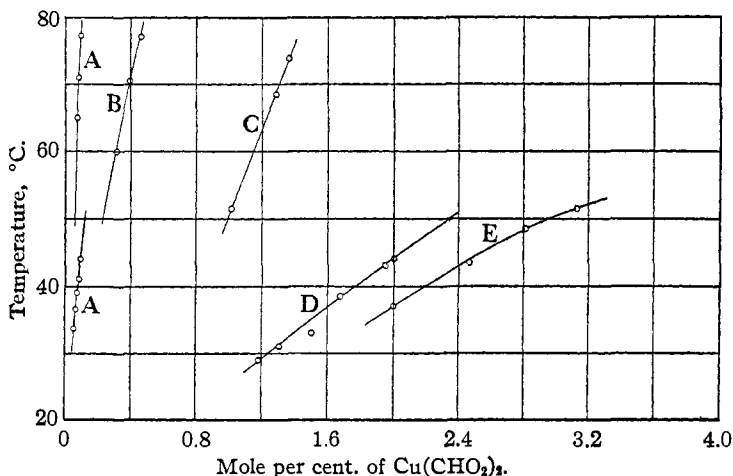


Fig. 2.—Solubility curves of $\text{Cu}(\text{CHO}_2)_2$ in HCHO_2 containing various concentrations of NH_4CHO_2 : A, $R = 0.10$; B, $R = 0.1973$; C, $R = 0.2975$; D, $R = 0.3354$; E, $R = 0.4375$. *

In series C, D and E, the solids isolated were pale blue in color. Qualitative analysis showed them to contain cupric formate and formic acid, but no ammonia. No acid cupric formate has been reported previously. Quantitative analysis gave the following results.

Series	% Cu	Mole % $\text{Cu}(\text{CHO}_2)_2$
C	28.65	40.26
D	27.78	37.96
E	28.11	38.82
Average	28.18	39.00
Calcd. for $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$	28.56	40.00

It was impossible to attain a very high degree of accuracy in the analyses of these solid phases, because of the very small amounts of crystals obtainable, the difficulty in freeing them from the rather viscous adhering mother liquor, and their tendency to lose formic acid in vapor form on exposure to the atmosphere. However, it is believed that the figures given satisfactorily establish that the three substances analyzed are identical and that they consist of a solvated cupric formate, probably of the formula $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$.

It is evident that the solubility of cupric formate in formic acid at a fixed temperature increases with increasing concentration of ammonium formate throughout the concentration range investigated, though not at a uniform rate. This is brought out more clearly in Fig. 3, which is an isotherm for 50° , plotted from the data of Fig. 2. At this temperature the solubility of cupric formate first increases as an almost linear function of R —the solid phase in this range being the bright blue compound of unknown degree of solvation—from 0.0068 mole per cent. in pure formic acid ($R = 0$) to 0.33 mole per cent. when R is 0.294. There a new solid phase—the pale blue solvate $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$ —appears, and the solubility then increases much more rapidly with increasing R , reaching a value of 2.95 mole per cent. at the highest concentration of ammonium formate investigated ($R = 0.4375$). A little beyond this point, at $R = 0.51$, NH_4CHO_2 appears as solid phase.

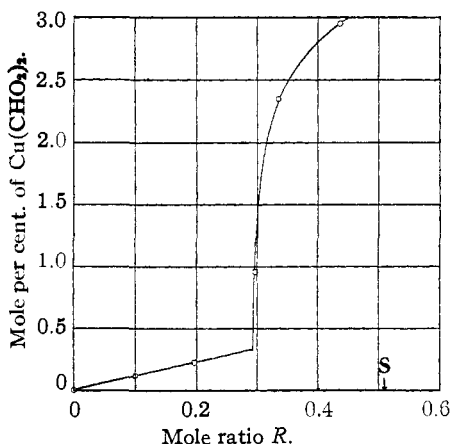


Fig. 3.—Effect of varying concentration of NH_4CHO_2 upon the solubility of $\text{Cu}(\text{CHO}_2)_2$ in HCHO_2 at a fixed temperature: isotherm at 50° . S indicates saturated solution of NH_4CHO_2 .

ammonium formate investigated ($R = 0.4375$). A little beyond this point, at $R = 0.51$, NH_4CHO_2 appears as solid phase.

In order to compare the solvent effect of potassium formate with that of ammonium formate, one further experiment, in which the former salt was used, was carried out. A solution in which R was 0.244 was found to dissolve 0.38 mole per cent. of cupric formate below 60° . This, as may be seen from the isotherm, is of the same order as the solubility of the cupric salt in ammonium formate solution under similar conditions.

Discussion

Comparison of Results with Data for the Corresponding Acetic Acid System.—It was shown in the previous article¹ referred to at the beginning of this paper that the solubility of cupric acetate in acetic acid at any

fixed temperature between 30 and 45° is at first increased by the addition of ammonium acetate, a solvated cupric acetate being the stable solid phase in contact with these solutions. The data obtained in the present investigation show that this behavior is paralleled in the corresponding ternary system in formic acid, although the solubility of the cupric salt at any given value of R is much smaller in the latter case than in the former.

In the acetic acid system, at higher concentrations of ammonium salt, a ternary compound of the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ appears as stable solid phase, and the concentration of cupric acetate in the saturated solution then diminishes with increasing concentration of ammonium acetate. We expected to come upon a similar ternary compound in the formic acid system, but no such substance appeared, and the solubility of cupric formate continued to increase with increasing ammonium formate concentration throughout the range studied. It is, indeed, possible that a ternary compound might have been obtained as solid phase at still higher concentrations of ammonium formate, but this region could not be satisfactorily investigated.⁸ It may be of interest to mention here that although no addition compound of cupric formate and ammonium formate appears to be known as yet, a compound of cupric formate and ammonia, having the formula $\text{Cu}(\text{CHO}_2)_2 \cdot 4\text{NH}_3$, has been reported.⁹ We confirmed the existence of this compound by passing ammonia over a weighed quantity of cupric formate at 0° until no further increase in weight occurred; the amount of ammonia taken up closely corresponded to the above formula, and the product was blue-violet in color.

One further point of similarity between the two systems remains to be mentioned. It was pointed out as a conspicuous property of the cupric acetate-ammonium acetate-acetic acid system that, on heating the solutions, a marked deepening of the blue color, accompanied by a change toward the violet, takes place. An exactly similar change was observed in the present investigation; at temperatures in the neighborhood of 100° for small values of R , or lower for the larger values, the ternary solutions attain a deep violet-blue color closely resembling that of aqueous cupric ammonia solutions; on cooling, they return to their original blue color. On the other hand, although solutions similar in color, at room tempera-

⁸ An attempt was made to employ as solvent a solution in which R was 0.50—an equimolecular mixture, that is, of ammonium formate and formic acid; but several circumstances made it impossible to obtain satisfactory results in this solvent. In the first place, since such a solution was supersaturated with respect to NH_4CHO_2 at temperatures up to 47°, the latter substance, rather than the copper compound, was likely to separate on cooling. Second, the very high viscosity of the solution promoted supercooling, as well as delayed the escape of air bubbles, and finally, the very deep blue color of the solution united with these other factors to make accurate observation of melting points a practical impossibility.

⁹ Ephraim and Bolle, *Ber.*, **48**, 1770 (1915).

ture, to those just discussed are readily obtained by the solvent action of potassium acetate and potassium formate upon the corresponding cupric salts in acetic acid and in formic acid, respectively, yet in these cases no color change whatever is observable on heating. The appearance of the violet-blue color in such solutions, therefore, is a phenomenon apparently occurring only in the presence of *ammonium* salts, is independent of the anion and may be due to the formation of some sort of cupric ammonia complex, as suggested previously.

Conclusions.—It was pointed out by Davidson and Griswold¹ that the water analog of the solubility of cupric acetate in acetic acid solutions of ammonium acetate at low temperatures is to be found in the solvent effect of the strong alkalis, rather than in that of ammonium hydroxide, upon cupric hydroxide, and it was suggested that only at temperatures above 100°, where the bond between the ammonia and the acetic acid may be supposed to be weakened, do the conditions approach those prevailing in an aqueous ammonium hydroxide solution at ordinary temperatures. The facts presented in this article are in complete accord with a similar hypothesis for formic acid solutions. Ammonium formate may obviously be regarded as a base in formic acid; here, it is true, there are no electrometric titration data available for comparing its basic strength with that of the corresponding potassium compound,¹⁰ but the conductivity measurements of Schlesinger and co-workers^{3,11} indicate that ammonium formate is highly dissociated, and give evidence of its being at least as strong a base as potassium formate, in this solvent. It is not surprising, therefore, that the solvent effects of the two bases upon cupric formate should be so nearly alike. However, the avidity of cupric formate for ammonia, on the one hand, and the characteristic violet-blue color, suggesting a cupric ammonia complex, that appears in hot cupric formate–ammonium formate solutions, on the other, make it seem probable that at high temperatures the free ammonia formed by dissociation also plays a part in the solvent action of ammonium formate.

Summary

1. The solubility of cupric formate in pure formic acid and in the presence of ammonium formate in concentrations up to 43.75 mole per cent. has been determined at various temperatures.

2. The solubility of cupric formate at a fixed temperature has been found to increase, throughout this range, with increasing concentration of ammonium formate.

¹⁰ Very recently, a study of the potentiometric titration of acids and bases in formic acid solution has been published by Hammett and Dietz, *THIS JOURNAL*, **52**, 4795 (1930). Ammonium formate was not investigated; urea, however, was found to behave as a strong base.

¹¹ Schlesinger and Calvert, *THIS JOURNAL*, **33**, 1924 (1911).

3. A solvated cupric formate of the formula $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$ has been isolated and analyzed.

4. The results here obtained have been compared with those previously reported for the corresponding ternary system in acetic acid. Attention has been called to the similarity between these two cases, and certain relationships with analogous aqueous systems have been pointed out.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH]

THE TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE. NEW DETERMINATIONS BY THE HITTORF METHOD AND A COMPARISON WITH RESULTS OBTAINED BY THE MOVING BOUNDARY METHOD

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We have obtained, in this Laboratory, by the moving boundary method a large amount of data, for the most part still unpublished, on the transference numbers of electrolytes. Many of these data differ so widely from the published values for transference numbers obtained by the Hittorf method that the question arose seriously in our minds as to whether the two methods (the Hittorf and moving boundary) obtain measures of the same property of the solutions of electrolytes. With potassium chloride, for instance, the measurements in dilute solutions by Jahn and associates² of the cation transference number by the Hittorf method gave values on the average 1% above the determinations by the moving boundary method. On the other hand, Dewey,³ working at 0.2 *N*, obtained *lower* values for this constant by the Hittorf method than those obtained by MacInnes and Brighton⁴ and Smith and MacInnes⁵ using the moving boundary procedure. We have, however, found it possible to interpret the conductance and transference data, as a whole, for a group of simple electrolytes provided the newer moving boundary results are used. This is far from being true with reference to most of the Hittorf data now published. These new data and their interpretation will be the subject of a series of papers from this Laboratory. It was evidently very important to find out whether the disagreement of the results of the two methods for obtaining transference numbers is due to

¹ Department of Chemistry, Northwestern University, Evanston, Illinois.

² Jahn and Bogdan, *Z. physik. Chem.*, **37**, 673 (1901); Jahn and Hertz, *ibid.*, **58**, 641 (1907). The "best values" of the "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 310, are largely based on this work.

³ Jane Dewey, *THIS JOURNAL*, **47**, 1927 (1925).

⁴ MacInnes and Brighton, *ibid.*, **47**, 994 (1925).

⁵ Smith and MacInnes, *ibid.*, **47**, 1009 (1925).