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

The Binary System Sodium Formate-Acetic Acid, with some Observations on Solutions of Sodium Acetate in Formic Acid[1]

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Although systems consisting of acetates and acetic acid have been studied extensively,[2] no detailed investigation has as yet been made of solutions of salts of other organic acids in this solvent. Because of the close relationship between formate and acetate ions, it was believed that a comparison of the behavior of solutions of sodium formate in acetic acid and of sodium acetate in formic acid would be of interest, especially in view of the data cited above and already available on solutions of formates in formic acid.[3]

The marked difference between acetic and formic acids as solvents for salts, due to their great disparity in dielectric constant and in self-ionization, has been pointed out by Hammett and Dietz.[4] Because of the large difference in the inherent acidities of the two compounds, the equilibrium constant for the protolytic reaction

$$\mathrm{HCHO_2 + C_2H_3O_2^- \rightleftharpoons HC_2H_3O_2 + CHO_2^-}$$

must have a large value; that is, this reaction must tend to proceed in the direction indicated by the equation, as read from left to right. Hence we should expect solvolysis in solutions of sodium formate in acetic acid to be inappreciable. In formic acid solutions of sodium acetate, on the other hand, a considerable solvolytic effect is to be anticipated.[5]

The behavior of the solutions studied was consistent with these expectations. The solvates which separated from the sodium formate–acetic acid solutions were addition compounds of the original components, and it was possible to determine the entire freezing point—concentration curve for this system. In the sodium acetate–formic acid solutions, however, the solid phase separating at ordinary temperatures proved to be a product of solvolysis rather than of simple solvation.

Method

Preparation of Materials.—Anhydrous acetic acid was prepared as described in previous papers from this Laboratory. Sodium formate and sodium acetate were prepared from the best available hydrated samples by means of recrystallization from water and drying for five days at 140°. The anhydrous sodium formate thus obtained had a melting point of 253°; the sodium acetate, of 323°.

Anhydrous formic acid was prepared from a sample of 90% acid by a modification of the method of Schlesinger and Martin.[6] After dehydration by means of powdered boric anhydride and distillation under reduced pressure, the product, which gave a slight test for borate ion, was fractionated at atmospheric pressure by means of a long and efficient column. The main portion of the distillate was found to have a freezing point of 8.40° and a refractive index $n^{20}\mathrm{D}$ 1.3715 $\pm$ 0.0001.[7] These values are in good agreement with those in the literature, 8.24 to 8.6° for the freezing point, and 1.371 for the refractive index.

Determination of Equilibrium.—The freezing point or synthetic method, as described in previous papers, was used in the study of the system sodium formate–acetic acid throughout the entire range of concentrations. At temperatures above 120°, small sealed bulbs were used instead of the freezing point tube. Each determination was made in duplicate, and the equilibrium temperatures reported are believed to be correct to within 0.1° for temperatures up to 50°, 0.2° between 50° and 100°, and 1° above 100°.

The same method was used to determine the freezing point depression curve for sodium acetate in formic acid, which was followed to a concentration of about 13 mole %. At higher concentrations, a solid phase containing a sodium salt separated out. Analysis of this phase, as described below, showed it to be a solvate of a composition which could not be expressed in terms of the two components sodium acetate and formic acid. In the concentration range in which this compound separated, therefore (13 to 24 mole % of sodium formate), the system must be regarded as one of three components (sodium formate–acetic acid–formic acid, for example). Hence the freezing points obtained at these higher concentrations will not be recorded here.[8]

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Dallas meeting of the American Chemical Society, April, 1938. Original manuscript received April 25, 1940.

[2] (a) Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921); (b) Davidson and McAllister, *ibid.*, **52**, 507 (1930); (c) Davidson and Chappell, *ibid.*, **55**, 3531, 4524 (1933).

[3] Schlesinger, *et al.*, *ibid.*, **41**, 1934 (1919), and previous papers.

[4] Hammett and Dietz, *ibid.*, **52**, 4795 (1930).

[5] Solvolysis in formic acid has been discussed previously by Schlesinger and Calvert, *ibid.*, **33**, 1924 (1911), for the case of ammonium chloride solution.

[6] Schlesinger and Martin, THIS JOURNAL, **36**, 1589 (1914).

[7] The refractive index was found to change rapidly, due to the absorption of moisture, on exposure of the acid to the atmosphere; the freezing point, however, changes but slowly under these conditions.

[8] The curve of equilibrium temperature against concentration, in the range referred to, is to be regarded as a cut, or section, of the freezing point surface of the metathetical ternary system, $\mathrm{NaC_2H_3O_2 + HCHO_2 \rightleftharpoons NaCHO_2 + HC_2H_3O_2}$; an equimolecular mixture of either pair of compounds thus must give the same equilibrium point and must show the same behavior after equilibrium has been reached, as has actually been observed. An adequate study of this ternary system, however, would require considerably more information than is at present available concerning the binary

Analysis of Solid Phases.—In solutions of sodium formate in acetic acid, the probable composition of each solid phase was clearly indicated by the course of the freezing point curve. In the case of each of the two addition compounds formed, however, samples of the solid were obtained, from solutions richer in acid than the solvate, by means of crystallization between suitable temperature limits; these were dried between porous tiles and analyzed acidimetrically, the acidity being calculated as acetic acid.

A more complex situation is presented by the solutions of sodium acetate in formic acid. Since, as a result of solvolysis, acetic acid is undoubtedly present in the solution, the possibility that the solid phase separating from dilute solutions may contain acetic acid also, in solid solution, is not excluded. No mention of such solid solutions was made by Baud[9] in his study of the system formic acid–acetic acid, but apparently no positive identification of the solid phases was undertaken by him. Hence, in the present work, an attempt (not entirely successful) was made to free from adherent mother liquor, at 0°, the solid in equilibrium with a solution containing 4.5 weight % of sodium acetate, and its composition was determined acidimetrically. The solid solvate separating at higher concentrations might also have consisted of a solid solution; in any case, because of the possibility of its being a product of solvolysis, determination of a single constituent would not have sufficed to establish its identity. Hence, after titration with alkali, the solution was evaporated to a small volume with sulfuric acid, transferred to a platinum crucible and evaporated to dryness after the addition of a few drops of concentrated sulfuric acid. The residue was ignited to low red heat and weighed as sodium sulfate. By subtraction of the amount of sodium sulfate corresponding to the added sodium hydroxide, the proportion of sodium in the sample was determined.

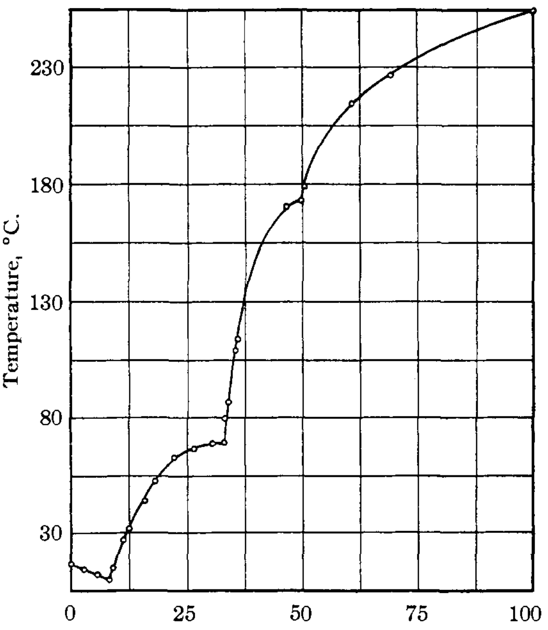

Fig. 1.—System sodium formate–acetic acid.

Results

1. System Sodium Formate–Acetic Acid.—In the following table S denotes the mole percentage of sodium formate, and T the corresponding equilibrium temperature. These data are presented graphically in Fig. 1.

TABLE I

SODIUM FORMATE–ACETIC ACID

S	T
(a) Solid phase $HC_2H_3O_2$	
0	16.60
0.54	16.15
1.33	15.60
2.96	14.25
3.74	13.50
4.78	12.75
5.79	11.80
7.27	10.60
8.14	9.70
(b) Solid phase $NaCHO_2 \cdot 2HC_2H_3O_2$	
8.75	14.55
9.24	17.70
11.08	27.10
12.22	32.25
14.61	40.10
15.73	44.35
18.18	53.0
19.76	56.2
22.36	63.1
(b) Solid phase $NaCHO_2 \cdot 2HC_2H_3O_2$ (cont.)	
26.34	66.5
28.32	68.2
30.42	69.0
32.17	69.2
32.80	69.2
(c) Solid phase $NaCHO_2 \cdot HC_2H_3O_2$	
33.09	80.0
33.51	83.0
33.98	87.0
35.24	109
35.73	114
46.46	171
49.81	173
(d) Solid phase $NaCHO_2$(?)	
50.17	179
60.48	215
68.93	227
100	253

Although the solid phase (b) proved to be stable almost up to its melting point, two samples obtained from solutions containing about 20 mole % of solute were nevertheless analyzed for acidity. The mean of these closely concordant analyses gave $HC_2H_3O_2$, 64.13% (calcd. for $NaCHO_2 \cdot 2HC_2H_3O_2$, 63.84%); since this agreement can scarcely be regarded as accidental, the compound is undoubtedly the disolvate. Similarly, the mean of two analyses of solid phase (c) from solutions containing about 36 mole % of solute gave $HC_2H_3O_2$, 46.77% (calcd. for $NaCHO_2 \cdot HC_2H_3O_2$, 46.89%); this compound is certainly a monosolvate. Solid phase (d), which was obtained only in sealed bulbs, could not be subjected to analysis, but the course of the curve makes it probable that it is the unsolvated salt.

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systems acetic acid–formic acid and sodium formate–sodium acetate, as well as isothermal equilibrium data. Since the object of the present work was merely the comparison of the formally binary solutions obtained by the dissolving of sodium formate in acetic acid, on the one hand, and sodium acetate in formic acid, on the other, no such complete study of the ternary system was undertaken.

(9) Baud, *Bull. soc. chim.*, [4] **13**, 435 (1913).

Each of the solvates here obtained undergoes transition just below its melting point; in each case the curve is much flattened in this region, and may be extrapolated readily to the ordinate corresponding to the composition of the compound. In this way the "true" melting point of the disolvate is found to be very close to 69.2°, and that of the monosolvate to be about 173°.

2. **Solutions of Sodium Acetate in Formic Acid.**—In the following table, S denotes the mole percentage of sodium acetate, and T the corresponding equilibrium temperature.

TABLE II

SODIUM ACETATE–FORMIC ACID

S	T	S	T
0	8.4	7.01	− 6.0
0.76	7.3	8.56	− 8.3
1.43	6.0	9.73	−12.0
2.39	4.5	10.71	−14.5
3.20	3.1	11.85	−18.2
4.17	0.9	12.42	−20.3
5.19	−1.5	13.11	−22.5
6.06	−3.7	13.61	−24.0 (metastable)

A solution containing 3 mole % of sodium acetate was cooled to 0°, and the solid was filtered off, dried on porous tile previously cooled to 0°, and subjected to acidimetric analysis. The mean of four closely concordant titrations gave acid H, 2.095% (calcd. for $HCHO_2$, 2.190%). Although this result does not altogether exclude the possibility of the presence of acetic acid in the solid, the fact that the crystals contained a detectable trace of sodium salt, due to the impossibility of freeing them completely from the rather viscous mother liquor at the necessarily low temperature, would appear adequately to account for the slightly low figure for acidity.

Samples of the solvate separating at concentrations above 13 mole % were obtained from two solutions of different concentrations, at two different temperatures, and analyzed for acidity. The results showed, respectively, acid H, 1.31 and 1.28% (calcd. for $NaCHO_2 \cdot 2HCHO_2$, 1.26%). On the second of these samples, the sodium content was determined also; the result showed Na, 14.53% (calcd. for $NaCHO_2 \cdot 2HCHO_2$, 14.37%). The facts that, despite the difficulty of complete separation of solid and solution, the acidity of the two samples was so nearly the same, and that both these figures and that obtained for sodium were so close to the calculated values for the solvate $NaCHO_2 \cdot 2HCHO_2$, appear to provide sufficient evidence that the solid phase consists not of a solid solution but of a pure disolvate of sodium *formate*. This solvate has, in fact, been isolated previously from sodium formate–formic acid solutions.[2a]

Discussion

1. **System Sodium Formate–Acetic Acid.**—The behavior of this system is strikingly similar to that consisting of sodium acetate and the same solvent, as reported by Kendall and Adler.[2a] In both cases a disolvate and a monosolvate are formed, each of which undergoes transition just before its melting point is reached. Transition point and solubility data for these four solvates are compared in Table III.

TABLE III

SOLVATES OF SODIUM ACETATE AND OF SODIUM FORMATE IN ACETIC ACID

Solvate	Transition temp., °C.	Composition of solution at transition (mole % solute)	Solubility (mole % solute)
$NaC_2H_3O_2 \cdot 2HC_2H_3O_2$	96.3	33.2	7.06 at 25°
$NaCHO_2 \cdot 2HC_2H_3O_2$	69.2	32.8	10.65 at 25°
$NaC_2H_3O_2 \cdot HC_2H_3O_2$	163	48.1	33.4 at 100°
$NaCHO_2 \cdot HC_2H_3O_2$	173	49.8	34.7 at 100°

Nowhere in the data for this system do we find evidence of solvolysis. The freezing point depressions produced by sodium formate are, it is true, slightly larger than those of sodium acetate at the same concentration, but interionic effects in this solvent are so large and vary so greatly with the specific nature of the ions, that the enhanced freezing point depressions cannot be considered as an indication of solvolytic reaction. It may be of interest to point out that the value of j, the freezing point divergence function, remains constant for sodium formate over a wide concentration range ($j = 0.35$ from 0.1 to 1.5 molal), as it does for sodium acetate[10] ($j = 0.51$ from 0.1 to 1 molal), and indeed for most other salts in this solvent. We can at present draw no conclusion from the difference in cryoscopic behavior between the two salts[11] further than that association into ion pairs must be somewhat less in the case of sodium formate than for sodium acetate.

2. **Solutions of Sodium Acetate in Formic Acid.**—The dielectric constant of formic acid, 62, is ten times that of acetic acid, and, indeed,

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(10) Webb, THIS JOURNAL, **48**, 2263 (1926).

(11) The relationships presented here are, of course, markedly different from those observed in aqueous solutions of the same salts; *cf.* Scatchard and Prentiss, *ibid.*, **56**, 807 (1934).

approaches that of water, so that interionic effects in formic acid solutions are relatively small. Hence it is possible to gain some information with regard to the molecular state of ionized solutes in this solvent from the magnitude of the freezing point depressions produced by them.

From a large scale plot of the freezing point depressions obtained by Kendall and Adler[2a] for sodium formate solutions, as well as of those here observed, it was found that the lowerings produced by the formate are almost equal to those calculated for a completely dissociated ideal solute; the acetate, however, gives depressions about $^3/_2$ as great as the ideal values. Thus, for example, the depression obtained by interpolation for a 1 molal solution of sodium acetate is 8.06°, as compared with 5.13° for sodium formate at the same concentration, and 5.34°[12] for an ideal binary salt. Thus the lowering due to the acetate is 1.57 times as large as for the formate, or 1.51 times the ideal value. Since the interionic effects would not diverge widely, in this solvent, for two salts of the same valence type, the most probable explanation of this large difference in cryoscopic effects appears to be that based upon solvolysis. Specifically, we may conclude that the solvolytic reaction represented by the equation

$$Na^+ + C_2H_3O_2^- + HCHO_2 \longrightarrow HC_2H_3O_2 + Na^+ + CHO_2^-$$

takes place to a very considerable extent (if, indeed, it does not go practically to completion) in these dilute solutions. Hence the separation, at somewhat higher concentrations, of a solvated sodium *formate* as solid phase, is readily accounted for.

Summary

1. A temperature–concentration curve has been obtained for equilibrium between solid and liquid phases in the binary system sodium formate–acetic acid.

2. Two new compounds, $NaCHO_2 \cdot 2HC_2H_3O_2$ and $NaCHO_2 \cdot HC_2H_3O_2$, have been isolated from these solutions, and their compositions confirmed by analysis.

3. The behavior of sodium formate in acetic acid solution has been shown to be markedly similar to that of sodium acetate in the same solvent.

4. Evidence is presented that sodium acetate is extensively solvolyzed in formic acid solution.

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[12] This is twice the molal freezing point constant, 2.67, calculated from the melting point, 8.4°, and the heat of fusion, 2713 calories ("International Critical Tables," Vol. V, p. 132).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Acylation of Aldoximes. VI. The Relative Ease and Mechanism of Conversion of Benzoyl-*syn*-aldoximes to Nitriles in the Presence of Pyridine and Pyridinium Chloride[1]

BY CHARLES R. HAUSER AND GERTRUDE VERMILLION

Although benzoyl-*syn*-aldoximes are stable in pure pyridine, they are gradually converted into nitriles (and benzoic acid) on standing in solutions of pyridine containing pyridinium chloride.[2] This conversion is considered to involve the intermediate formation of benzoyl-*anti*-aldoximes, which, like other acyl *anti*-derivatives,[3] would doubtless be decomposed readily by pyridine to form nitriles. The isomerization of benzoyl-*syn*-aldoximes to their *anti*-isomers is assumed to take place through the medium of their acid salts, the precedent for this being the well-known isomerization of the acid salts of *syn*-aldoximes.[4] The reactions may be represented by the following ionic equations, in which Y represents a meta or para substituent.

The effect of various meta and para substituents (Y) in benzoyl-*syn*-benzaldoximes, on their ease of conversion to nitriles has been determined by allowing a series of the compounds in pyridine solutions containing pyridinium ion to stand under the same conditions and then isolating unchanged *syn*-benzoates; in cases in which the nitriles formed were solids they also were isolated. The percentage yields of these substances

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[1] Presented before the division of Organic Chemistry of the American Chemical Society, Detroit Meeting, September, 1940.

[2] See Vermillion and Hauser, THIS JOURNAL, **62**, 2939 (1940).

[3] See Hauser and Jordan, *ibid.*, **58**, 1772 (1936).

[4] See, for example, Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Company, New York, N. Y., 1937, p. 361.