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

Amphoteric Acetates in Acetic Acid as Solvent[1]

BY ARTHUR W. DAVIDSON AND ERNEST GRISWOLD

It has been reported in previous papers[2] from this Laboratory that zinc and cupric acetates are readily soluble in acetic acid solutions of sodium and ammonium acetates, respectively, and that in each case an addition compound is formed between the alkali acetate and that of the heavy metal. It has also been pointed out[2] that such increased solubility and compound formation might be regarded as manifestations of a type of amphoterism analogous to that shown by the hydroxides of these metals in aqueous solution. Recent work on amphoteric hydroxides, to be referred to later, has served to strengthen this analogy. The investigation of solubility and compound formation in the systems potassium acetate–cupric acetate–acetic acid and ammonium acetate–zinc acetate–acetic acid reported in the present paper, was undertaken in order that the effects of ammonium and alkali acetates upon the same heavy metal acetate might be compared, and with the hope of throwing further light upon the behavior of amphoteric bases in general.

Method

Anhydrous acetic acid and the acetates used were all prepared as described in previous papers. Because of the highly deliquescent nature of potassium acetate, it was found necessary, in making up solutions of this salt, to dry each sample before weighing, by heating it to 180° for several hours after it had been transferred to the tube in which it was to be used.

Solubility determinations were made by the synthetic method; that is, the temperature of disappearance of solid phase in a solution of known concentration was observed, as described in previous papers. Calibrated thermometers were employed, and each equilibrium temperature reported represents the mean of at least two determinations.

In the potassium cupric acetate system, analyses of solid phases were made both upon crystals which had been freed from mother liquor by filtration and pressing between porous tiles, and

upon wet residues, the results of the latter analyses being used according to the familiar method of Schreinemakers. In either case, copper was first determined by electrolytic deposition; if potassium was present also, it was determined by treating the remaining solution with sulfuric acid, evaporating and heating in a platinum dish until complete conversion to potassium sulfate had taken place, and weighing the residue. In the ammonium zinc acetate system, solid phases were analyzed for zinc by potentiometric titration with potassium ferrocyanide solution, and for ammonia by treatment of another portion with sodium hydroxide solution, followed by distillation into standard hydrochloric acid.

Results

I. System $KC_2H_3O_2-Cu(C_2H_3O_2)_2-HC_2H_3O_2$.— The solutions were of a greenish-blue color, changing toward blue with increasing concentration of potassium acetate; unlike the corresponding solutions containing ammonium acetate,[2b] they showed no appreciable change in color upon heating. In the following table the mole fraction

TABLE I

SOLUBILITY OF CUPRIC ACETATE IN POTASSIUM ACETATE SOLUTIONS

S	T	S	T	S	T
A. $R = 0.0146$		B. $R = 0.0254$		C. $R = 0.0486$	
Solv.		Solv.		S. D. A.	
0.350	31.8	0.392	31.3	0.530	32.0
.476	38.3	.435	34.0	.623	36.8
.557	42.3	.594	42.0	.711	41.0
.632	45.3	.752	48.0	.800	44.0
.723	48.3	.843	51.0	.916	48.0
D. $R = 0.0590$		E. $R = 0.0657$		F. $R = 0.0738$	
S. D. A.		S. D. A.		S. D. A.	
0.440	29.8	0.378	27.0	0.373	26.0
.520	35.7	.495	35.5	.497	35.5
.706	44.2	.599	41.5	.676	45.8
.804	48.5	.745	48.5	.746	49.0
1.100	58.5	1.100	60.5	.814	52.0
G. $R = 0.107$		H. $R = 0.116$		I. $R = 0.144$	
S. D. A.		S. D. A.		S. D. A.	
0.409	27.1	0.454	29.3	0.800	43.6
.557	38.3	.549	36.8	.923	49.1
.654	44.6	.706	45.7	.980	51.7
.817	52.3	.832	51.8	1.110	57.3
.927	56.8	1.100	62.0	1.240	61.3

of potassium acetate in the binary solvent is represented by R, while S denotes the mole percentage of cupric acetate in the ternary solution which was in equilibrium with solid phase at the temperature T. The abbreviation "Solv." is used to indicate that the stable solid phase is the solvate $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, and "S. D. A.," similarly, to denote the solvated double acetate $KC_2H_3O_2 \cdot 2Cu(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$.

These results were plotted in a series of curves, not reproduced here, from which were obtained data for the 45° isotherm shown in Fig. 1.
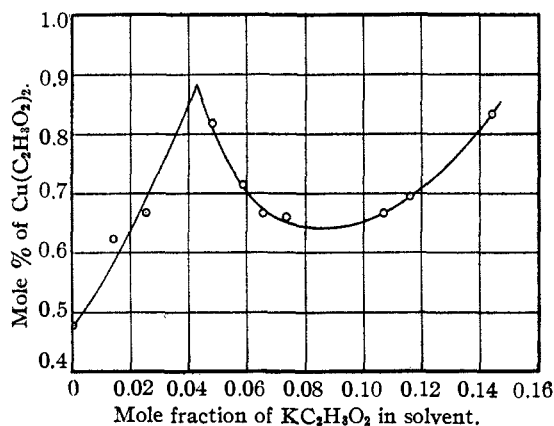

Fig. 1.—Solubility of cupric acetate in acetic acid solutions of potassium acetate at 45°.

The solid phase obtained in series A and B was light blue-green in color. Analyses showed it to contain no potassium, and gave a mean value of 24.5% of copper (calcd. for $Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, 26.3%). This compound is evidently the same as that which occurs as solid phase in the binary system $Cu(C_2H_3O_2)_2 - HC_2H_3O_2$ at temperatures below 50°.

In series C to I, the solid which separated out was of a light greenish-blue color and contained potassium. It was both deliquescent and unstable; these facts, together with the high viscosity of the mother liquor, made the accurate analysis of a dried sample impossible. Four direct analyses on samples obtained from solutions of different compositions were supplemented by three determinations made by the method of algebraic extrapolation of tie-lines through corresponding compositions of original complex and wet residue. The mean of all the results, expressed in mole %, gave the following figures: $KC_2H_3O_2$, 21.5; $Cu(C_2H_3O_2)_2$, 37.9; $HC_2H_3O_2$, 40.6%. This indicates that the solid phase is probably a compound of the composition KC_2H_3-

$O_2 \cdot 2Cu(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (calcd.: $KC_2H_3O_2$, 20; $Cu(C_2H_3O_2)_2$, 40; $HC_2H_3O_2$, 40%).

It is evident that the behavior of this system is, in general, similar to that of the corresponding one with ammonium acetate as solvent salt. The solubility of cupric acetate at a fixed temperature, as long as solvated cupric acetate is the stable solid phase, increases with increasing concentration of potassium acetate; on the appearance of a ternary compound, the proportion of cupric acetate in the saturated solution begins to decrease with increasing concentration of alkali salt. At 45°, as shown by Fig. 1, the increase is from 0.478 mole % in pure acetic acid to a maximum of about 0.88 mole % when R is 0.043; here the new solid phase appears, and the solubility falls off somewhat, rising again to 0.83% for $R = 0.144$.

II. System $NH_4C_2H_3O_2 - Zn(C_2H_3O_2)_2 - HC_2H_3$-$O_2$.—In the following table, R denotes the mole fraction of ammonium acetate in the solvent, and S the mole percentage of zinc acetate in the saturated solution at the temperature T. "U." is used to denote unsolvated $Zn(C_2H_3O_2)_2$ as solid

TABLE II

SOLUBILITY OF ZINC ACETATE IN AMMONIUM ACETATE SOLUTIONS

S	T	S	T	S	T
A. $R = 0.0414$		B. $R = 0.0838$		C. $R = 0.134$	
U.		U.		U.	
1.105	37.3	2.58	41.0	5.14	48.8
1.216	46.0	2.79	48.0	5.50	56.0
1.358	55.0	3.01	56.0	5.92	64.0
1.627	69.0	3.77	71.8	. 6.40	74.3
D. $R = 0.155$		E. $R = 0.169$		F. $R = 0.196$	
(a) U.		(a) U.		(a) U.	
5.75	42.0	6.89	53.0	8.59	57.0
6.19	49.3	7.40	61.5	8.87	62.0
6.71	60.0	8.18	73.5	9.19	67.0
7.10	67.3	8.62	80.0	9.69	73.0
7.52	72.3	(b) S. D. A.		10.97	88.0
(b) S. D. A.		2.23	32.1	(b) S. D. A.	
2.09	30.4	3.31	35.8	1.00	23.8
3.10	34.0	4.37	37.5	1.99	32.0
4.10	36.0	5.41	38.6	3.69	38.5
5.07	36.9	6.42	39.1	5.64	42.0
6.19	37.0	7.40	39.1	8.71	43.8
G. $R = 0.223$		H. $R = 0.253$		H (b)	
S. D. A.		(a) U.		(continued)	
1.04	23.1	11.64	57.0	1.93	29.8
2.05	30.9	12.29	67.0	3.92	38.3
4.02	38.7	12.85	74.0	5.08	41.3
5.91	42.0	13.35	80.0	7.32	44.5
7.77	43.6	(b) S. D. A.		9.58	45.8
9.53	44.0	1.00	25.3	11.92	45.8

phase, and "S. D. A." for the solvated double acetate $Zn(C_2H_3O_2)_2 \cdot 2NH_4C_2H_3O_2 \cdot 6HC_2H_3O_2$.

From the series of curves obtained by plotting these results, data were taken for the 39° solubility isotherm shown in Fig. 2.

The solid phase obtained in series A, B, C, D(a), E(a), F(a) and H(a) consisted of fine colorless crystals. Analysis showed ammonia to be absent, and gave 35.59% of zinc (calcd. for $Zn(C_2H_3O_2)_2$, 35.64%). This result, together with the similarity of the corresponding freezing point curves, establishes the identity of the compound as unsolvated zinc acetate.

The solid which crystallized out in series D(b), E(b), F(b), G and H(b) was quite different in appearance from the one just discussed, consisting of slender colorless needles. The solubility of this substance changed with temperature very much more rapidly than did that of the zinc acetate. The crystals were fairly stable, and three analyses on samples obtained from solutions of different composition gave the following mean results, in mole %: $Zn(C_2H_3O_2)_2$, 10.97; $NH_4C_2H_3O_2$, 24.12; $HC_2H_3O_2$ (by difference), 64.91. These values indicate that the compound is $Zn(C_2H_3O_2)_2 \cdot 2NH_4C_2H_3O_2 \cdot 6HC_2H_3O_2$ (calcd.: $Zn(C_2H_3O_2)_2$, 11.11; $NH_4C_2H_3O_2$, 22.22; $HC_2H_3O_2$, 66.67%).

Here the results are of the same general nature as in the sodium zinc acetate system studied previously. At 39° the solubility of zinc acetate increases from 0.0049 mole % in pure acetic acid to a maximum of 6.21 mole % when R is 0.169, after which the ternary compound appears as solid phase, and the solubility falls off.

Discussion

The results of this work, considered in connection with those previously reported, show no marked difference between the effects of ammonium acetate and an alkali acetate upon either the zinc or the cupric salt. There is no evidence, at least in the temperature range here studied, of any specific effect due to ammonia; ammonium acetate behaves merely as a strong base, as would be expected in view of its stability in acetic acid solution.[3]

In dissolving either in alkali acetate or in ammonium acetate solutions, then, the heavy metal acetates are exhibiting amphoteric behavior analogous to that of the corresponding hydroxides in dissolving in aqueous alkali solutions. The latter

(3) Davidson, *Chem. Reviews*, **8**, 182 (1931).

phenomenon is usually explained in terms of the traditional theory that amphoteric hydroxides have weakly acid properties and are neutralized by strong bases to give soluble salts. The evidence for such a mechanism is, however, far from
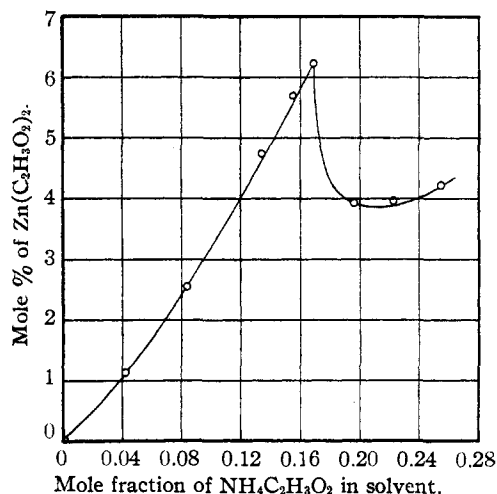

Fig. 2.—Solubility of zinc acetate in acetic acid solutions of ammonium acetate at 39°.

conclusive, and the alternative explanation first suggested by Pfeiffer[4] seems preferable. According to Pfeiffer's theory the dissolving of an amphoteric hydroxide in a solution of an alkali is due to the formation of a hydroxo salt by an addition reaction, rather than to neutralization; thus in the case of zinc, for example, the main reaction is

$$Zn(OH)_2 + NaOH = Na[Zn(OH)_3], \text{ or}$$
$$Zn(OH)_2 + OH^- = Zn(OH)_3^-$$
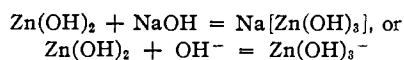
In support of this theory, Scholder and his co-workers,[5] in a recent series of articles, have given evidence to show that the crystalline products obtained from such solutions are actually hydroxo salts, while Brintzinger and Wallach[6] have shown that hydroxo ions are present in the solutions. In the case of the double acetates, no evidence has been obtained as yet as to the existence of complex anions; nevertheless, it is of interest to compare the formulas of the four compounds which have been obtained in our work with some of the hydroxo compounds tabulated by Scholder, as follows:

(4) Pfeiffer, *Ber.*, **40**, 4036 (1907); see also Seward, *J. Chem. Ed.*, **11**, 567 (1934).

(5) Scholder, *Z. angew. Chem.*, **46**, 509 (1933); Scholder and Weber, *Z. anorg. allgem. Chem.*, **215**, 355 (1933); Scholder, Felsenstein and Apel, *ibid.*, **216**, 138 (1933); Scholder and Weber, *ibid.*, **216**, 159 (1933); Scholder and Pätsch, *ibid.*, **216**, 176 (1933).

(6) Brintzinger and Wallach, *Z. angew. Chem.*, **47**, 61 (1934).

Water system	Acetic acid system
$Na_2Zn(OH)_4$	$Na_2Zn(OAc)_4{}^7 \cdot 4HOAc$
$Na_2Zn(OH)_4 \cdot 2HOH$	$(NH_4)_2Zn(OAc)_4 \cdot 6HOAc$
$BaZn(OH)_4 \cdot HOH$	$(NH_4)_4Cu(OAc)_6 \cdot 4HOAc$
$Ba_2Cu(OH)_6$	$KCu_2(OAc)_5 \cdot 2HOAc$

The marked resemblances among these formulas lend support to the theory that the chemical behavior of amphoteric bases in these two very different solvents is substantially the same.[8]

The isolation of the above addition compounds in the solid state leaves small room for doubt that such compounds exist in solution also, and this fact could scarcely fail to play an important part in increasing the solubility[9] of the heavy metal acetates in acetic acid. Yet the possibility that the observed increases may be due largely to the familiar "salt effect" should not be overlooked.
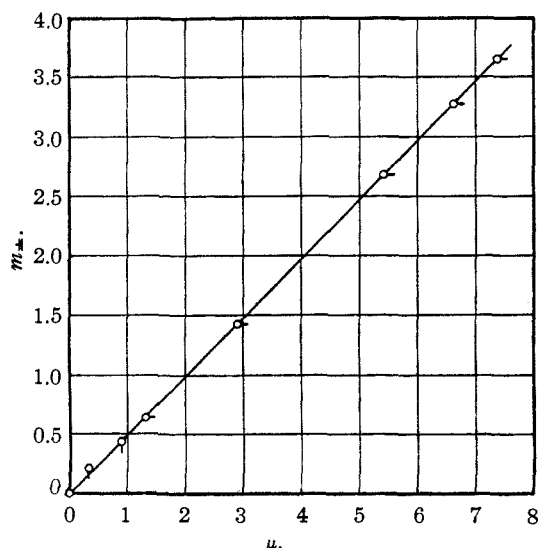

Fig. 3.—Variation of the mean molality of the ions of zinc acetate with the total ionic strength: O, no added salt; ⊘, added salt sodium acetate; O-, added salt ammonium acetate.

In aqueous solution, it is true, the solubilities of amphoteric hydroxides in alkaline solutions are generally far too great to be accounted for by interionic effects alone; but because of the low dielectric constant of acetic acid, the activity coefficients of salts in this solvent decrease much more rapidly with increasing ionic strength than

(7) "Ac" is used here as an abbreviation for the acetyl group.

(8) It may be noted here that, due to the instability of ammonium hydroxide at ordinary temperatures, hydroxo salts of ammonium have not been obtained, although of course ammonia complexes are abundant. It is conceivable that such ammonium salts, analogous to those of the acetic acid system, might be stable at very low temperatures.

(9) See Kendall, Davidson and Adler, THIS JOURNAL, **43**, 1495 (1921); Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, 1924, pp. 178-179.

in water, even in the absence of specific chemical effects.[10] It therefore seemed desirable to include in this discussion a very brief consideration of some of our results from the thermodynamic viewpoint. The data for zinc acetate are best suited for such a study, since the unsolvated salt is obtained as solid phase over a wide concentration range.

Figure 3 was constructed from the solubility data at 39° in order to show how the mean molality, $m_\pm$, of the ions (that is, the cube root of the solubility product) of zinc acetate varies with the total ionic strength, μ. It is evident that the points corresponding to sodium acetate and to ammonium acetate as solvent fall on the same line, a fact which gives further support to the statement that there is no essential difference in chemical behavior between the alkali acetates and ammonium acetate at this temperature. The activity coefficient, γ, of zinc acetate, must be inversely proportional to $m_\pm$. The data do not extend to sufficiently dilute solutions to make it possible to evaluate the proportionality constant; nor can the Debye–Hückel equation in any form be used, at these concentrations, to calculate the theoretical change, due to interionic effects, of γ with μ. We may, however, compare the rate of change of activity coefficient observed here with that found experimentally for a salt of the same valence type in a binary solution. For this purpose the change in activity coefficient with concentration was calculated by the method of Lewis and Randall from the freezing point data for barium acetate.[11] The divergence function j for this salt remaining nearly constant, for molalities between 0.1 and 1 (μ = 0.3 to 3), at 0.65, it follows that γ, over this range, is approximately proportional to $1/\mu^{0.65}$. In the case of zinc acetate, it is evident from Fig. 3 that in the same concentration range $m_\pm$ is proportional to μ, or γ to $1/\mu$. Hence it is obvious that the activity coefficient of zinc acetate in the alkali acetate solutions falls off much more rapidly with increasing ionic strength than does that of barium acetate in solution alone; in the case of barium acetate $\gamma_{\mu=3}/\gamma_{\mu=0.3} = 0.23$, whereas for zinc acetate this ratio has a value of only 0.10.

While the distinction between physical and chemical effects in solution is admittedly an imperfect one, it seems reasonable to conclude in this

(10) See, for instance, Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932); Scholl, Hutchison and Chandlee, *ibid.*, **55**, 3081 (1933).

(11) Davidson and McAllister, *ibid.*, **52**, 507 (1930).

case that the increased solubility of zinc acetate is not due to the general salt effect alone, but that specific chemical effects, as suggested above, must be an important factor. Hence the application of the term "amphoteric" to this acetate, and to others which exhibit similar properties, appears to be justified.

Summary

1. The solubilities of cupric acetate in potassium acetate solutions in acetic acid, and of zinc acetate in ammonium acetate solutions, have been determined over a wide range of temperatures and concentrations.

2. In each instance the solubility of heavy metal acetate, at a fixed temperature, has been found to vary with the concentration of alkali acetate in the same general manner as in the cases previously reported.

3. Two new ternary addition compounds, $KC_2H_3O_2 \cdot 2Cu(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ and $Zn(C_2H_3O_2)_2 \cdot 2NH_4C_2H_3O_2 \cdot 6HC_2H_3O_2$, have been isolated and analyzed.

4. Resemblances between the ternary compounds obtained in these studies and analogous compounds of the water system have been pointed out, and their significance, from the point of view of theories of amphoteric behavior, has been discussed.

5. It has been shown that the effects of sodium and ammonium acetates upon the solubility product of zinc acetate are approximately the same, and that the activity coefficient of zinc acetate in the presence of alkali acetates falls off much more rapidly with increasing ionic strength than does that of barium acetate in binary solution.

6. The large increases in solubility observed in these studies have been attributed mainly to specific chemical effects, analogous to those which occur in solutions of amphoteric hydroxides in aqueous alkalies.

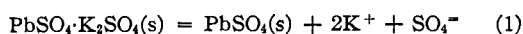# Potassium Lead Sulfate, Lead Sulfate, Lead Iodide, Potassium, Sulfate and Iodide Ions at 25°
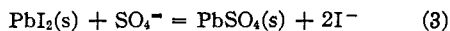
BY MERLE RANDALL AND DONALD L. SHAW

In this paper we shall give measurements of the equilibrium at 25° of the reaction

$$PbSO_4 \cdot K_2SO_4(s) = PbSO_4(s) + 2K^+ + SO_4^- \quad (1)$$

in which the double potassium lead sulfate is decomposed into lead sulfate and aqueous potassium sulfate. This equilibrium combined with our measurements of the reaction

$$PbI_2(s) + 2SO_4^- + 2K^+ = PbSO_4 \cdot K_2SO_4(s) + 2I^- \quad (2)$$
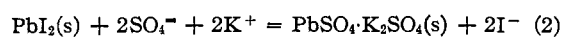
gives a new determination of the reaction

$$PbI_2(s) + SO_4^- = PbSO_4(s) + 2I^- \quad (3)$$

which was studied by Findlay[1] in the presence of sodium ion.

Equilibrium was obtained by rotating in sealed flasks about 20 g. of each of the pure solid phases with about 250 ml. of solution at 25°, after the procedure of Randall and Vietti.[2] A dilute solution of pure lead nitrate was added slowly with

mechanical stirring to a solution of sodium sulfate, all in conductivity water. Lead iodide was similarly prepared.

Potassium lead sulfate was prepared by allowing solutions containing known weights of lead acetate to react with solutions containing the quantities of saturated potassium sulfate solution calculated to form $PbSO_4 \cdot K_2SO_4$. The compound formed was dried by suction and all possible moisture removed by pressure between absorbent papers. It was then dried and weighed. The filtrate always contained only a slight excess of either lead or sulfate ions and the composition of the double salt thus formed corresponded to the formula, $PbSO_4 \cdot K_2SO_4$.

Samples of the filtered equilibrium solutions were weighed for analysis from a weight buret. Iodide ion was determined by slowly adding a standardized solution of silver nitrate from a weight buret while the flask was shaken vigorously. When the precipitation was complete a small excess of silver nitrate was added and the

(1) (a) Findlay, Z. physik. Chem., 34, 409 (1900); (b) Stoffella [Boll. chim. farm., 64, 481 (1925), through C. A., 20, 346 (1926)] studied this reaction in the presence of zinc ion. The latter measurements are qualitative; (c) see Brönsted, Z. physik. Chem., 77, 315 (1911).

(2) Randall and Vietti, THIS JOURNAL, 50, 1528 (1928).