

SOME STUDIES IN THE TERNARY SYSTEM:
COPPER FORMATE - AMMONIUM FORMATE -
FORMIC ACID

by

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Introduction

The work here reported has been carried out with the intention of extending the data on the solubility of a salt of the type CuX_2 in a solvent HX , and the effect upon this solubility of measured quantities of the salt NH_4X . This type of system in acetic acid has already been studied by Griswold¹ in this laboratory, and it was found that by addition of ammonium acetate, a very marked increase in the solubility of copper acetate in acetic acid is obtained. Obviously, this is analogous to the well known behavior of copper hydroxide in water when ammonium hydroxide is added to the system. In each case, in fact, the problem might be formulated in terms of the effect of ammonia, NH_3 , upon the solubility of the copper

¹Unpublished work

compound, since the dissolved ammonium acetate might be regarded simply as a solution of ammonia in acetic acid. The fact that this similarity does occur in the two systems brings up the question as to whether this behavior is general, and if so, to what extent. It seemed desirable, therefore, to study the analogous system in another solvent. For this purpose formic acid was chosen. It is a considerably stronger acid than acetic acid, it can be quite readily prepared in the pure state, and it is a representative of the simple type of solvent, HX, in which we are especially interested.

The solubility of copper formate in pure formic acid has been reported by Kendall and Adler² to be less than 0.10 mole % at 140°. No other work has been done upon this system. In the present research a solubility curve for copper formate in formic acid has been obtained, and the effect upon this solubility of the addition of definite amounts of ammonium formate has been determined. In addition, the effect of using

²Kendall and Adler, J. Am. Chem. Soc, 43, 1470 (1921).

potassium formate was observed at one concentration and the results compared.

Experimental Method

Preparation of Materials:-

The formic acid was prepared by treatment of 90 % C. P. acid with finely powdered boric anhydride (B_2O_3)³. It was found that in the presence of a slight excess of boric anhydride over that which had been calculated to remove the water present, approximately a week was required for maximum efficiency in dehydration. The percentage of water in the original acid had been previously determined by comparing its freezing point with data given by Faucon.⁴ The acid was then distilled and again treated with a small quantity of boric anhydride. After this mixture had stood for three or four days the solution was separated from the boric acid and unused anhydride in the bottom of the flask, and was distilled under reduced pressure. The resulting acid froze at from

³Schlesinger and Martin, J. Am. Chem. Soc, 36, 1589 (1914)

⁴Faucon, Ann. chim. phys. (8) 19, 70 (1910)

8.3° to 8.5°C. and from the data of Faucon, this represents acid that is from 99.9 % to 100 % pure.

The ammonium formate was prepared by a method similar to that described by Adler. Dry ammonia was passed into 100 % acid until complete solidification had taken place. The resulting substance was desiccated over 99 % sulfuric acid and the final product gave a melting point of 117° - 118° which agrees with that reported by Adler, - 117.5°.

In the preparation of pure copper formate more difficulties were encountered than with any of the other compounds which it was necessary to prepare. Basic copper carbonate was treated with a 50 % solution of formic acid. The resulting solution was heated to free it from carbon dioxide and was then cooled, when a hydrate of copper formate, undoubtedly, $\text{Cu}(\text{OOCH})_2 \cdot 4\text{H}_2\text{O}$ separated out. This was dehydrated in an oven at 80° for fifteen hours. Analyses for copper content on the resulting product indicated that the bright blue compound was the neutral salt and that it was of sufficient purity to be used in the determinations.

Later attempts, however, to prepare the neutral salt by the same method were unsuccessful. The attempts to dehydrate the crystals that separated from the solution upon cooling resulted in the darkening of the salt, though analyses at this stage indicated that dehydration was not complete. The substance when examined under the microscope showed black masses among the bright blue crystals, these black masses increasing in number as the dehydration was continued. The composition of this black substance is not known.

After four unsuccessful attempts to duplicate the original method, it was decided to attempt to bring about separation of the anhydrous salt at an elevated temperature and thus eliminate the destructive dehydration process. Voss⁵ states that the anhydrous salt separated from a slowly evaporating acid solution of the salt in water at 75° - 85°C., while a dihydrate separates out between 50° and 60°C. The following method was therefore employed. The crystals separating from

⁵Voss, Ann., 266, 33 (1891)

a solution kept at 80°C. were quickly separated from the mother liquor, pressed between porous tiles and then placed in a drying oven at about 75°C. After drying for ten or twelve hours the resulting bright blue compound was analyzed and proved to be pure copper formate. It dissolved to give a clear blue solution in cold water and appeared uniform under the microscope, just as the product in the first method of preparation had done. No explanation is available for the fact that in one case the dehydration of $\text{Cu}(\text{OOCH})_2 \cdot 4\text{H}_2\text{O}$ proceeded normally while in all other cases it was accompanied by a chemical change of unknown nature.

The potassium formate was prepared by treating the C.P. carbonate with 90 % acid and heating to expel the carbon dioxide. The solution was evaporated in the open for a time and then placed in a drying oven at 150°C. for several days. At the end of this period the melting point indicated that the potassium formate was not yet thoroughly dehydrated. Consequently, it was heated at a temperature of about 20° above the melting point of the pure salt for about an hour. After this

treatment it was desiccated over 99 % sulfuric acid for several days. The final product melted at 169°C . $\pm 1^{\circ}$, which compares favorably with the value recorded by Adler, $-167.5^{\circ}\text{C} \pm 0.5^{\circ}$.

The Freezing Point Method:-

The solubility determinations were made in freezing point tubes which were about one inch in diameter and six inches long and which were fitted with thermometers and stirrers in such a manner that moisture was excluded. An amount of solute which had previously been determined to be approximately correct for the amount of solvent present, was introduced into the tube. The tube was then placed in a water bath heated by a low flame and the mixture was constantly agitated by means of the stirrer until complete solution had taken place. The tube was then cooled in a suitable freezing bath until a finely divided solid phase had appeared. For these baths a variety of cooling agents were used, depending on the requirements: salt and ice mixtures, liquid ammonia, and solid carbon dioxide in gasoline.

The freezing point tube was now placed in another water bath and the temperature of this was slowly raised, the mixture meanwhile being constantly stirred, until the last fine crystals disappeared. This temperature was taken as the melting point of the solid phase. All points determined in this manner were checked by repeating the procedure.

The set of thermometers used in the experimental procedure consisted of three precision thermometers of the following ranges: -12° to 52° , -6° to 106° , and -10° to 250° and one ordinary thermometer of the range 0° to 100° . These thermometers had been previously compared at six degree intervals with a set of certified thermometers calibrated by the Bureau of Standards, and were also corrected for emergent stem at these points. The precision of the thermometers in all of of the determinations was considerably greater than the accuracy of the melting points, due in some cases to the fact that the solid phase obtained consisted only of a faint cloudiness, while in other cases the deep blue coloration of the solutions prevented accurate observations. However, the melting points are believed to be reliable to $\pm 0.5^{\circ}$.

In the determinations on the effect of ammonium formate on the solubility of copper formate several "solvents" were made up by dissolving various known amounts of ammonium formate in formic acid. The solubility of copper formate in these prepared "solvents" was then determined by exactly the same procedure as for the solubility in formic acid.

Identification of Solid Phases;-

In most instances the solid phases for which equilibrium temperatures were determined could be obtained in sufficient quantity so that analyses were possible. The crystals were filtered off, dried between porous tiles, and placed in a small weighing bottle. These operations were performed as quickly as possible to eliminate any loss of formic acid of solvation, or absorption of moisture, before weighing.

Since none of the solid phases gave a qualitative test for ammonia, the possible compounds were limited to anhydrous copper

formate and its solvates. To decide which of these was present in a particular case, it was only necessary to make a quantitative determination of copper. These determinations were carried out by the electrolytic method.

In two of the systems which were studied it was impossible to crystallize out a sufficient quantity of the solid phase for analysis. However, the composition of the solid phases in these instances is believed to be accurately known, both from the appearance of the crystalline compounds as compared with those in other systems that were analyzed, and also from their behavior in the solution, since a change in the solid phase present would be accompanied by a distinct change in direction of the solubility isotherm.

Results

The results obtained in the experimental procedure are given in the following tables and are also presented graphically in the accompanying diagrams.

Binary System $\text{Cu}(\text{OOCH})_2 - \text{HOCH}$

Solid phase $\text{Cu}(\text{OOCH})_2$ (?)

$\text{Cu}(\text{OOCH})_2$ %	0.0045	0.0048	0.0066	0.0075
T	35	42	49	52.2

Ternary System $\text{Cu}(\text{OOCH})_2 - \text{NH}_4\text{OOCH} - \text{HOCH}$

A. Mole % of NH_4OOCH in Solvent = 10

a. Metastable solid phase

$\text{Cu}(\text{OOCH})_2$ %	0.055	0.066	0.076	0.083	0.0978
T	33.6	36.5	39	41	44

b. Stable solid phase $\text{Cu}(\text{OOCH})_2$

$\text{Cu}(\text{OOCH})_2$ %	0.076	0.083	0.0978
T	65	71	77.3

B. Mole % of NH_4OOCH in Solvent = 19.73

Solid phase $\text{Cu}(\text{OOCH})_2$ (?)

$\text{Cu}(\text{OOCH})_2$ %	0.319	0.399	0.465
T	60	70.5	77.2

C. Mole % of NH_4OOCH in Solvent = 29.75

Solid phase $\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$

$\text{Cu}(\text{OOCH})_2$ %	1.016	1.286	1.365
T	51.5	68.5	74

D. Mole % of NH_4OOCH in Solvent = 33.54

Solid phase $\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$

$\text{Cu}(\text{OOCH})_2$ %	1.179	1.508	1.501	1.680	1.950	2.004
T	29 <u>+1</u>	51	53	58.5	43	44

E. Mole % of NH_4OOCH in Solvent = 43.75

Solid phase $\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$

$\text{Cu}(\text{OOCH})_2$ %	1.990	2.470	2.816	3.151
T	37	43.5	48.5	51.5

The copper contents determined by analyses of the solid phases isolated in the various systems/^{are} compared in the following table with theoretical values for the compounds which they are thought to represent.

System	Compound	Copper content in %	
		Experimental	Theoretical
A	$\text{Cu}(\text{OOCH})_2$	41.1 %	41.39 %
C	$\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$	28.1	25.89
D	$\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$	28.6	25.89
E	$\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$	27.8	25.89

Discussion of Results

In the above table which gives the analyses of solid phases it will be noticed that the copper content of the compound assumed to be $\text{Cu}(\text{COOCH})_2 \cdot 2 \text{HOOCH}$, was found in each case to be somewhat above the theoretical percentage of copper for a compound of that formula. This may be explained by the fact that the solvate is not exceedingly stable and when exposed to the atmosphere loses formic acid, this change being accompanied by a change in color from the pale blue of the solvate to the bright deep blue of the unsolvated salt. It is therefore probable that a slight amount of formic acid might have been lost in the manipulations succeeding the drying process and that for this reason the percentage of copper is higher than it should be.

In the data for the binary system it will be noticed that copper formate is quite insoluble in formic acid. This extreme insolubility makes it very difficult to secure reliable freezing points, first because of the necessity of weighing

minute quantities of the salt in making up the samples and secondly, because of the difficulty in observing the exact solution temperature for the very thin suspension of the solid phase, which can obviously not separate out in very large quantity from such a dilute solution. Because of this fact also, it was impossible to analyze the solid phase. However, from its appearance it is believed to be the unsolvated copper formate.

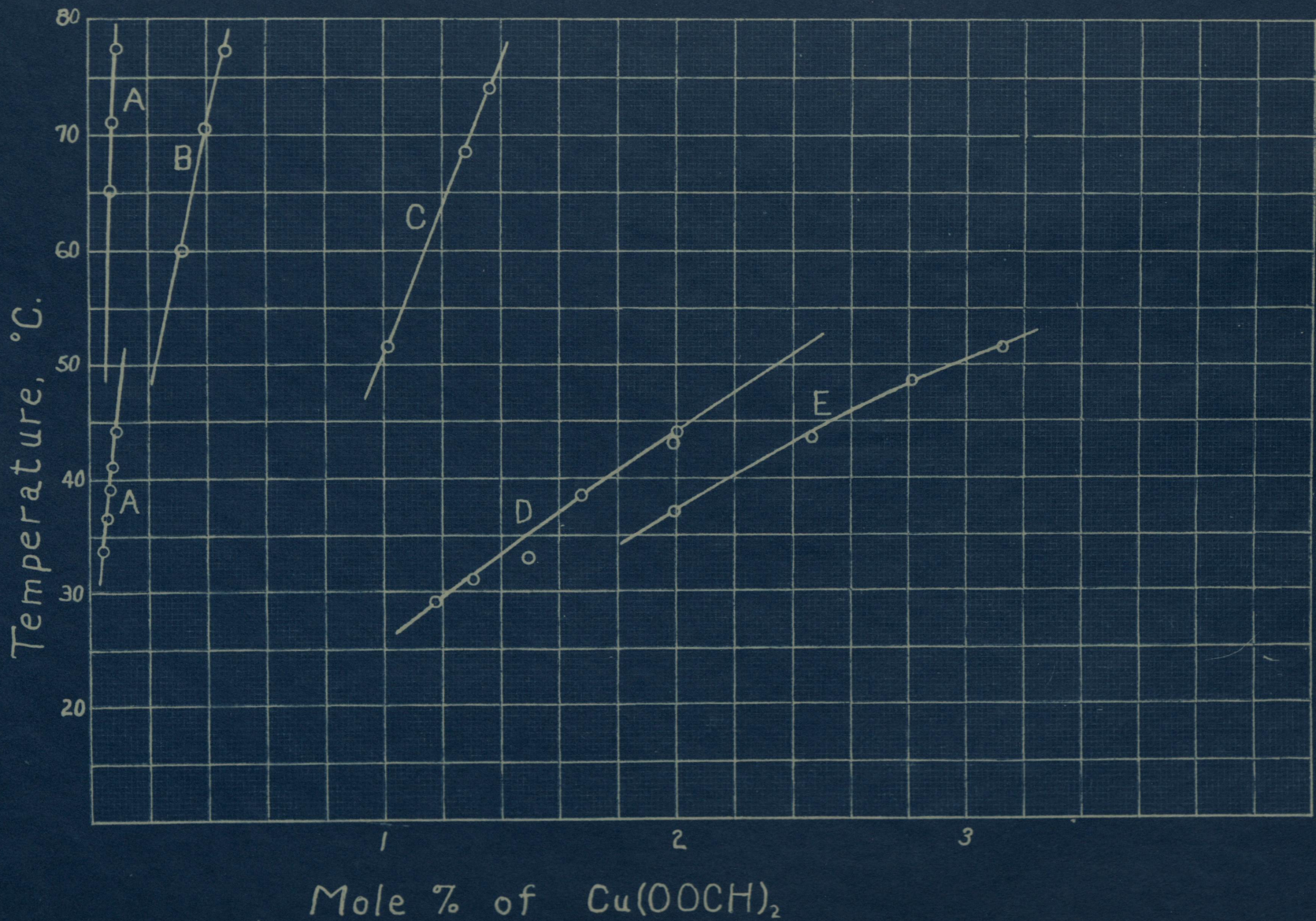
The data for the ternary system indicate a decided increase in solubility of copper formate with increasing concentration of ammonium formate in formic acid solution. In the ternary system it had been expected that at a high concentration of ammonium formate, a ternary compound, $\text{Cu}(\text{OOCH})_2 \cdot n \text{NH}_4\text{OOCH} \cdot n \text{HOOCH}$, would appear as the solid phase, and that the solubility would then decrease from the maximum reached at an intermediate concentration of ammonium formate. Such a compound and such behavior have been observed by Griswold in the acetic acid system. However, in the case of formic acid no such

compound could be isolated and the solubility of copper formate increased with increasing concentration of ammonium formate throughout the entire range in which the system could be conveniently studied. Since the solutions become deeply colored as the amount of copper increases, which is probably due to some free ammonia present by dissociation of ammonium formate, it was considered that results at much higher concentrations of ammonium formate might be rather inaccurate because of the difficulty of observation of the solution temperature. Indeed a solution containing 50 mole per cent. of ammonium formate was prepared, but attempts to secure satisfactory melting points failed for this reason.

Since the solubility of copper formate in the various solvents varies over such a wide range it is convenient to show the relations between these solubilities by means of two separate graphs. Figure 1 shows the equilibrium curve for copper formate in pure formic acid and also in the system where the mole % of ammonium formate in the solvent is 10 (A). Figure 2 shows the equilibrium curves for the ternary systems A, B, C, D, and E.

Figure 1

Figure 2



In Figure 1 it will be noticed that in system A, two solubility curves are given, the one curve representing a metastable solid phase whose composition is unknown. In this system, if the melting point was determined by raising the temperature directly from that of the freezing bath, the metastable phase would give a definite melting point; but occasionally after this point was reached and the solution had cleared, it would suddenly become cloudy again indicating that the stable phase had come out of solution. This phase dissolved at a considerably higher temperature. If the solution from which crystals had been frozen out, was allowed to stand for some time before taking the melting point, only the higher of the two points could be obtained, indicating that a transition to the more stable phase had occurred.

The more stable of the phases was analyzed and is evidently the unsolvated copper formate. The other modification could not be secured in sufficient quantity for analysis, but it is possible that it is simply a different crystalline form of the same compound.

In the ternary system containing the next higher concentration of ammonium formate in the "solvent", (B), the solid phase was not secured in large enough quantity for analysis. However, a comparison of the calor of the solid phase separating out in this solution with the anhydrous copper formate found in system A, and with the disolvate of the copper salt found in solutions containing higher concentrations of ammonium formate, led to the conclusion that the solid phase in B was the former compound. More evidence in favor of this decision is available if we consider the isotherm showing the change in solubility of copper formate with increasing concentration of ammonium formate in the solvent at 50°. This isotherm is illustrated in Figure 3.

Figure 3

The values for the solubility of copper formate, expressed in molecular per cent., are plotted as ordinates against the molecular per cent. of ammonium formate in the solvent as abscissae. The solubility values for copper formate at 50°C were obtained by extrapolation of the experimental curves of Figures 1 and 2, where these curves did not already cross the 50° axis. Since the curves are regular and usually extend to within a few degrees of this axis, this extrapolation was considered sufficiently accurate. Figure 3 indicates an abrupt change in solubility with change in solid phase, as the percentage of ammonium formate increases. As long as the solid phase is $\text{Cu}(\text{OOCH})_2$ the solubility increases practically as a straight line function with respect to the percentage of ammonium formate, but when the solid phase changes to $\text{Cu}(\text{OOCH})_2 \cdot 2 \text{H} \text{OOCH}$ the solubility increases very sharply. The fact that the solubility of the solid phase in B does not coincide with the solubility of the disolvate as indicated by the curve, but does coincide with

the solubility of the unsolvated salt, leads to the conclusion that the solid phase is the latter.

Ammoniated Copper Formate:-

It was mentioned earlier in this discussion that the ternary compound containing copper formate, ammonium formate and formic acid could not be isolated in this system. To test more thoroughly whether or not an ammoniated copper formate existed, it was decided to attempt passing dry ammonia over anhydrous copper formate. A quantity of copper formate was consequently placed in a U-tube and ammonia gas from liquid ammonia that had been treated with metallic sodium was passed over it, precautions being taken so that the moisture of the atmosphere was excluded. The U-tube was immersed in an ice bath in order to facilitate absorption. After ammonia had passed through for a short period of time, the copper formate began to lose its deep blue color and took on a lighter, purple shade. In some portions of the tube the absorption of ammonia was so great that drops of a solution of the salt in liquid ammonia collected on the sides of the tube. This

liquid phase disappeared when the tube was allowed to attain room temperature. The change in color was accompanied by a decided increase in volume, and these facts suggested that probably a compound had formed. To verify this point a quantitative test was run by using a weighed quantity of copper formate and recording the gain in weight as ammonia was passed over it. It was found that the absorption occurred very rapidly at first but after ammonia had been passed over the substance for several days the rate had decreased until it was negligible. This is clearly shown by the fact that during the first ten hours a sample of copper formate weighing 4.658 grams absorbed 1.097 grams of ammonia, while in the last ten hours of the run, it gained only .011 gram. At this point a total of 2.028 grams of ammonia had been absorbed. The final product therefore represents a compound containing 1 mole of $\text{Cu}(\text{OOCH})_2$ to 3.94 moles of NH_3 , and this is believed to be sufficient evidence for assigning to the compound, the formula $\text{Cu}(\text{OOCH})_2 \cdot 4 \text{NH}_3$.

At this point it may be of interest to note that there seems to be some common relation existing between the number of moles of solvent taken up by a mole of copper formate in its various solutions. It was mentioned earlier that it forms two hydrates: $\text{Cu}(\text{OOCH})_2 \cdot 2 \text{H}_2\text{O}$ and $\text{Cu}(\text{OOCH})_2 \cdot 4 \text{H}_2\text{O}$. The former corresponds to the solvate obtained in the formic acid system: $\text{Cu}(\text{OOCH})_2 \cdot 2 \text{HOOCH}$, and the latter is related to the ammoniated compound whose preparation is described above: $\text{Cu}(\text{OOCH})_2 \cdot 4 \text{NH}_3$.

Comparison between solvent action of potassium formate and ammonium formate:—

An interesting phenomenon of which no special mention has hitherto been made is the deepening of color of the solutions containing copper and ammonium formates when the temperature was raised. The usual blue of the copper ion which was observed in the cold solution changed to the deep characteristic bluish purple of the copper ammonia ion in water, when the solution was heated to a temperature of about 90° or 100° . Indeed in the more concentrated solutions of

ammonium formate the color tended toward this shade of blue even at ordinary temperatures. The same behavior was mentioned previously for acetic acid solutions⁶ and has been further studied in such solutions by Griswold.

Now, if we consider the water system, the solubility of copper hydroxide is attributed to the formation of the copper ammonia ion made possible by the fact that ammonium hydroxide is highly dissociated into ammonia and water. In the formic and acetic acid systems, however, since an increase in solubility of the copper salts is observed even at temperatures so low that only a slight dissociation of the ammonium salt into ammonia and the acid can occur, the increase in solubility must be attributed to some other factor. Recalling the effect of a strong base on an amphoteric hydroxide and the consequent solution of the hydroxide, it may not be unreasonable to suppose that in the system under consideration, ammonium formate may be a

⁶A. W. Davidson, J. Am. Chem. Soc., 50 1890 (1928)

relatively strong base and may dissolve the copper formate by virtue of some amphoteric properties of that salt. In fact conductivity measurements⁷ on solutions of the metal formates in formic acid and of ammonium formate show that ammonium formate is even more highly dissociated than potassium formate and the formates of the other alkali metals. Titrations in acetic acid using potassium acetate and ammonium acetate as bases indicate that their basic strengths are very nearly the same.⁸

In order to more thoroughly test this hypothesis, a solution of potassium formate in formic acid was prepared and its solvent action upon copper formate noted. It was found that at a temperature below 60° a solution containing 24.4 mole per cent. of potassium formate in formic acid dissolved 0.38 mole per cent. of copper formate. From the curve of Figure 3, it can be estimated that at this concentration of ammonium formate in formic acid, one would expect that "solvent" to dissolve 0.37 mole

⁷Kendall, Adler, and Davidson, J. Am. Chem. Soc. 43, 1846 (1921). In this article references to earlier work by Schlesinger and others is also given.

⁸Dr. Norris F. Hall in private communication with Dr. A. W. Davidson

per cent. of copper formate at 50°. This indicates that so far as their effect in increasing the solubility of copper formate in formic acid is concerned, potassium formate and ammonium formate are strikingly similar.

The curves in Figure 2 indicate that as the concentration of ammonium formate in the "solvent" increases, not only does the solubility of copper formate become greater but the slopes of the curves also become less abrupt. In other words, the solubility increases more rapidly with rise in temperature at the higher concentrations of ammonium formate. This behavior is readily accounted for if we recall that at high temperatures the deep bluish purple color of the solutions indicated that something analogous to the copper ammonia ion, $\text{Cu}(\text{NH}_3)_4^{++}$, may have been present. It has already been mentioned that at high concentrations of ammonium formate this deep color was observed even at room temperatures. By increasing the concentration of ammonium formate, then, we have in reality also increased the concentration of ammonia, NH_3 , in the solution, since slight dissociation of the salt into ammonia

and formic acid evidently occurs. In these more concentrated solutions of ammonium formate, the solubility of copper formate depends as in the other systems, upon the strong basic properties of ammonium formate and perhaps also upon the solvent effect of ammonia, which latter factor is evident only at higher temperatures in more dilute solutions of ammonium formate.

The similarity of the effect of potassium and ammonium formates upon the solubility of copper formate in formic acid brings up several interesting questions with respect to basic strengths and amphoterism. It has just been shown that the increase in solubility by the addition of ammonium formate cannot be due to any great extent, at low temperatures, to the formation of a copper ammonia complex. If copper formate may be considered as an amphoteric substance, a concept with which we are not familiar in connection with copper salts, an increase in its solubility by addition of potassium formate is readily accounted for. Since ammonium formate behaves in an analogous manner we have further evidence for believing that it too is strongly basic in the formic acid system.

It has often been suggested that if it

were not for the fact that ammonium hydroxide is so highly dissociated into ammonia and water in a water solution, it would be a relatively strong base comparable even to the hydroxides of the alkali metals. This theory might be further supported by a brief consideration of the substituted ammonias. Methyl amine is a substance very much like ammonia except that with its higher molecular weight are associated a lower vapor pressure and a higher boiling point than ammonia. Also, its escaping tendency from a water solution is less than that of ammonia, as is shown by a consideration of solubility data, and this would seem to indicate that mono-methyl ammonia hydroxide has a lesser tendency to dissociate into water and methyl amine than ammonium hydroxide into water and ammonia. For a given concentration of ammonia and methyl amine in water solutions, the latter would therefore give a greater concentration of hydroxyl ion due to the greater amount of the hydroxide present and should be the stronger base. It is well known that methyl ammonium hydroxide is a considerably stronger base than ammonium hydroxide, since it is a sufficiently strong base to dissolve aluminum hydroxide. As we still further increase the molecular weight we should continue to decrease the escaping

tendency of the amine from the solution and thereby strengthen the basic properties. Tetra methyl ammonium hydroxide is a very strong base and behaves like potassium hydroxide in water solutions. Considering these facts it seems probable to suppose that the extreme basic strength of these solutions is due at least partly to an increased concentration of the substituted ammonium hydroxide in the solution made possible by ^{the} substituting groups rather than entirely to the chemical properties of these substituting groups. In acetic and formic acids, where ammonia is much more firmly held than in water, even the unsubstituted ammonium compounds are strong bases.

From the above reasoning it would be logical to suppose that aqueous ammonium hydroxide would be a very strong base providing a concentrated solution of it might be obtained. Further light might be thrown upon this question by a study of the behavior of aqueous solutions of ammonium hydroxide at very low temperatures, where the degree of dissociation into ammonia and water is doubtless much smaller than under ordinary conditions.

Summary

1. The solubility of copper formate in pure formic acid has been determined over a range of temperatures.
2. Solubility curves for copper formate in solutions of various known concentrations of ammonium formate in formic acid have been obtained.
3. A comparison has been made of the effect of potassium formate upon the solubility of copper formate in formic acid with that observed for ammonium formate.
4. In the course of the investigation two compounds have been isolated which have not been previously reported: $\text{Cu}(\text{OOCH})_2 \cdot 2\text{HOOCH}$ and $\text{Cu}(\text{OOCH})_2 \cdot 4 \text{NH}_3$.
5. Some speculations have been put forward as to the basic strength of ammonium formate and the amphoteric nature of copper formate in the formic acid system.