

# AN INTRODUCTION TO THE CHEMISTRY OF ACETIC ACID SOLUTIONS

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## I. ACETIC ACID AS A SOLVENT FOR ELECTROLYTES

Acetic acid has been familiar to chemists for so long a time, is so readily obtainable in a pure state, and is a liquid over so wide and convenient a range of temperature ( $16.6^{\circ}$  to  $118^{\circ}$ ), that it seems strange that its properties as a solvent for inorganic substances should have remained, until recently, so little known. But when Raoult (1), in 1884, made a study of freezing point depressions in this solvent, he limited himself almost entirely to organic solutes, and Beckmann (2), reporting its ebullioscopic behavior twenty-three years later, made the statement that acetic acid was not a very suitable solvent for inorganic substances. Whether or not it was these precedents that acted as a deterrent to further investigation, it is, of course, impossible to determine; it is a fact, however, that data concerning the solubilities and reactions of electrolytes in acetic acid remained, for many years, meager and unorganized. Several addition compounds were reported, a few solubilities were determined, and conductivity measurements were made on solutions of the alkali acetates and of several other salts; much of this data was compiled by Walden, in 1924, in his "Elektrochemie Nichtwässriger Lösungen" (3).

Within the last few years, interest in this solvent appears to have revived. In 1926, Webb (4), using the freezing point method, studied the activity coefficients of several salts in acetic acid solution, and in the following year Hall and Conant (5), using an electrometric method for the determination of hydrogen ion activity, showed how the properties of acids and bases in

glacial acetic acid might be studied in a very thorough and interesting manner. Selected references to work in this field up to 1928 were given in the first paper of a series by the present writer (6); in this paper, also, there were reported the results of preliminary experiments, of a qualitative nature, on the solubilities of salts in anhydrous acetic acid. It immediately became evident, not only that this liquid was capable of dissolving a much larger number of salts than had been previously supposed, but also that the chemical properties of these salt solutions were of sufficient variety and interest to repay further study. Without undertaking to give a complete list of soluble salts, it may be stated that these include not only many of the acetates (which are to be regarded as bases in acetic acid, as will be shown later), but a large number of nitrates, halides (particularly iodides), cyanides and thiocyanates as well; in many cases, stable solvates have been isolated in the solid state from these solutions. When to this list are added water, ammonia, and some of the common acids, such as perchloric, sulfuric, hydrochloric, orthophosphoric, and hydrogen sulfide, all of which are readily soluble in acetic acid, it is clear that we have at our disposal a group of acids, bases and salts large and varied enough to enable us to acquire at least a general idea of the chemistry of acetic acid solutions.

## II. METATHETIC REACTIONS OF SALTS, ACIDS AND BASES IN ACETIC ACID AS SOLVENT

The early conductivity measurements on salts in acetic acid solution, together with the freezing point determinations of Webb and the electrode potential measurements of Hall and Conant, leave no room for doubt that, in spite of its rather low dielectric constant (about 6 at 25°), typical acids, bases and salts are dissociated into ions in this medium. That the dissociation can hardly be regarded as complete (or that the effect of interionic attraction must be large) is a point which need not concern us here. We should expect, therefore, that ordinary metathetical reactions would proceed smoothly in acetic acid. Experiment showed (6) that such reactions do take place, in many cases as readily as in water, with the formation of slightly soluble or un-

dissociated substances. It appears that practically all salts that are difficultly soluble in water are insoluble in acetic acid also.<sup>1</sup> In accordance with this rule, it was found, for instance, that solutions of soluble salts of the heavy metals gave immediate precipitates upon the introduction of hydrogen sulfide gas; some of the sulfides so precipitated dissolved readily in a dilute solution of hydrogen chloride. (No sulfide precipitates were obtained, however, with salts of the alkali or alkaline earth metals, or of aluminum.) Similarly, a solution of silver nitrate readily yielded precipitates with solutions of soluble chlorides, bromides, iodides, cyanides or thiocyanates, and zinc chloride with a solution of sodium oxalate or of orthophosphoric acid, just as in aqueous solution. It would serve no purpose to extend this list further.

On the other hand, a number of salts which are easily soluble in water are practically insoluble in acetic acid. The most familiar group of salts in this class are the sulfates of the metals, all of which, even those of the alkalis, are difficultly soluble in acetic acid. Using a solution of anhydrous sulfuric acid in acetic acid as the precipitant, a sulfate or an acid sulfate can be precipitated from a solution of almost any soluble metal salt. The acetates of many of the less positive metals are insoluble, and can be precipitated from solutions of soluble salts by the addition of sodium acetate. And as a final example of a reaction which has no close parallel in aqueous solution it may be mentioned that barium nitrate is sufficiently insoluble to be precipitated upon mixing solutions of sodium nitrate and barium iodide.

Certain salts which are known to be only slightly dissociated in aqueous solution give evidence of but slight dissociation in acetic acid also. Thus the very deeply colored ferric thiocyanate is just as readily formed by metathesis in acetic acid as in water. Antimony trichloride and stannic chloride (if the latter may be called a salt) give no precipitates with sulfuric acid or with silver nitrate, presumably due to their being almost undissociated. It may be mentioned here that on mixing stannic chloride and acetic acid, an unparalleled increase in viscosity is observed, the

<sup>1</sup> Mercuric iodide, which is fairly soluble in acetic acid, constitutes the only exception to this rule which has so far been observed.

mixture being enormously more viscous than either component in the pure state. This phenomenon has been studied quantitatively by Stranathan and Strong (7), and a solid solvate of stannic chloride has been isolated from such a mixture by the writer (8).

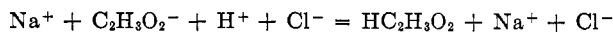
The most interesting group of metathetical reactions, however, consists of those which, while not identical with reactions in aqueous solution, are found to be entirely analogous to them when the nature of the medium is taken into consideration. Outstanding examples of acetic acid analogs of phenomena familiar in aqueous solution are to be found in reactions involving acids and bases. The general concepts of acidity and basicity have been the subject of much discussion within the last few years (9) and need not be considered at length here. In considering acetic acid solutions, we may safely follow Hall and Conant (5), who employ hydrogen ion activity as the criterion of acidity. These authors showed that, on this basis, the familiar acids such as perchloric, sulfuric and hydrochloric have strongly acid properties in acetic acid also. On the other hand, the purely formal analogy between the metal acetates,  $MC_2H_3O_2$ , in acetic acid,  $HC_2H_3O_2$ , and the hydroxides,  $MOH$ , in water,  $HOH$ , is immediately obvious, and might be interpreted as an indication that the metal acetates are bases in the acetic acid system of compounds, just as the metal hydroxides are bases in the water system, or the metal amides in ammonia (10). A formal resemblance of this nature, as Walden (11) has pointed out, is hardly sufficient justification for classifying the substances in question as bases; some real evidence of their basic function is required also. Such evidence was again supplied by Hall and Conant, who showed that sodium acetate (as well as a large number of organic compounds of a basic nature) does indeed decrease hydrogen ion activity when added to acetic acid solutions, and is therefore actually a base in this solvent. Hall and Werner (12) carried out the electrometric titration of sodium acetate with acids in acetic acid solution, and Hall (13) has found that the acetates of the other alkali metals behave in a similar manner. Expressing these facts in terms of Brönsted's conception of acids and bases (14), we might say that in all these cases the actual base is the acetate ion, which shows an avidity

for the hydrogen ion, or proton, similar to that exhibited by the hydroxyl ion.

The process of neutralization, then, takes place readily in acetic acid solutions, and follows the course illustrated by the equation



Since pure acetic acid is probably only very slightly dissociated into ions, its specific conductivity being even smaller than that of water, we may write this in the ionic form (neglecting, as we commonly do in the case of reactions in aqueous solution, the solvation of the ions), as follows:



The occurrence of reactions of this type can be observed in various ways besides the electrometric method which has already been mentioned. It is perfectly practicable to follow the course of the neutralization by means of indicators (15, 16, 17). It must be noted, however, that the hydrogen ion activity at the "neutral" point in acetic acid is far higher than in water, corresponding, according to Hall (13), to a pH value in the neighborhood of zero; so that, for the titration of a strong acid with a strong base in acetic acid, an indicator showing a color change in this region (such as crystal violet, methylene blue or picric acid, to mention only a few) would have to be employed, those commonly used for similar titrations in aqueous solution being entirely unsuitable.

Still another means of observing these neutralization reactions is, of course, available in the event of a marked difference in solubility between the salt produced and one or both of the reactants. Thus the neutralization of sodium acetate by hydrochloric acid is accompanied by the precipitation of sodium chloride. On the other hand, the very insoluble zinc acetate readily dissolves upon the addition of a solution of hydrogen chloride, just as zinc hydroxide dissolves in aqueous hydrochloric acid; while hydroferrocyanic acid, difficultly soluble in acetic acid, dissolves fairly readily in sodium acetate solution.

Further examples of acetic acid analogs of reactions familiar in aqueous solution will be given later.

## III. SOLUBILITIES OF ACETATES IN ACETIC ACID

As was pointed out in the preceding section, the metal acetates are the analogs in acetic acid of the metal hydroxides in water. Now, one of the most conspicuous features of the group of hydroxides, in relation to the solvent water, is the enormous variation in solubility from the extremely soluble alkalis, at one end of the scale, to the very insoluble aluminum and ferric hydroxides, at the other. Kendall and coworkers (18, 19, 20) have shown that such variation, far from being peculiar to aqueous solutions,

TABLE 1  
*Solubility of acetates in acetic acid*

METAL	SOLVATES ISOLATED	SOLUBILITY, MOLE PER CENT AT 25°	MOLES OF ACETIC ACID PER MOLE OF ACETATE IN SOLID PHASE
K	$\text{KC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ , $\text{KC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	12.29	2
Na	$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ , $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	7.06	2
Li	$\text{LiC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	9.37	1
Ba	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{HC}_2\text{H}_3\text{O}_2$ , $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$	3.48	3
Ca	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	0.068	1
Zn	None	0.0018	0
Pb	None	31.9	0
Fe(-ic)	None	Practi- cally 0	0
Cu	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$	0.166	1
Ag	None	0.094(76°)	0

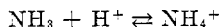
is found in several series of systems of the type HX:MX. The order of solubility of a series of sulfates in sulfuric acid, or of formates in formic acid, is very similar to that of the corresponding hydroxides in water. More recently, Fredenhagen and Cadenbach (21) have shown the same thing to be true for solutions of fluorides in anhydrous hydrogen fluoride. An explanation of this regularity, in terms of the effect of addition compound formation on solubility, is offered by Kendall in one of the articles just referred to (20). The results of accurate measurements on a number of acetates in acetic acid (17, 19) fall in line with the analogous cases in other solvents. As is shown in table 1, where

some of these results are summarized briefly, the acetates of the alkali metals and of barium exhibit marked solvation and are readily soluble, while the solubility of the acetates of most of the less electropositive metals is small, lead acetate constituting a very marked exception.

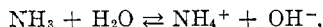
#### IV. AMMONIA AND WATER AS BASES IN ACETIC ACID SOLUTION

The large group of organic bases will not be considered in this article, but any discussion of basicity in acetic acid solution would be incomplete without mention of the two additional inorganic basic substances, ammonia and water.

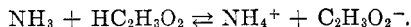
The basic nature of ammonia may be regarded from two different points of view. According to the ideas of Brönsted (14), ammonia is to be regarded as a base because of its tendency to combine with a hydrogen ion, or proton, to form ammonium ion:



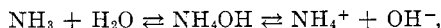
More specifically, in aqueous solution, we might write



where  $\text{NH}_3$  and  $\text{OH}^-$  are both bases. A corresponding formulation for ammonia in acetic acid solution would be



Despite the advantages of this viewpoint, too close adherence thereto might, it appears to the writer, have the undesirable effect of obscuring the very close similarity between ammonium compounds and those of the alkali metals, especially potassium. In order to emphasize this similarity, it would seem preferable to formulate the above reactions as follows:



and



Ammonium acetate is, of a course, a well-known salt, which is quite stable with respect to ammonia and acetic acid, not only at

room temperature, but up to its melting point,  $113^{\circ}$ ; and it is quite unlikely that it is *completely* dissociated into its ions in acetic acid solution. Moreover, the freezing point curve for ammonium acetate in acetic acid is quite similar to that for potassium acetate (17), and Hall (13) has found that the two compounds behave quite similarly on titration with acids. There is every indication, then, that in acetic acid solution ammonia combines completely with the solvent, and that the resulting ammonium acetate is as strong a base as potassium acetate. Considering the aqueous solution of ammonia from the same point of

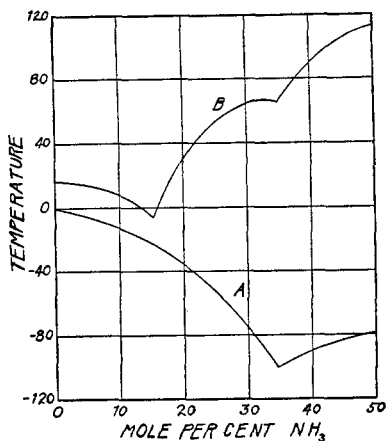


FIG. 1. FREEZING POINT CURVES OF AMMONIA IN WATER (A) AND IN ACETIC ACID (B)

view, the compound ammonium hydroxide should not be regarded merely as a convenient, though probably fictitious, postulate, as some authors have done (22), since it also is capable of existence as a stable solid, though at low temperatures only. In this connection, the freezing point curves of ammonia in water (23) and in acetic acid (17) as solvents may profitably be compared. In figure 1 these curves (for concentrations of ammonia up to 50 mole per cent) are plotted on the same scale, and the enormous difference in stability between the addition compounds  $\text{NH}_3 \cdot \text{H}_2\text{O}$  or ammonium hydroxide, on the one hand, and  $\text{NH}_3 \cdot \text{HC}_2\text{H}_3\text{O}_2$  or ammonium acetate, on the other, is clearly brought



out. Whatever may be the cause of this difference, it seems altogether reasonable to advance the hypothesis that at very low temperatures ( $-90^{\circ}$  or thereabouts) a solution of ammonium hydroxide might behave in an entirely analogous manner to one of potassium hydroxide. However, the rather flat maximum in the freezing point curve indicates that ammonium hydroxide is somewhat dissociated into ammonia and water even at  $-79^{\circ}$ , and the extent of this dissociation doubtless increases with increasing temperature, so that the weakness of ammonium hydroxide as a base under ordinary conditions may reasonably be ascribed to the instability of the compound with respect to ammonia and water.

Whereas ammonia in acetic acid solution, as has just been mentioned, exhibits strongly basic properties, the closely related substance water, though also a basic solute, is only weakly so. This is indicated both by the potential measurements of Hall and Conant (5) and by observations on the effect of water upon indicators in acetic acid (17). The weakly basic nature of water is accounted for, in terms of Brönsted's ideas, by the hypothesis that, although the water molecule will combine with a proton to form the oxonium ion,  $\text{H}_3\text{O}^+$ , the tendency for this reaction to take place is considerably less than in the case of the ammonia molecule. Or, if we choose to formulate the behavior of water as a solute in a manner entirely analogous to that used for ammonia, we might write



However, the existence of the addition compound, which may be called oxonium acetate, is open to question, since, unlike ammonium acetate, it is unknown in the solid state at ordinary temperatures. In figure 2 the freezing point curves (up to a concentration of 50 mole per cent of solute) for water (24) and for ammonia (17) as solutes in acetic acid are plotted on the same scale. It is evident that oxonium acetate cannot be isolated as a solid even at very low temperatures. Nevertheless, the identity between the cryoscopic effects of the two substances in moderately dilute solutions, as shown by the exact coincidence of the two

curves in this region, points toward a similar state of solvation at these low concentrations, and makes it seem probable that oxonium acetate is capable of existence *in solution* and that it is actually formed, to some extent, when water is dissolved in acetic acid. Again it seems entirely reasonable to explain the low basicity of water in acetic acid solution as compared to ammonia, in terms of the instability of oxonium acetate as compared to ammonium acetate.

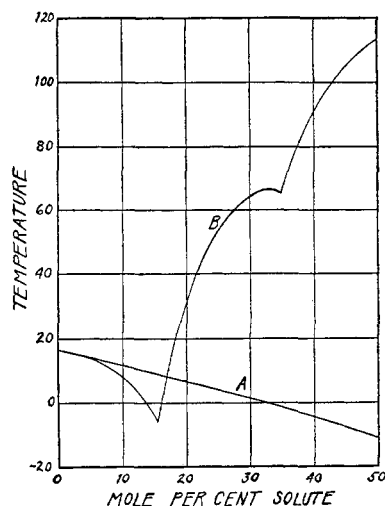
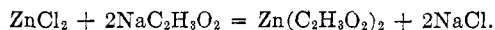


FIG. 2. FREEZING POINT CURVES OF WATER (A) AND OF AMMONIA (B) IN ACETIC ACID

#### V. THE EFFECT OF SODIUM AND AMMONIUM ACETATES UPON THE SOLUBILITY OF OTHER ACETATES IN ACETIC ACID

When a small amount of sodium acetate solution is added to a solution of zinc chloride in acetic acid,<sup>2</sup> a precipitate of zinc acetate is formed, the reaction being expressed by the equation



This reaction is, of course, analogous to the precipitation of zinc hydroxide by the addition of sodium hydroxide to an aqueous

<sup>2</sup> Prepared by heating a solution of hydrogen chloride with an excess of zinc acetate and filtering.

solution of a zinc salt. Now, just as the precipitate of zinc hydroxide dissolves in an excess of sodium hydroxide solution, so does the precipitate of zinc acetate, in acetic acid, dissolve in an excess of sodium acetate solution. Detailed investigation of this phenomenon (25) showed that the analogy between the two cases is far from being merely a superficial one. The solubility curve of zinc acetate in acetic acid solutions containing varying concentrations of sodium acetate, at a constant temperature, is

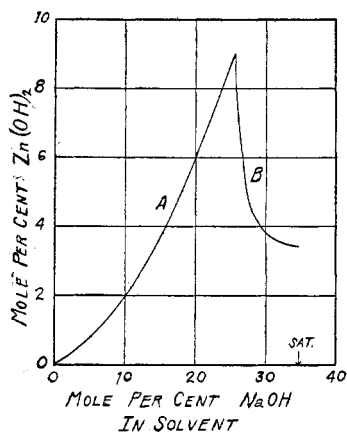


FIG. 3

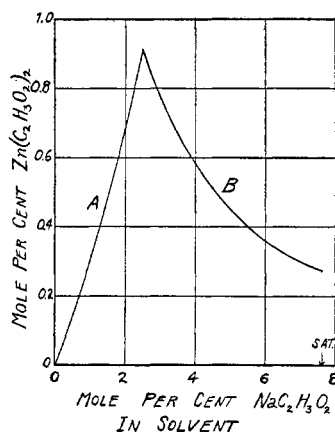


FIG. 4

FIG. 3. EFFECT OF  $\text{NaOH}$  UPON THE SOLUBILITY OF  $\text{Zn}(\text{OH})_2$  IN  $\text{H}_2\text{O}$  AT  $30^\circ$

A—solid phase  $\text{Zn}(\text{OH})_2$ ; B—solid phase  $\text{Zn}(\text{OH})_2 \cdot 2\text{NaOH} \cdot 2\text{H}_2\text{O}$

FIG. 4. EFFECT OF  $\text{NaC}_2\text{H}_3\text{O}_2$  UPON THE SOLUBILITY OF  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$  IN  $\text{HC}_2\text{H}_3\text{O}_2$  AT  $28.5^\circ$

A—solid phase  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; B—solid phase  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NaC}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$

strikingly similar to the curve for zinc hydroxide in aqueous sodium hydroxide solutions, as may be seen by a comparison of figure 3, plotted from the data of Goudriaan (26), and figure 4, from the investigation (25) just referred to. In each case the solubility of the zinc compound increases with increasing concentration of sodium compound until a maximum is reached,<sup>3</sup> at

<sup>3</sup> In figure 3 this branch of the curve shows the solubility of zinc hydroxide, although this compound is metastable with respect to zinc oxide under these conditions.

which point a new solid phase appears; beyond this point the concentration of zinc compound in the saturated solution decreases with increasing concentration of sodium compound. The solid phase which appears at high concentrations of sodium compound may be formulated, in each case, as a ternary addition compound of the three components of the solution. The composition of these two ternary compounds is very similar, as is evident from the following comparison: in water— $\text{Zn}(\text{OH})_2 \cdot 2\text{NaOH} \cdot 2\text{H}_2\text{O}$ , or  $\text{Na}_2\text{ZnO}_2 \cdot 4\text{H}_2\text{O}$ ; in acetic acid— $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NaC}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ , or  $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ . In the aqueous system zinc hydroxide is said to be amphoteric, and the ternary com-

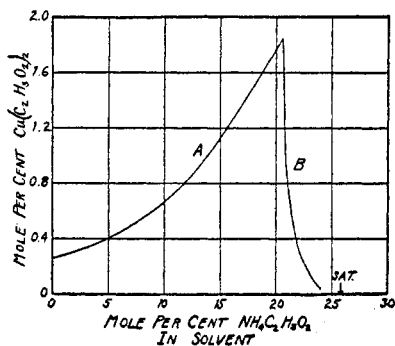


FIG. 5. EFFECT OF  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  UPON THE SOLUBILITY OF  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  IN  $\text{HC}_2\text{H}_3\text{O}$  AT  $33.5^\circ$

A—solid phase  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$ ;  
 B—solid phase  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$

pound is thought of as a sodium zincate. An answer to the question of whether or not this name, or some modification thereof, such as sodium acetozincate, would also be suitable for the ternary compound in the acetic acid system, must wait upon further investigation of the properties of this substance.

The solubility of cupric acetate in acetic acid, though considerably greater than that of zinc acetate, is still rather low. It was found, however, that cupric acetate dissolves very readily in an ammonium acetate solution, and a quantitative study of this phenomenon (27) again led to interesting results. Figure 5 shows the variation in the solubility of cupric acetate with varying con-

centration of ammonium acetate in acetic acid, at a constant temperature. The solubility of cupric acetate rises to a maximum, at which point a ternary addition compound appears; with further increase in ammonium acetate concentration, the concentration of cupric acetate in the saturated solution falls off. The composition of the ternary addition compound in this case may be represented by the formula  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$ .

The writer was at first disposed to regard these facts as exactly analogous to the solubility of cupric hydroxide in aqueous ammonium hydroxide solution. There is, indeed, a marked resemblance between the two cases; the solubility of cupric hydroxide increases with increasing concentration of ammonium hydroxide, and, although there is no satisfactory evidence as to the composition of the solid phase in equilibrium with solutions of high ammonia content, the compound  $\text{Cu}(\text{OH})_2 \cdot 4\text{NH}_3$  is commonly supposed to be present in the solution. Further consideration, however, has led to a somewhat altered viewpoint. It has been mentioned above that ammonium acetate in acetic acid, unlike aqueous ammonium hydroxide, is as strong a base as the corresponding potassium compound; moreover, qualitative experiments have shown (27) that cupric acetate readily dissolves in potassium acetate solution also. It therefore seems preferable to regard the effect of ammonium acetate on the solubility of cupric acetate in the same light as the effect of sodium acetate on zinc acetate, discussed above, and to seek the water analog of this phenomenon in the effect of the alkali hydroxides, rather than of ammonium hydroxide, upon cupric hydroxide. Although cupric hydroxide is not ordinarily considered to be amphoteric, it is appreciably soluble in concentrated aqueous solutions of alkalis. In fact, Müller (28), in a quantitative study of its solubility in sodium hydroxide solution, obtained a solubility isotherm of the same type as those of figures 3, 4 and 5, with an addition compound which he called sodium cuprite appearing as solid phase at very high concentrations of alkali.<sup>4</sup> It may be mentioned here that

<sup>4</sup> The investigation of such systems in aqueous solution is extremely troublesome because of the high viscosity of the concentrated alkali solutions which

many addition compounds of this nature have been obtained from solutions in liquid ammonia, and have been discussed by Franklin (10).

One further property of these cupric acetate-ammonium acetate-acetic acid solutions remains to be noted. On heating them to a temperature of 100° or higher, they exhibit a very marked deepening of their blue color. At the boiling point they attain a very intense shade of violet-blue, which is practically identical with the familiar color characteristic of aqueous solutions containing the so-called cupric ammonia ion. The resemblance is so close that it seems unlikely that it could be merely fortuitous, especially since the cupric acetate-potassium acetate solutions show no color change whatever on heating. It would therefore seem a reasonable hypothesis that at these elevated temperatures a solution of ammonium acetate in acetic acid approaches the state of an aqueous ammonium hydroxide solution at ordinary temperatures; that is, that the ammonia is but loosely held by the solvent, and is therefore available for the formation of other ammonia complexes which are more stable at the temperature in question. If this supposition is correct, then the violet-blue color of the hot cupric acetate-ammonium acetate solutions may be due to a complex ion,  $\text{Cu}(\text{NH}_3)_n^{++}$ , very similar to that which gives rise to the same color in aqueous solutions.

Several other facts have been observed which also seem to point toward a loosening of the bond between dissolved ammonia and acetic acid at temperatures in the neighborhood of the boiling point of the solvent. For instance, silver chloride does not dissolve in an acetic acid solution of ammonium acetate in the cold, as it does in aqueous ammonia, but does dissolve when the mixture is heated to boiling. Similarly, mercurous chloride, which is quite insoluble in acetic acid, shows no change of color when ammonium acetate is added at room temperature, but turns gray on being heated. And finally, the fact that the distillate from a concentrated solution of ammonium acetate in acetic acid

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have to be employed, and the difficulty of obtaining substances like cupric hydroxide or zinc hydroxide in crystalline forms of constant composition. In the acetic acid systems, these difficulties do not arise.

contains perceptible quantities of ammonia (29), shows that the vapor pressure of ammonia in such a solution, which must be practically zero at room temperature, becomes appreciable at the boiling point of the solution. The conclusion may be drawn, then, that while ammonium acetate in acetic acid at 25° is comparable to potassium hydroxide rather than to ammonium hydroxide in aqueous solution, yet above 100° it begins to exhibit properties similar to those of an aqueous ammonium hydroxide solution at low temperatures.

Some of the phenomena which have been discussed in this article have so far been studied only superficially, and further investigation will be necessary for a better understanding of the facts observed and a more thorough confirmation of the hypotheses advanced; while many other possible reactions and relationships have not been touched upon at all. Nevertheless, it appears to the writer that the value of the study of non-aqueous solutions, as a means of broadening our perspective of general chemistry, is further demonstrated by these first steps toward the development of the chemistry of acetic acid solutions.

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