the tube dissipated, the reaction mixture solidified. Fractional recrystallizations of the crude material from alcohol yielded 60% of the theoretically calculated amount of 10-methylphenothiazine; m. p. 99–100°, known m. p. 99–100°.[4]

An identical run was made using absolute ethyl alcohol. In this case, only 35% of the calcd. 10-ethyl compound was isolated; m. p. 101–102°, known m. p. 101–102°.[4]

Similar reactions were run with *n*-butyl, *i*-butyl, *s*-butyl, *t*-butyl, *n*-amyl, and benzyl alcohols. In all but the last case, however, phenothiazine was recovered quantitatively, even at temperatures of 180° for forty-eight hours. A 1–2 cc. water layer always formed in the course of these reactions and the characteristic odor of olefin could be detected upon opening the tubes. In the case of the *n*-butyl alcohol run, besides olefin formation, 3 cc. of a liquid having the characteristic odor of di-*n*-butyl ether, b. p. 135–140°, was isolated by fractional distillation from an initial charge of 10 cc. of the alcohol. The benzyl alcohol run gave an unworkable red oil.

10-Ethylphenothiazine Sulfone.—To 20 cc. of boiling water was added 1.0 g. of 10-ethylphenothiazine. The mixture was stirred until the ethyl compound had completely melted and a potassium permanganate solution containing 1.5 g. of permanganate and 45 cc. of water was added over a period of an hour. The reaction mixture was cooled, filtered, and the residue extracted with boiling alcohol. The combined extracts were then diluted with water and the resultant precipitate recrystallized from alcohol; wt. 0.65 g. (57% of the calcd.), m. p. 162–163°.

Anal. Calcd. for $C_{14}H_{13}O_2NS$: C, 65.14; H, 5.02. Found: C, 64.84; H, 5.06.

10-Toluenesulfonylphenothiazine Sulfoxide.—An attempt to oxidize 10-tosylphenothiazine by the above procedure failed in aqueous media. Therefore, acetone was used as a solvent to increase its solubility. To a refluxing acetone solution of 1.0 g. of the tosyl compound was added, dropwise, a saturated aqueous potassium permanganate solution until the purple color remained. The reaction mixture was diluted with water and then treated in an analogous manner to the 10-ethyl-sulfone above except that acetone was used in the extractions. Recrystallization from alcohol yielded 0.75 g. (74% of the calcd.), m. p. 246–248°.

Anal. Calcd. for $C_{19}H_{15}O_3NS_2$: C, 61.78; H, 4.06. Found: C, 61.81; H, 3.97.

Attempts to prepare the above sulfoxide and 10-*p*-acetylaminophenothiazine sulfoxide by Barnett's method[7] failed, no observable reaction having occurred after 3 g. samples of the tosyl and acetylamino compounds had been bottled and allowed to stand for two weeks in a solution consisting of 20 cc. of 30% hydrogen peroxide, an equal volume of acetone, and a few drops of a sodium ethoxide solution.

When a glacial acetic acid solution of the acetylamino compound was treated with chromic acid, a black, tarry oxidate was formed with 50% recovery of the unreacted starting material. Shriner had previously found this procedure satisfactory in the oxidation of various sulfides.[12]

Sulfone of Ethyl 10-Phenothiazine-carboxylate.—To a refluxing solution containing 300 cc. of glacial acetic acid, 100 cc. of water, and 60 g. of ethyl 10-phenothiazine-carboxylate,[8] was added 65 g. of potassium permanganate dissolved in 300 cc. of water. The permanganate solution was preheated to about 90° and was added slowly enough to prevent frothing. The mixture was refluxed for twenty minutes, cooled, diluted with water, and filtered. The residue was extracted with acetone, the extracts poured into water and the resulting precipitate recrystallized from acetone. The pure sulfone, wt. 55 g., m. p. 215–216°, was obtained in 83% yield.

Anal. Calcd. for $C_{15}H_{13}O_4NS$: C, 59.41; H, 4.39. Found: C, 60.43, 58.97; H, 4.39, 4.82.

Phenothiazine Sulfone.—To 50 g. of the above sulfone dissolved in an excess of alcohol, 30 g. of potassium hydroxide was added and the reaction mixture refluxed for thirty minutes. The reaction could be followed by the precipitation of potassium carbonate. The hot solution was cooled and diluted with water and the precipitated phenothiazine sulfone recrystallized from alcohol; wt. 35 g. (90% of the calcd.), m. p. 257–258°, known m. p. 258°.[8]

Summary

1. Several 10-substituted phenothiazines including 10-sulfanilylphenothiazine have been prepared.

2. 10-Methyl- and 10-ethylphenothiazine were prepared by the action of the corresponding alcohols on phenothiazine.

3. Phenothiazinesulfone has been prepared by a new and superior method and it has been suggested that the ease of oxidation of 10-substituted phenothiazines is dependent upon the nature of the 10-substituent.

[12] Shriner, Struck and Jorison, This Journal, 52, 2060 (1930).

CHICAGO 16, ILLINOIS RECEIVED JUNE 30, 1944

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

Amphiprotic Substances. I. The Systems Acetamide–Ammonia and Acetamide–Acetic Acid

BY HARRY H. SISLER, ARTHUR W. DAVIDSON, RAYMOND STOENNER AND LUTHER L. LYON

It is a well-known experimental fact that ammonia and simple amines stand high in the Brønsted scale of basicity. This has been explained in terms of the high electron-donating or proton-accepting tendency which, because of the unshared pair of electrons on its nitrogen atom, resides in the amide group. That the acid amides are much less basic is equally well known, and this fact has been attributed to the electron affinity of the carbonyl group, which serves to decrease markedly the electron density about the nitrogen atom. Acetamide, like other simple acid amides, shows so little tendency to accept protons from the strongest acid available in aqueous solution, *viz.*, the hydronium ion, and so little tendency to release protons to the strongest base available in aqueous solution, *viz.*, the hydroxyl ion, that it is ordinarily thought of as a neutral substance. Conductivity studies of solutions of acetamide and barium hydroxide in water have shown that the acid dissociation constant of acetamide is 8×10^{-16}, which is of the same order of magnitude as that of water itself.[1]

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[1] Branch and Clayton, This Journal, 50, 1680 (1928).

In less basic solvents, however, which afford acids stronger than the hydronium ion, these acid amides show appreciably basic properties. For instance, the study of the potentiometric titration of acetamide with perchloric acid in glacial acetic acid has shown that acetamide behaves as a weak base in acetic acid solution.[2,3,4]

In liquid ammonia, on the other hand, where bases much stronger than the hydroxyl ion are available, acetamide and other simple acid amides take part in many reactions which justify their classification as aquo-ammono carboxylic acids.[5] Metallic amides, imides, or nitrides have been found to react with liquid ammonia solutions of acetamide to form metallic salts, as illustrated by the equation[6,7]: $CH_3CONH_2 + NaNH_2 \rightarrow CH_3CONHNa + NH_3$. Likewise, solutions of acetamide in liquid ammonia react with active metals with the evolution of hydrogen and the formation of aquo-ammono acetates.[8] Acetamide also has been found to give a slightly conducting solution in liquid ammonia.

However, in spite of the above evidences for the amphiprotic nature of acetamide, no attempt has thus far been made to study the systems acetamide–acetic acid and acetamide–ammonia through the entire range of concentrations. Yet these systems are of special interest because of the close relationship of acetamide both to acetic acid and to ammonia; specifically, acetamide may be regarded either as the acetyl derivative of ammonia, or, in terms of the Franklin[5] point of view, as aquo-ammono acetic acid. The present work consists principally of freezing point studies of these systems and has indicated the existence of 1–1 addition compounds of acetamide both with acetic acid and with ammonia.

The work of Davidson and Griswold[9] has shown that, in exact analogy with the effect of ammonia on the solubility of cupric hydroxide in water, the presence of ammonia greatly increases the solubility of cupric acetate in acetic acid. Moreover, a dark violet-blue color, reminiscent of that of aqueous solutions of the cupric ammonia complex, is obtained when these ternary solutions are heated. Since the present work, as well as that of Hall and his co-workers,[2,3,4] indicates that the behavior of acetamide in acetic acid is in many respects analogous to that of ammonia, it seemed of interest to determine the effect, if any, of acetamide on the solubility of cupric acetate in acetic acid. The results obtained indicate that the presence of acetamide does indeed increase such solubility.

Experimental

Materials.—The anhydrous acetic acid was prepared by the method of Kendall and Gross[10] from synthetic glacial acetic acid and its purity checked by its freezing point. No sample used varied from the reported freezing point of 16.60° by more than 0.03°.

The acetamide was purified by the method described by Wagner.[11] This method invariably yielded a product which melted at 80.2 ± 0.2° in poor agreement with the melting point of 82° reported by Wagner. The lower melting point, however, is in accord with other published results, such as those of Peterson.[12] Further, in accordance with observations first reported by Kahrs[13] and by Korber,[14] and recently confirmed by Peterson and others, it was found that when acetamide is heated to a temperature well above the melting point of the stable form, and then rapidly cooled, it is converted to a metastable modification which melts at 69°.

The ammonia was synthetic anhydrous ammonia with a stated purity of 99.95%. Its freezing point was found to be −77.5 ± 0.4°, in good agreement with the values of −77.7 to −77.8° found in the literature.[15]

Anhydrous cupric acetate was prepared by recrystallization of the monohydrate from solution in dilute aqueous acetic acid and dehydration at 90° until no water remained. Samples of the resulting dark bluish-green product were analyzed for copper by the iodimetric method and gave closely concordant results. Calcd. for $Cu(C_2H_3O_2)_2$: Cu, 35.00. Found: Cu, 35.14.

The System Acetamide–Acetic Acid.—This system was studied by means of the freezing point or synthetic method as described in previous papers from this Laboratory. While the accuracy of this method varies considerably with the slope of the temperature–concentration curve, as well as with the interval between the freezing point and room temperature, the data reported for this system are believed to be accurate to ±0.5°. An unsuccessful attempt was made to establish points in the freezing point curve for the metastable form of acetamide in acetic acid. It was found that when mixtures containing high concentrations (above 88 mole %) of acetamide were heated above 80° and cooled rapidly, crystals of the metastable modification were indeed obtained. However, when the

TABLE I

ACETAMIDE–ACETIC ACID

S	*T*
(a) Solid phase CH_3CONH_2	
0.0	80.2
8.0	75.8
11.5	72.5
14.3	69.6
16.2	68.0
20.9	63.0
30.0	51.9
40.2	35.6
51.5	8.0
(b) Solid phase $CH_3CONH_2 \cdot HC_2H_3O_2$	
51.9	−0.2
53.6	− .5
55.8	− .6
57.9	−1.8
60.3	−2.6
62.5	−3.9
68.2	−9.2
(c) Solid phase $HC_2H_3O_2$	
69.9	−11.7
70.0	−11.1
71.8	− 9.4
76.7	− 2.2
78.9	0.0
81.8	3.0
87.0	7.7
89.0	8.9
94.2	12.9
95.3	13.4
96.4	14.2
97.5	14.9
100.0	16.6

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(2) Conant and Hall, THIS JOURNAL, **49**, 3047 (1927).

(3) Hall and Werner, *ibid.*, **50**, 2367 (1928).

(4) Hall, *ibid.*, **52**, 5115 (1930).

(5) Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1931, Chapter XXIX.

(6) Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902).

(7) Franklin, THIS JOURNAL, **37**, 2279 (1915).

(8) Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

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

(10) Kendall and Gross, *ibid.*, **43**, 1426 (1921).

(11) Wagner, *J. Chem. Education*, **7**, 1135 (1930).

(12) Peterson, *Proc. Iowa Acad. Sci.*, **46**, 195 (1939).

(13) Kahrs, *Z. Krist.*, **40**, 477 (1905).

(14) Korber, *Z. physik. Chem.*, **82**, 45 (1913).

(15) Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

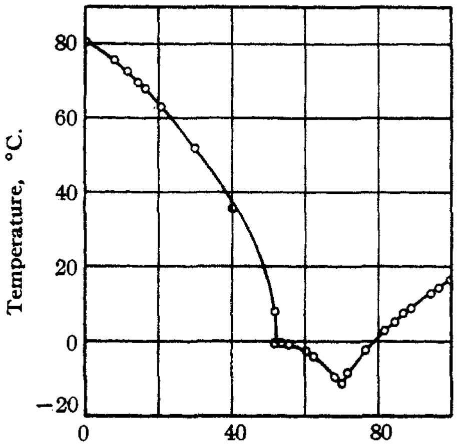

Fig. 1.—System acetamide–acetic acid.

mixture was warmed, the acetamide always reverted to the stable form before the melting point was reached.

The data obtained for the acetamide–acetic acid system are listed in Table I and recorded graphically in Fig. 1. In Table I, *S* denotes the mole % of acetic acid and *T* the corresponding equilibrium temperature.

Although the compositions of the various solid phases in equilibrium with the solution are evident from the course of the curve in Fig. 1, the composition of solid phase (b) was checked by analysis. Samples of this solid phase were obtained by filtration at appropriate temperatures and were dried as quickly and thoroughly as possible by means of pressure between porous tiles; weighed portions of the solid were then titrated with standard alkali. Calculated for $CH_3CONH_2 \cdot HC_2H_3O_2$: $HC_2H_3O_2$, 50.40. Found: $HC_2H_3O_2$, 49.91, 49.98, 50.26.

The Ternary System Acetamide–Acetic Acid–Cupric Acetate.—In the study of this system, acetic acid solutions were prepared containing 5.0, 9.2, and 16.4 mole % of acetamide. To these solutions increasing amounts of cupric acetate were added, and the equilibrium temperatures (which increased very rapidly with increasing concentration of cupric acetate) were determined just as in the binary system acetamide–acetic acid. The data for each concentration of acetamide were plotted on the same scale and the point where each curve cut the 35° abscissa was taken as representing the solubility of cupric acetate at 35° in the respective solution. Data obtained for this ternary system are presented in Table II.

TABLE II

5.0% Acetamide		9.2% Acetamide		16.4% Acetamide	
% $Cu(C_2H_3O_2)_2$	*T*	% $Cu(C_2H_3O_2)_2$	*T*	% $Cu(C_2H_3O_2)_2$	*T*
0.42	20	0.54	26	0.75	18
.43	34	.56	40	.78	36

From the lines (not reproduced here) plotted from these data, the values for the 35° isotherm given in Table III were obtained. These data are plotted in Fig. 2, along with the data of Davidson and Griswold[9] on the solubility of cupric acetate in solutions of ammonia in acetic acid for comparison. The mole % of cupric acetate is plotted in curve *A* against the mole ratio $NH_3/[NH_3 + HC_2H_3O_2]$; in curve *B*, against the mole ratio $CH_3CONH_2/[CH_3CONH_2 + HC_2H_3O_2]$.

TABLE III

Mole ratio $\frac{CH_3CONH_2}{CH_3CONH_2 + HC_2H_3O_2}$	Mole % $Cu(C_2H_3O_2)_2$ in satd. soln. at 35°
0.000	0.31
.050	.43
.092	.55
.164	.78

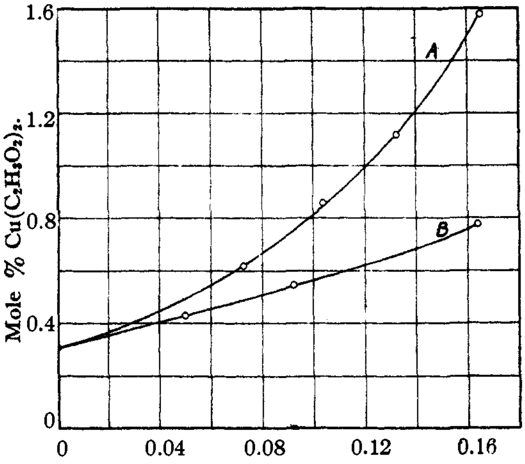

Fig. 2.—Ternary systems: (A) cupric acetate–ammonia–acetic acid; (B) cupric acetate–acetamide–acetic acid.

The ternary solutions of acetamide, acetic acid, and cupric acetate did not exhibit the characteristic violet-blue color observed in hot solutions of ammonia, acetic acid, and cupric acetate, as well as in solutions of ammonia, water and cupric hydroxide. The dark green color of the acetamide–acetic acid–cupric acetate solutions remained unchanged even when the solutions were heated to the boiling point. Neither was any ternary solid compound obtained, as in the case of ammonia–acetic acid solutions, in this system, even at high concentrations of acetamide; the only phase which separated out was the familiar $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$.

The System Acetamide–Ammonia.—The methods used for the determination of freezing points in this system were similar to those employed in the study of the system acetic acid–ammonia,[16] recently reported from this Laboratory. For mixtures of freezing point higher than +5° (0.0 to 62.2 mole % of ammonia) the procedure was the same as that employed for mixtures of intermediate ammonia content in the acetic acid–ammonia study, except that instead of U-shaped tubes of uniform diameter, small ampoules (60 × 13 mm.) attached at one end to glass tubing of smaller bore (7 mm.) were used. This modification was made in order to allow the use of samples of larger mass, with a smaller amount of space for vapor. Such precaution was found to be necessary because acetamide–ammonia mixtures of low ammonia content had, at their freezing points, vapor pressures so high as to introduce considerable error into freezing-point determinations in tubes providing a relatively large vapor space. A sample of acetamide (0.6 to 0.7 g.) was introduced into one of these ampoules, which was then immersed in a bath of chloroform, carbon tetrachloride, and solid carbon dioxide, and dry ammonia was passed in. The quantity of ammonia condensed was controlled by the maintenance of a constant rate of flow and the regulation of the time of condensation, which varied, in different samples, from five seconds to four minutes. With the ampoule still in the cold-bath, the glass tubing was sealed off about 30 mm. above the body of the ampoule. The sample was then allowed to come to room temperature, and was weighed to determine the amount of ammonia condensed. It was then warmed until liquefaction, except for one or two small crystals,[17] had taken place, and was allowed to crystallize

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(16) Davidson, Sisler and Stoenner, THIS JOURNAL, 66, 779 (1944).

(17) In order to obtain the stable form of acetamide on solidification, it was found necessary in the region of low ammonia content (<33 mole %) to allow at least one crystal to remain unmelted. This precaution was taken on each sample in this range until the freezing point of the stable form for that particular sample had been established.

slowly. The freezing point was then determined as that temperature at which the last trace of crystals disappeared when the tube was again slowly heated. The data thus obtained constituted the freezing point curve for the stable form of acetamide.

The freezing point curve for the metastable form was established for the region 0.0 to 32.9 mole % of ammonia by the following procedure. After the freezing point of the stable form had been established by the above method, the ampoules were heated to a temperature above 80° and were rapidly cooled. The solid was then heated, as above, until the last crystal disappeared, the temperature at which this took place being taken as the equilibrium temperature for the metastable form. Once the metastable form was obtained, attempts to change back to the stable form were unsuccessful. Attempts to obtain the metastable form for the mixtures of ammonia content greater than 32.9 mole % were also unsuccessful. Each freezing point was determined at least twice, and data thus obtained are believed to be correct to ±0.5°.

For mixtures of freezing point below +5.0° the procedure followed was almost identical with that used for the corresponding portion of the acetic acid–ammonia system. This method involved the determination of the freezing point by means of cooling curves which were recorded by a Leeds and Northrup Micromax recorder. The cell used in the present work was identical with that previously described except that a second side arm of large bore was attached to permit more convenient introduction of solid acetamide. Data for this part of the curve are believed to be correct to ±1.5°.

Data obtained for the system acetamide–ammonia are reported in Table IV and recorded graphically in Fig. 3. *S* denotes the mole % of ammonia, *T* the equilibrium temperature for the stable form of acetamide, and *T′* the equilibrium temperature for the metastable form. Because of the very high vapor pressure of acetamide–ammonia mixtures, direct analysis of the solid phase would have been altogether impracticable.

TABLE IV

ACETAMIDE–AMMONIA

S	*T*	*T′*
(a) Solid phase CH_3CONH_2		
0.0	80.2	69.0
6.2	75.8	64.7
11.9	72.1	60.6
13.4	71.2	59.2
21.7	65.4	52.6
24.6	62.8	49.6
27.7	60.2	46.6
29.9	58.0	44.2
31.8	56.2	42.0
32.9	54.3	40.0
34.9	52.0	
37.8	48.8	
40.3	45.0	
42.2	42.5	
44.3	39.8	
45.6	37.5	
47.3	35.0	
48.9	32.5	
50.6	30.0	
52.2	27.0	
53.7	24.5	
56.2	20.0	
58.6	14.8	
60.8	9.5	
62.2	7.0	
62.9	5.0	
66.0	−5.0	
68.8	−9.0	
(b) Solid phase $CH_3CONH_2 \cdot NH_3$ (?)		
67.3	−31.0	
68.0	−32.0	
68.7	−32.5	
71.4	−35.5	
74.0	−40.0	
77.8	−43.0	
80.4	−46.0	
82.5	−50.0	
84.4	−53.0	
85.4	−56.0	
87.2	−61.0	
88.6	−66.0	
89.7	−69.0	
(c) Solid phase NH_3		
91.4	−82.0	
92.5	−82.0	
95.7	−80.0	
97.0	−79.0	
97.7	−78.5	
100.0	−77.5	

Discussion of Results

System Acetamide–Acetic Acid.—It is evident from the course of the curve in Fig. 1, as well as from the analytical data, that acetamide and acetic acid form a solid addition compound in which the mole ratio is 1:1. This compound does not melt congruently, but undergoes transition to acetamide and solution just below its melting point, at −0.2°. The curve is much flattened in this region, indicating considerable dissociation into acetamide and acetic acid even at this low temperature; from a very short extrapolation, we may conclude that the melting point of the compound is about 0°. A eutectic point occurs at 70.0 mole % of acetic acid; a mixture of this composition is in equilibrium with the solid compound and solid acetic acid at −11.7°.

The addition compound $CH_3CONH_2 \cdot HC_2H_3O_2$ or $[CH_3CONH_3][OOCCH_3]$, which is obviously formally analogous to ammonium acetate, $NH_3 \cdot HC_2H_3O_2$ or $[NH_4][OOCCH_3]$ (m. p. 117°), might appropriately be called acetylammonium acetate. The enormous difference in stability between the two compounds is accounted for by the much lower basicity of acetamide as compared with ammonia. In other words, the reaction

$$CH_3CONH_2 + HC_2H_3O_2 \rightleftharpoons CH_3CONH_3^+ + C_2H_3O_2^-$$

must be supposed to proceed toward the right at ordinary temperatures, to a small extent only.

Comparison of curves A and B, Fig. 2, shows that although acetamide, like ammonia, increases the solubility of cupric acetate in acetic acid, the effect of the former is considerably smaller. It has been shown previously[18] that the solvent effect brought about by the addition of ammonia is presumably due mainly to the presence of acetate ion; only at elevated temperatures does there appear to be a specific effect due to ammonia as such, heralded by a change in color of the solution to violet-blue. Hence the smaller solvent effect of acetamide may again be attributed to its lower degree of basicity; whereas the absence of a color change when the acetamide–cupric acetate solutions are heated to 100° appears to indicate the non-existence of a complex cupric-acetamide ion analogous to the familiar cupric-ammonia complex.

System Acetamide–Ammonia.—Although it is apparent from the middle portion of the curve in Fig. 3 that acetamide forms a solid addition compound with ammonia also, the fact that this compound undergoes transition considerably short of its melting point, together with the impracticability of direct analysis of the solid phase, makes it impossible to ascertain its formula beyond all doubt. However, by analogy with other systems, as well as by consideration of the course of the curve, it may be concluded that it is very probably a 1:1 compound, $CH_3CONH_2 \cdot NH_3$.

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[18] Davidson and Griswold, THIS JOURNAL, **57**, 423 (1935).

It undergoes transition to acetamide and solution at about −31°, and extrapolation indicates that its melting point would be in the neighborhood of −25°. A eutectic point with ammonia occurs at a composition of 92 mole % of ammonia, and a temperature close to −82°.

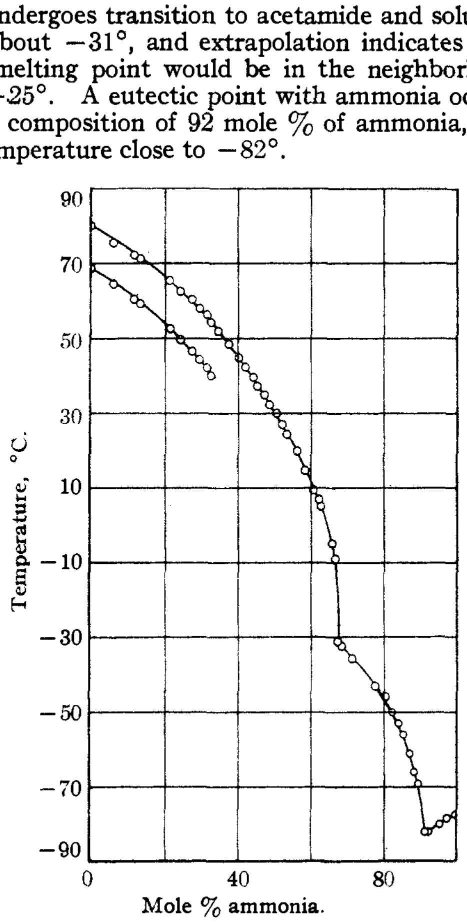

Fig. 3.—System acetamide–ammonia.

This compound, whose formula may be written [CH_3CONH] [NH_4], also shows a formal analogy to ammonium acetate, [CH_3COO] [NH_4], and might be called ammonium aquo-ammono acetate. Its instability is to be accounted for in terms of the very low acidity of acetamide; in other words, the equilibrium point in the reaction

$$CH_3CONH_2 + NH_3 = CH_3CONH^- + NH_4^+$$

must be supposed to be far toward the left.

Freezing Point Depressions.—It seems worthy of mention that in none of the dilute solutions included in the systems here studied (ammonia or acetic acid in acetamide, acetamide in ammonia or in acetic acid) does the depression of the freezing point differ markedly from that calculated for an ideal solution. Thus, for example, with acetamide as solvent, the experimental freezing points for solutions containing up to 11.9 mole % of ammonia (2.29 molal) fall exactly on the curve corresponding to the equation for ideal solutions in acetamide calculated from the data of Peterson[12]

$$\log N = (347.2/T) + 7.609 \log T - 20.732$$

while those for solutions containing up to 11.5 mole % of acetic acid fall very close to the same curve. Despite the much lower temperatures involved, solutions of acetamide in acetic acid up to 11 mole % (2.06 molal) and even in liquid ammonia up to the eutectic concentration (5.11 molal), show freezing point depressions only very slightly greater than the normal values for an unsolvated and undissociated solute. Although it would be unwarranted to attempt to draw quantitative conclusions from such evidence, especially for solutions in a liquid of so low a dielectric constant as that of acetic acid,[19] yet the freezing point data obviously support the previous conclusion as to the small extent of ionization in these systems.

Summary

1. Temperature–concentration curves for the systems acetamide–acetic acid and acetamide–ammonia have been determined throughout the entire range of concentrations.

2. A new compound, $CH_3CONH_2 \cdot HC_2H_3O_2$, for which the name acetylammonium acetate is suggested, has been isolated from the first of these systems, and its composition confirmed by analysis.

3. In the second system, the existence of an addition compound, presumably $CH_3CONH_2 \cdot NH_3$, for which the name ammonium aquo-ammono acetate is suggested, has been demonstrated.

4. It has been found that the solubility of cupric acetate in acetic acid is markedly increased by the presence of acetamide.

5. The existence of the above addition compounds is cited as evidence for the amphiprotic nature of acetamide, while their low stability, as compared with that of ammonium acetate, is regarded as additional evidence for the low basicity of acetamide as compared to ammonia, and its low acidity as compared to acetic acid.

LAWRENCE, KANSAS RECEIVED AUGUST 17, 1944

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(19) *Cf.* Davidson and Chappell, THIS JOURNAL, **55**, 3531 (1933).