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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. II. SOLUBILITIES OF ACETATES[1]

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Introduction

In the first paper of this series,[2] it was pointed out that anhydrous acetic acid is a far better solvent for salts than had been previously supposed, and existing data concerning solubilities and reactions of salts in this solvent were summarized. In the present investigation the solubilities of a number of typical acetates in acetic acid were measured over a wide range of temperature, and the compositions of all the compounds appearing as solid phases in these systems were determined. Although a number of addition compounds of acetates with acetic acid have been reported in the literature,[3] only two such systems, namely, those consisting of sodium and silver acetates in acetic acid, have been accurately investigated at more than one temperature.[4] In the present paper data are given for the acetates of potassium, ammonium, lithium, lead, barium and calcium. Other systems will be reported on in subsequent papers.

It has been shown by Kendall and co-workers[5] that, in polar solutions, compound formation between solute and solvent, or solvation, is a major factor in determining solubility, and further that in several series of systems of the type HX:RX, where the solute and solvent have a common anion, both solvation and solubility increase with increasing diversity in electropositive character between the metal R and hydrogen. It is to be expected, therefore, that in such a series solvation and solubility will be found to be greatest in the case of the salts of the alkali metals, less for those of the alkaline earth metals, while the salts of other metals, with few exceptions, are likely to be little solvated and not very soluble. The data here presented afford further opportunity for testing the validity of this view-point.

It has been repeatedly pointed out that any salt RX in solution in its own acid HX may be considered, formally at least, as a base.[6] That this

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[1] The material presented in this paper is from part of a thesis submitted by Walter H. McAllister to the Graduate School of the University of Kansas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Davidson, THIS JOURNAL, **50**, 1890 (1928).

[3] References to these will be given later, in connection with the particular system under consideration. Hydrated compounds, however, will not be referred to.

[4] Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921).

[5] Kendall, Davidson and Adler, *ibid.*, **43**, 1481 (1921). *Cf.* Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, **1924**, pp. 118–120, 169–170.

[6] See, for instance, Schlesinger and Calvert, THIS JOURNAL, **33**, 1924 (1911); also Ref. 5, p. **1494**.

conception is of real significance, and not merely a matter of nomenclature, has recently been brought out very strikingly by the work of Hall and Werner,[7] who showed that sodium acetate could be titrated electrometrically with perchloric acid in acetic acid solution to a perfectly definite point of complete neutralization. According to Brönsted's conception of acids and bases,[8] the basicity of acetates is due to the strong tendency for the acetate ion to unite with a proton. Further evidence of the actual basicity of acetates in acetic acid will be presented in the latter part of this article.

Method

The freezing-point method was employed in this work for the determination of compound formation and solubility relationships. Solutions of known composition were prepared, cooled until crystallization occurred and then heated slowly, the temperature at which the last trace of crystals disappeared being recorded as the freezing point of the solution.[9] Freezing points below 100° were determined in large test-tubes provided with a thermometer and stirrer, suitable precautions being taken to exclude moisture. For solutions in which the equilibrium temperature was above 100°, small sealed bulbs were employed. Eight mercury thermometers were used, each of them having been calibrated either at fixed points or by comparison with certified thermometers. All temperatures were corrected for exposed stem. Each freezing point was determined at least twice.

Pure anhydrous acetic acid was prepared by the addition of the required amount of acetic anhydride to a special grade of C. P. glacial acetic acid, as described by Kendall and Gross.[10] The acid used in the determinations had a freezing point of 16.5 to 16.6°, which agrees with that given by Kendall and Gross for acetic acid of minimum conductivity.

Analysis of solvated compounds was unnecessary in those cases where the congruent melting point could be determined. In other cases, the compound was obtained in crystalline form by cooling a solution of appropriate composition, filtered off with the aid of suction and dried as rapidly as possible between porous tiles. The dried sample was then weighed and the acetic acid of solvation determined, except in the case of ammonium acetate, by titration with standard sodium hydroxide solution, using phenolphthalein as indicator. Neutral and solvated ammonium acetates were analyzed by adding concentrated sodium hydroxide solution to a weighed sample in a Kjeldahl flask, distilling the liberated ammonia into a measured amount of standard hydrochloric acid and titrating the excess acid with sodium hydroxide.

The results for the various systems are given below, and are represented also in the accompanying diagrams. Compositions are expressed in molecular percentages throughout; T denotes the equilibrium temperature.

Results

System Potassium Acetate–Acetic Acid.—Although no thorough study has been made of this system previously, two addition compounds

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[7] Hall and Werner, THIS JOURNAL, **50**, 2367 (1928).

[8] Brönsted, *Chemical Reviews*, **5**, 231 (1928), and previous papers.

[9] Details regarding method, apparatus and limits of accuracy have been given in earlier papers and need not be repeated here. See, for instance, Kendall and Landon, THIS JOURNAL, **42**, 2131 (1920).

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

have been reported, $KC_2H_3O_2 \cdot HC_2H_3O_2$,[11] melting at 148°, and $KC_2H_3O_2 \cdot 2HC_2H_3O_2$,[12] said to melt at 112°. The location of the eutectic point has also been studied.[13]

The salt used was prepared by neutralizing a solution of pure acetic acid with potassium hydroxide, crystallizing the salt from the solution and maintaining it at 180° for several days. The product had a melting point of 292°, agreeing with that previously reported.[14] Since this salt is quite deliquescent, each sample was heated in the previously weighed freezing-point tube at 105° for several hours before weighing.

(a) Solid Phase $HC_2H_3O_2$

$KC_2H_3O_2$, %	0.0	1.22	2.11	6.70	7.62	9.10	10.03
T	16.50	15.82	15.30	10.95	9.71	7.45	5.95

(b) Solid Phase $KC_2H_3O_2 \cdot 2HC_2H_3O_2$

$KC_2H_3O_2$, %	10.97	11.36	12.71	13.30	15.75	15.94	17.00
T	14.76	17.95	28.03	32.02	49.90	51.50	55.50
$KC_2H_3O_2$, %	17.92	18.71	19.00	20.48	23.72	23.85	
T	60.1	64.1	65.9	73.5	83.1	83.6	

(c) Solid Phase $KC_2H_3O_2 \cdot HC_2H_3O_2$

$KC_2H_3O_2$, %	28.44	28.69	30.67	31.45	32.47	
T	99.0	101.2	110.0	114.0	118.0	
$KC_2H_3O_2$, %	33.44	33.94	34.41	34.65	35.00	35.27
T	121.0	121.5	124.5	125.5	126.0	126.0
$KC_2H_3O_2$, %	39.50	44.88	45.62	48.30	50.22	52.32
T	137.0	145.0	146.0	147.5	148.0	147.5

(d) Solid Phase $KC_2H_3O_2$

$KC_2H_3O_2$, %	58.45	61.40	64.16	65.21	70.05	76.50	100.0
T	170	191	206	207	230	249	292

The curve for this system is given in Fig. 1. Analyses of the solid phase (b) gave a mean value for the acid content of 66.9 mole %, corresponding to the compound $KC_2H_3O_2 \cdot 2HC_2H_3O_2$.

The existence of the two acid salts previously reported has been confirmed. The melting point of 112° reported for the compound $KC_2H_3O_2 \cdot 2HC_2H_3O_2$ is erroneous, however, as this compound undergoes transition below its melting point, which, as indicated by extrapolation, would be about 100°. The compound $KC_2H_3O_2 \cdot HC_2H_3O_2$ is stable up to its melting point, which is 148°, as reported by Melsens.

System Ammonium Acetate–Acetic Acid.—This system has not been studied previously, although isotherms for the ternary system ammonium

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[11] Melsens, *Compt. rend.*, **19,** 611 (1844).

[12] Lescoeur, *Ann. chim. phys.*, [6] **28,** 245 (1893).

[13] Vasiliev, *J. Russ. Phys.-Chem. Soc.*, **41,** 753 (1909).

[14] Schaffgotsch, *Pogg. Ann.*, **102,** 293 (1857).

acetate–acetic acid–water have been determined at 16 and 25°.[15] The compound $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$, melting at 66.5°, has been reported.[16] Two different melting points have been reported for unsolvated $NH_4C_2H_3O_2$, 89° (which still is found in a number of standard reference books) and 112.5–114°.[16] The results of this work show the former to be entirely erroneous.

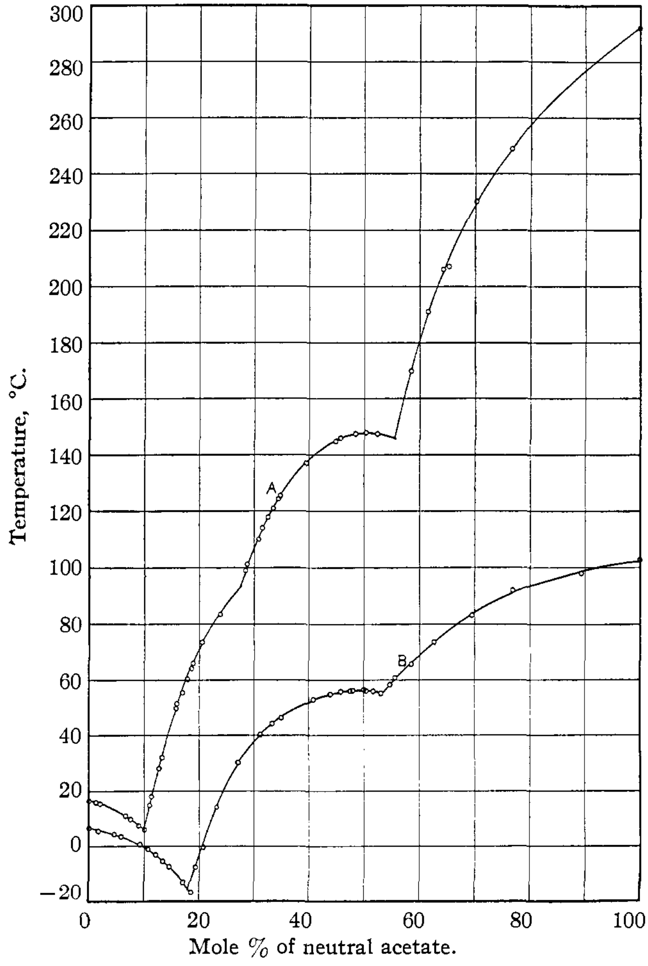

Fig. 1.—A, system $KC_2H_3O_2$–$HC_2H_3O_2$; B, system $NH_4C_2H_3O_2$–$HC_2H_3O_2$, add 10° to temperature scale.

No satisfactory method for the preparation of pure anhydrous ammonium acetate was found in the literature. The salt used was prepared

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[15] Sugden, *J. Chem. Soc.*, 960 (1926).

[16] Reik, *Monatsh.*, **23,** 1033 (1902).

by passing dry ammonia gas (produced by the evaporation of liquid ammonia, to which metallic sodium had been added until the solution remained a deep blue color) over pure acetic acid contained in an evaporating dish over soda lime in a vacuum desiccator. After the mixture had solidified, it was pulverized and the process was continued for several days. The product obtained always analyzed within a few tenths of one per cent. of the theoretical 22.1% ammonia, and melted, in a sealed capillary tube, at 112–113°.

(a) Solid Phase $HC_2H_3O_2$

$NH_4C_2H_3O_2$, %	0. 0	1.76	4.64	5.85	9.35	10.72
T	16.50	15.65	14.20	13.40	10.45	9.00
$NH_4C_2H_3O_2$, %	12.03	13.46	14.54	16.84	17.08	18.54
T	6.90	4.51	2.80	−2.5	−3.0	−6.5

(b) Solid Phase $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$

$NH_4C_2H_3O_2$, %	19.43	20.67	23.15	27.06	31.10	33.43
T	2.5	9.6	24.0	40.1	50.1	54.2
$NH_4C_2H_3O_2$, %	34.95	40.80	43.97	45.05	45.84	47.66
T	56.4	63.0	64.9	65.5	65.9	66.0
$NH_4C_2H_3O_2$, %	48.06	50.00	50.41	51.75	53.20	
T	66.2	66.5	66.2	66.0	65.2	

(c) Solid Phase $NH_4C_2H_3O_2$

$NH_4C_2H_3O_2$, %	54.83	55.60	58.70	62.63	69.50
T	68.5	70.8	75.7	83.6	93.0
$NH_4C_2H_3O_2$, %	76.84	89.25	100.0		
T	102	108	113		

The curve for this system is given in Fig. 1. The existence of the acid salt $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$, which has been previously reported, is confirmed. This compound has a congruent melting point at 66.5°. The melting point of unsolvated $NH_4C_2H_3O_2$ is 113°.

System Lithium Acetate–Acetic Acid.—The compound $LiC_2H_3O_2 \cdot HC_2H_3O_2$, said to melt at 99°, has been reported.[17] The present work has shown this melting point to be erroneous. The location of the eutectic point in this system has been determined also.[13]

The salt used was prepared from a C. P. hydrate, which was recrystallized and then kept at 150° for three days. Its melting point, not previously reported, was found to be 272°.

(a) Solid Phase $HC_2H_3O_2$

$LiC_2H_3O_2$, %	0.0	3.56	3.81	5.01	5.72
T	16.50	14.85	14.80	14.16	13.75
$LiC_2H_3O_2$, %	6.86	7.57	7.70	8.45	
T	13.15	12.90	12.75	12.10	

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[17] Lescoeur, *Bull. soc. chim.*, **24,** 517 (1875); see also Ref. 12.

(b) Solid Phase $LiC_2H_3O_2 \cdot HC_2H_3O_2$

$LiC_2H_3O_2$, %	8.61	9.15	9.53	11.20	12.28	13.07
T	16.7	22.1	25.0	41.5	51.0	55.6
$LiC_2H_3O_2$, %	14.42	16.24	18.31	20.25	23.82	27.64
T	63.2	70.0	78.0	83.0	91.0	98.0
$LiC_2H_3O_2$, %	30.41	35.34	38.48	39.83	41.84	44.41
T	101.3	106.5	108.0	109.0	110.0[18]	111.0
$LiC_2H_3O_2$, %	45.32	45.74	46.77	48.76	50.06	
T	111.5	112.0	112.0	112.5	112.5	

(c) Solid Phase $LiC_2H_3O_2$

$LiC_2H_3O_2$, %	43.95	44.92	46.04	47.57	48.22	49.22
T	136.0	140.0	147.5	156.0	161.0	165.0
$LiC_2H_3O_2$, %	52.41	55.89	56.90	70.87	100.0	
T	178.5	188.0	192.0	221	272	

The curve for this system is given in Fig. 2. Analysis of the solid phase (b) gave a value for the acid content of 50.06 mole %, corresponding to the compound $LiC_2H_3O_2 \cdot HC_2H_3O_2$. The existence of the acid salt previously reported is thus confirmed. This compound undergoes transition before its melting point is reached, but its metastable melting point can readily be determined; it is 112.5°. The melting point of unsolvated lithium acetate is 272°.

System Lead Acetate–Acetic Acid.—This system has not been thoroughly studied previously, although a large part of the isotherm for the ternary system lead acetate–acetic acid–water at 25° has been determined.[19] Sandved states that it is impossible to bring about crystallization in very concentrated solutions of lead acetate in acetic acid. This was not found to be the case in the present work, although such solutions were exceedingly viscous and exhibited an enormous degree of supercooling, so that a great deal of patience was required in order to obtain satisfactory results with them.

The salt used was prepared from a c. p. hydrate by recrystallizing from dilute acetic acid and then drying over phosphorus pentoxide in a vacuum desiccator to constant weight, which required about six weeks. The product melted at 204°, agreeing with the figure previously reported.[20]

(a) Solid Phase $HC_2H_3O_2$

$Pb(C_2H_3O_2)_2$, %	0.0	0.54	5.18	8.42	11.53	19.78
T	16.50	16.33	15.52	14.24	13.40	9.55

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[18] Although the temperatures given here for systems containing from 40 to 50% $LiC_2H_3O_2$ correspond to a metastable equilibrium, these temperatures were invariably far easier to determine than those corresponding to the stable equilibrium between unsolvated $LiC_2H_3O_2$ and solution in this region. In fact, $LiC_2H_3O_2$ could be obtained from these solutions as solid phase only by seeding them with a crystal of this compound.

[19] Sandved, *J. Chem. Soc.*, 2967 (1927).

[20] Petersen, *Z. Elektrochem.*, **20**, 328 (1914).

$Pb(C_2H_3O_2)_2$, %	21.99	32.97	33.52	34.21	37.48
T	8.05	−0.3	−0.8	−1.2	−3.1

(b) Solid Phase $Pb(C_2H_3O_2)_2$

$Pb(C_2H_3O_2)_2$, %	35.69	38.27	38.46	41.43	41.75	44.95
T	49.0	68.0	70.2	87.3	88.0	100.5
$Pb(C_2H_3O_2)_2$, %	52.08	59.55	71.83	90.20	100.0	
T	119	139	165	192	204	

The curve for this system is given in Fig. 2. Since it is a smooth curve from eutectic to melting point, no analysis was necessary. There are evidently no stable solvates. The melting point of $Pb(C_2H_3O_2)_2$ is 204°.

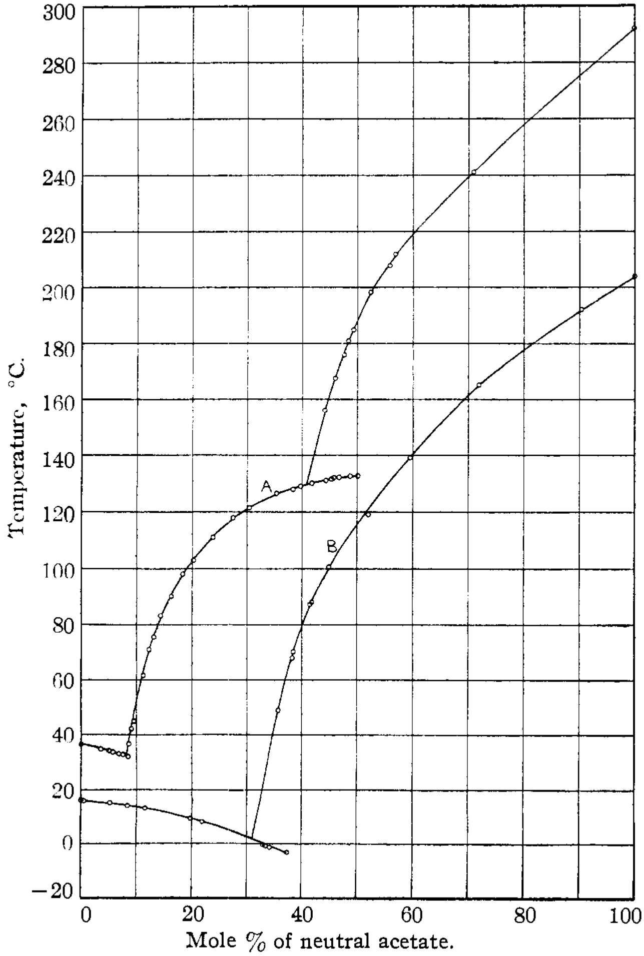

Fig. 2.—A, system $LiC_2H_3O_2$–$HC_2H_3O_2$, subtract 20° from temperature scale; B, system $Pb(C_2H_3O_2)_2$–$HC_2H_3O_2$.

System Barium Acetate–Acetic Acid.—No previous work has been done on this system. A compound $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ has been reported.[21] The salt used was prepared by recrystallizing a C. P. hydrate from dilute acetic acid at 100° and keeping the product at 105° for several days.

(a) Solid Phase $HC_2H_3O_2$

$Ba(C_2H_3O_2)_2$, %	0.0	1.27	1.59	1.91	2.32	3.04
T	16.50	15.60	15.43	15.30	15.00	14.63
$Ba(C_2H_3O_2)_2$, %	3.40	4.77	5.55	6.84	7.47	7.76
T	14.2	13.4	12.5	11.4	10.5	9.4

(b) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$

$Ba(C_2H_3O_2)_2$, %	2.67	3.16	4.48	5.05	5.18	6.21
T	19.0	22.5	31.8	35.2	36.0	41.1
$Ba(C_2H_3O_2)_2$, %	6.86	7.53	8.11	8.62		
T	44.0	47.3	48.0	49.0		

(c) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (Stable Modification)

$Ba(C_2H_3O_2)_2$, %	6.82	7.53	8.11	8.53	8.62	8.74	9.84
T	32.0	40.8	48.0	51.5	54.0	55.0	64.0
$Ba(C_2H_3O_2)_2$, %	11.37	11.70	12.46	14.06	15.08	15.58	
T	72.3	74.1	77.9	84.0	88.0	90.3	

(d) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (Unstable Modification)

$Ba(C_2H_3O_2)_2$, %	8.11	9.70	10.78	11.37	11.88	12.38
T	13.8	19.9	24.3	27.1	29.8	32.0

The curve for this system is shown in Fig. 3. Analyses of the solid phase (b) gave a mean value for the acid content of 75.46 mole %, corresponding to the compound $Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$. This compound has not been reported previously. Analyses of the solid phase (c) gave a mean value of 66.57 mole %, and of the solid phase (d), 65.69 mole % of $HC_2H_3O_2$, showing both these phases to consist of the compound $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$. The latter compound thus exists in two different crystalline modifications, one of them being metastable throughout the temperature range studied.

It was considered inadvisable to attempt to continue this curve beyond 16% $Ba(C_2H_3O_2)_2$ because of the high vapor pressure of acetic acid at the elevated temperatures required to bring about complete solution, in any reasonable time, at this concentration.

System Calcium Acetate–Acetic Acid.—Calcium acetate was reported to be little soluble in glacial acetic acid by Lescoeur.[22] Kendall and Adler[23] found its solubility to be less than 0.35 mole % of $Ca(C_2H_3O_2)_2$ at 30°. A compound $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ has been reported by Colson.[24]

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[21] Iwaki, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **1**, 81 (1914); *C. A.*, **10**, 574 (1916).

[22] Ref. 12, p. 253.

[23] Ref. 4, p. 1478.

[24] Colson, *Compt. rend.*, **137**, 1061 (1903).

The salt used here was prepared in the same manner as the barium acetate.

(a) Solid Phase $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Ca(C_2H_3O_2)_2$, %	0.0594	0.0670	0.0933	0.0968	
T	21.5	23.8	36.2	37.2	
$Ca(C_2H_3O_2)_2$, %	0.1576	0.2210	0.2823	0.3726	
T	52.5	60.9	67.5	75.1	
$Ca(C_2H_3O_2)_2$, %	0.4005	0.4935	0.5398	0.5573	
T	77.5	82.8	84.5	85.2	
$Ca(C_2H_3O_2)_2$, %	0.6287	0.6290	0.7082	0.9128	1.386
T	88.0	89.0	91.0	97.8	111.0

The curve for this system is shown in Fig. 3. Analyses of the solid phase (a) gave a mean value for the acid content of 50.66 mole %, corresponding to the compound $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, which has been reported

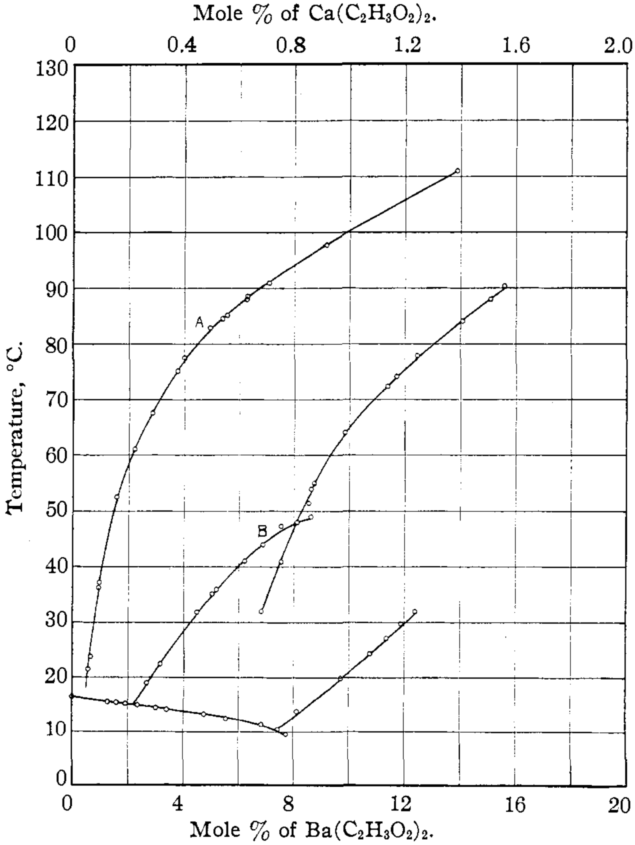

Fig. 3.—A, system $Ca(C_2H_3O_2)_2$–$HC_2H_3O_2$ (use upper concentration scale); B, system $Ba(C_2H_3O_2)_2$–$HC_2H_3O_2$ (use lower concentration scale).

previously. The curve was not continued beyond 1.4% of $Ca(C_2H_3O_2)_2$, for the same reason as in the case of the barium salt.

System Thallous Acetate–Acetic Acid.—The compound $TlC_2H_3O_2 \cdot HC_2H_3O_2$ has been reported.[25] Thallous acetate was prepared by the reaction between barium acetate and thallous sulfate in aqueous solution. After it had been dried for several days in a desiccator, the compound was found to melt at 127° (not 110°, as previously reported). The solubility was not accurately determined because of the limited quantity of salt available and its ready decomposition in sunlight. However, a rough determination showed the solubility to be approximately 2 mole % at 25°. The composition of the solid phase was not determined.

Summary of Data on Solvation and Solubility in Acetate–Acetic Acid Systems.—For ready comparison, the solvates which have been isolated in these systems, and the solubilities of acetates in pure acetic acid at 25°, are tabulated herewith.

Metal	Solvates isolated	Soly., mole per cent. at 25°	Moles of $HC_2H_3O_2$ per mole of acetate in solid phase
K	$KC_2H_3O_2 \cdot 2HC_2H_3O_2$, $KC_2H_3O_2 \cdot HC_2H_3O_2$	12.29	2
NH_4	$NH_4C_2H_3O_2 \cdot HC_2H_3O_2$	23.46	1
Na[2]	$NaC_2H_3O_2 \cdot 2HC_2H_3O_2$, $NaC_2H_3O_2 \cdot HC_2H_3O_2$	7.06	2
Li	$LiC_2H_3O_2 \cdot HC_2H_3O_2$	9.37	1
Tl (-ous)	$TlC_2H_3O_2 \cdot HC_2H_3O_2$[25]	About 2	1
Ba	$Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$ (not previously reported) $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (2 modifications)	3.48	3
Ca	$Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$	0.068	1
Zn[26]	None	0.0018	0
Pb	None	31.9	0
Fe (-ic)[2]	None	Practically 0	0
Cu[26]	$Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$	0.166	1
Ag[2]	None	0.094 (76°)	0

Discussion of Results

It is evident from the above table that solvation is most marked, and solubility is greatest, for the acetates of the most electropositive metals. Only two of the acid salts isolated have been found to be sufficiently stable to reach their melting points before undergoing transition, namely, the 1:1 compounds of potassium and ammonium. The 1:2 compound of potassium, and the 1:1 compound of lithium (like the corresponding sodium compounds) undergo transition just before the melting point is reached. The high solubility of ammonium acetate is, of course, related to its low melting point. The solubility of lead acetate, even when its low melting point is taken into consideration, is surprisingly great.[27] This fact is

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[25] Ref. 12, p. 249.

[26] From unpublished work in this Laboratory.

[27] *Cf.* Sandved, Ref. 19, p. 2974.

in line with the comparatively high solubility of the lead salts in other similar series, which was pointed out previously.[28]

Basic Properties of Acetates and of Water in Acetic Acid Solution.—Hall and Conant[29,30] studied the hydrogen-ion activity of glacial acetic acid solutions by means of the chloranil electrode and by their action upon indicators, and reached the tentative conclusion that the hydrogen-ion activity of pure glacial acetic acid can be represented by a P_{H} value in the neighborhood of zero[31] on a scale which is as yet an arbitrary one for this solvent, but which, it is hoped, may be found ultimately to coincide very nearly with the P_{H} scale in water. In the present investigation, qualitative experiments were made with a number of indicators which, according to Clark,[32] show color changes in water solution at a P_{H} value of about zero. We shall not take space here to report in detail the results of these experiments, especially since the names of the indicators are inadequate for complete identification, but shall merely summarize briefly the observations which we believe to be of interest. Acetic acid solutions of most of the indicators tried[33] showed definite color changes, in the direction of greater acidity (lower P_{H}), upon the addition of a small amount of a solution of dry hydrogen chloride in the same solvent. The original color of the indicator solution could then be restored, in every case, by the addition to the acid solution of a small amount of a solution of sodium or ammonium acetate. Other indicators[34] showed distinct color changes in the direction of greater basicity upon the addition of sodium or ammonium acetate, the original color being restored upon addition of hydrogen chloride solution. The acetates evidently act as bases in neutralizing acids in this solvent, the acetate ion of the base reacting with hydrogen ion of the acid to form undissociated acetic acid.

In this connection, it also seems worthy of mention that the behavior of water toward indicators was found to be similar to that of acetates, though less marked. Indicators in dilute solutions of dry hydrogen chloride or of anhydrous sulfuric acid in acetic acid could be restored to their "neutral" colors by the addition of a few drops of water. In other words, water, in acetic acid solution, behaves as a weak base. Such behavior is not surprising, since it has been pointed out repeatedly, in the work of Hantzsch and others, that water possesses basic properties be-

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[28] Kendall, Davidson and Adler, Ref. 5, p. 1501.

[29] Hall and Conant, This Journal, **49**, 3047 (1927).

[30] Conant and Hall, *ibid.*, **49**, 3062 (1927).

[31] We wish to express our indebtedness to Dr. Hall for a private communication touching upon this point.

[32] Clark, "The Determination of Hydrogen Ions," 3d ed., The Williams and Wilkins Co., Baltimore, **1928**, pp. 76–86.

[33] Including crystal violet, methylene blue, alizarin blue, azorol green and safranine.

[34] Including methylene blue, benzopurpurin 4B and picric acid.

cause of its tendency to combine with hydrogen ion to form oxonium ion, OH_3^+.[35] In this respect water is quite analogous to ammonia, although the former is a somewhat weaker base because the OH_3^+ ion gives up its extra hydrogen ion, or proton, more readily than does the NH_4^+ ion. The behavior of ammonia and of water in acetic acid solution may be represented by the parallel equations

$$NH_3 + HC_2H_3O_2 \rightleftharpoons NH_4C_2H_3O_2 \rightleftharpoons NH_4^+ + C_2H_3O_2^-$$
$$H_2O + HC_2H_3O_2 \rightleftharpoons OH_3C_2H_3O_2 \rightleftharpoons OH_3^+ + C_2H_3O_2^-$$

In the latter case, the addition compound, which might be called oxonium acetate, must, indeed, be regarded as hypothetical, since it cannot be isolated in the solid state, even at low temperatures.[36] However, the existence of such a compound *in solution* appears quite probable from the fact that the cryoscopic effect of water in moderately dilute solution in acetic acid is practically identical with that of ammonia.[37] Thus, the curve obtained by plotting the freezing-point data of Rüdorff[38] for solutions of water in acetic acid, after recalculating the concentrations in terms of mole per cent. of $OH_3C_2H_3O_2$, coincides within the limit of experimental error, up to 5 mole per cent. of solute, with the curve found in the present investigation for $NH_4C_2H_3O_2$.[39] Although this method of comparison is admittedly imperfect,[40] and it is impossible to determine the degree of solvation of either ammonia or water in acetic acid solution from freezing-point depression data, nevertheless the exact coincidence of the two curves may be taken as a strong confirmation of the hypothesis that in this instance again, as in so many others, the parts played by water and by ammonia are essentially the same.

Summary

1. Freezing-point curves have been determined for binary systems consisting of acetic acid with the acetates of potassium, ammonium, lithium, lead, barium and calcium, and a number of addition compounds have been isolated and analyzed. Incidentally, a method has been given

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[35] For an outline of Hantzsch's results and other evidence for the existence of oxonium ion, see Hammett, THIS JOURNAL, **50**, 2666 (1928). *Cf.* also Conant and Hall, Ref. 30, p. 3068.

[36] The complete freezing-point curve for the system H_2O–$HC_2H_3O_2$ is given by Faucon, *Ann. chim. phys.*, [8] **19**, 70 (1910). No compound appears as solid phase. *Cf.* Kremann, *Monatsh.*, **28**, 893 (1907).

[37] The data of Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907), show the same thing to be true for solutions in sulfuric acid.

[38] Rüdorff, *Ber.*, **3**, 390 (1870).

[39] Obviously, the system $NH_4C_2H_3O_2$–$HC_2H_3O_2$ might have been regarded as a portion of the system NH_3–$HC_2H_3O_2$, in which case $NH_4C_2H_3O_2$ would have appeared as a 1:1 compound. The study of the latter system in its entirety is, however, beyond the scope of this work; it seemed preferable to choose $NH_4C_2H_3O_2$ and $HC_2H_3O_2$ as components in order to emphasize the analogy between ammonium and the alkali metals.

[40] *Cf.* Kendall, Booge and Andrews, THIS JOURNAL, **39**, 2308 (1917).

for the preparation of pure ammonium acetate, and the uncertainty as to the melting point of this salt has been cleared up.

2. Solvation and solubility in these systems, and in others of the same type for which data are available, have been found to be closely related, in accordance with the theories of Kendall.

3. Attention has been called to the basic properties of acetates in acetic acid solution, and to the similarity in function between ammonia and water in this solvent.

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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. III. ZINC ACETATE AND SODIUM ZINC ACETATE[1]

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Introduction

The solubility of zinc acetate in acetic acid was found by Kendall and Adler[2] to be very small, the saturated solution at 130° containing only about 0.1 mole per cent. of zinc acetate; no further data are given by these authors. In the first article of this series,[3] mention was made of the fact that the solubility of zinc acetate is greatly increased by the presence of sodium acetate, and it was pointed out that this was analogous to the behavior of zinc hydroxide, in aqueous solutions, upon the addition of sodium hydroxide; no quantitative work, however, has been done previously upon the ternary system sodium acetate–zinc acetate–acetic acid. In the present investigation the solubility of zinc acetate in acetic acid over a range of temperatures has been measured, both in the absence of sodium acetate and in the presence of increasing concentrations of the latter solute. Comparison of the results of these measurements with data given in the literature for the corresponding aqueous system has established the analogy between the two cases upon a firmer basis, and has made possible its further development, as will be shown below.

Method

Preparation of Materials.—The acetic acid employed was prepared as described in the preceding paper of this series. The sodium acetate was prepared by recrystallizing a C. P. hydrate from water and dehydrating it at 150° for about a week. Zinc acetate, it was found, could not be dehydrated even at temperatures as low as 90° without slow partial decomposition to a basic salt. The pure salt was made by re-

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[1] The material presented in this paper is from part of a thesis submitted by Walter H. McAllister to the Graduate School of the University of Kansas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Kendall and Adler, THIS JOURNAL, **43**, 1470 (1921).

[3] Davidson, *ibid.*, **50**, 1890 (1928).