[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SOUTH DAKOTA]

The Solvent Effect of Lithium Acetate on Zinc Acetate in Acetic Acid

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Previous studies of the solvent action of certain salts on zinc acetate in acetic acid have indicated that specific chemical effects are predominantly involved in some instances, while salt effects probably figure largely in others. Both sodium acetate[1] and ammonium acetate[2] have been found to increase the solubility of zinc acetate in acetic acid to a very marked extent, and ternary addition compounds have been isolated in both cases. Specific chemical interaction is thus clearly evident here. On the other hand, the solvent effect of lithium nitrate,[3] although distinctly manifested, is nevertheless much weaker than that of the acetates mentioned. Moreover, no addition compound was obtained in this case. This behavior, although not conclusive proof of the operation of salt effect, does strongly suggest it. In the present investigation the solubility of zinc acetate in acetic acid solutions of lithium acetate of various concentrations and over a range of temperatures has been determined. Comparison of the solvent effect of lithium acetate with that of other acetates on the one hand, and with that of lithium nitrate on the other, is thus made possible.

Experimental

Materials.—Anhydrous acetic acid was prepared according to the method previously described.[4] The melting point of the product, as determined by a thermometer recently certified by the U. S. Bureau of Standards, was 16.6°. Zinc acetate was prepared by the method of Davidson and McAllister.[1] Analysis of the final product gave 35.61% zinc (calcd., 35.63). Lithium acetate was prepared by recrystallizing a C. P. hydrate and drying at 150° for two weeks. Analysis gave 10.53% lithium (calcd., 10.52).

Method.—The synthetic or freezing point method was used in obtaining the solubility data.. A series of solutions, each containing a known proportion of lithium acetate in acetic acid, were made up, and the solubility curve of zinc acetate in each of the binary solvents so prepared was determined.

To establish the identity of the solid phases, samples were filtered out, superficially dried between porous plates, and analyzed. The solvated double salt was analyzed by treating a weighed sample with sulfuric acid in a platinum dish, evaporating and heating until complete conversion to the mixed sulfates had taken place, and weighing the residue. The zinc content of the residue was then determined by potentiometric titration with standard potassium ferrocyanide solution. Preliminary analysis of mixtures containing known amounts of pure lithium acetate and zinc acetate showed this method to be entirely satisfactory. The unsolvated zinc acetate was simply analyzed for zinc by the method mentioned above, as was the purified zinc acetate used in this work. The purified lithium acetate used was analyzed by conversion to lithium sulfate.

(1) Davidson and McAllister, THIS JOURNAL, **52**, 519 (1930).
(2) Davidson and Griswold, *ibid.*, **57**, 423 (1935).
(3) Griswold, Ash and McReynolds, *ibid.*, **67**, 372 (1945).
(4) Griswold and Olson, *ibid.*, **59**, 1894 (1937).

Results

In Table I, R represents the mole percentage of lithium acetate in the binary solvent, while S denotes the mole percentage of zinc acetate in the ternary saturated solution at the temperature T. "Z" is used to represent $Zn(C_2H_3O_2)_2$ occurring as the solid phase, while "L. Z. A." denotes the solvated lithium zinc acetate, $Zn(C_2H_3O_2)_2 \cdot 2LiC_2H_3O_2 \cdot 4HC_2H_3O_2$, as solid phase.

TABLE I

SOLUBILITY OF ZINC ACETATE IN LITHIUM ACETATE SOLUTIONS AT VARIOUS TEMPERATURES

S	T
A. R = 2.50%	
Z	
0.705	35.0
.800	47.0
1.106	75.3
1.170	79.5
B. R = 5.00%	
1.565	37.9
1.572	38.0
1.604	42.0
1.887	59.5
1.897	63.5
2.416	83.8
2.445	84.7
C. R = 7.97%	
(a) Z	
2.04	36.7
2.13	39.7
2.35	47.6
3.07	66.6
3.31	72.6
3.45	75.8
4.14	90.1
(b) L. Z. A.	
1.44	14.0
1.82	18.3
2.09	20.9
2.25	21.2
2.35	22.9
D. R = 10.00%	
(a) Z.	
2.70	41.8
2.99	52.6
3.07	56.7
3.27	61.8
3.53	69.2
3.55	69.6
3.81	77.3
3.99	81.5
(b) L. Z. A.	
1.43	16.5
2.03	22.0
2.16	22.6
2.33	23.8
2.50	25.3
2.78	26.8
E. R = 12.50%	
(a) Z	
3.45	51.5
3.96	67.0
4.28	74.6
4.61	82.9
4.77	86.6
5.08	93.0
(b) L. Z. A.	
2.53	28.4
2.86	30.5
3.69	35.1
3.96	36.9
4.03	36.7
4.28	37.4

Curves, not reproduced here, were plotted from the results given in the table, and from them were obtained by interpolation the data from which the isotherms shown in Fig. 1 were constructed.

The solid phase obtained in series A, B, C(a), D(a), and E(a) in the table, and thus the solid phase represented in the solubility isotherms of Fig. 1, occurred in the form of fine white crystals. Determination of the zinc content of samples of the crystals gave values which came close to the percentage of zinc calculated for $Zn(C_2H_3O_2)_2$, leaving little doubt that this solid phase is simply unsolvated zinc acetate.

The second solid phase, appearing in C(b), D(b), and E(b), occurred as fine colorless needles. The solutions in which these crystals formed were quite viscous, and it was rather difficult to effect a satisfactory separation of the solid for analysis. However, two samples obtained from solutions of

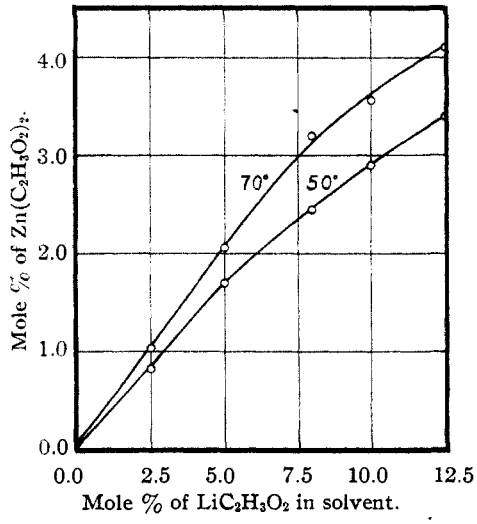

Fig. 1.—Solubility of zinc acetate in acetic acid solutions of lithium acetate at 50 and at 70°.

different composition were analyzed, and gave the following mean results, expressed in mole %: $Zn(C_2H_3O_2)_2$, 13.63; $LiC_2H_3O_2$, 27.63; $HC_2H_3O_2$ (by difference), 58.74. These values appear to conform most nearly to the formula $Zn(C_2H_3O_2)_2 \cdot 2LiC_2H_3O_2 \cdot 4HC_2H_3O_2$ (calcd., $Zn(C_2H_3O_2)_2$, 14.29; $LiC_2H_3O_2$, 28.57; $HC_2H_3O_2$, 57.14%).

Because of the viscous character of the solutions at the lower temperatures and their tendency to remain supersaturated, it was difficult to extend the solubility data by this method to temperatures much below those reported. It is therefore not possible to construct from these results a solubility isotherm which will show branches representing both of the solid phases, without making some long and uncertain extrapolations. It seems clear from the data, however, that at a given temperature the solubility of the solvated double salt becomes less as the concentration of lithium acetate is increased. Thus interpolation at 20°, with the ternary compound as solid phase, shows the concentration of zinc acetate in the saturated solution to be about 2.2 mole % when R is 7.97, but only 1.8 mole % when R is 10.00. It will be noted, also, that the effect of temperature upon solubility is much more pronounced with the ternary compound than with zinc acetate.

Discussion

The results of this study show that the effect of lithium acetate is closely similar to the effects of sodium and ammonium acetates previously described by others. This similarity is brought out clearly by a comparison of the formulas of the ternary compounds obtained at high concentrations of the solvent salts. The compound $Zn(C_2H_3O_2)_2 \cdot 2LiC_2H_3O_2 \cdot 4HC_2H_3O_2$ found in this investigation has the same formulation as $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$ reported by Davidson and McAllister, and is very similar to $Zn(C_2H_3O_2)_2 \cdot 2NH_4C_2H_3O_2 \cdot 6HC_2H_3O_2$ reported by Davidson and Griswold. Still another similar compound, $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2$, has been obtained by Lehrman and Skell[5] from the binary system zinc acetate–sodium acetate. Moreover, the increase in solubility of zinc acetate produced by lithium acetate is of the same order of magnitude as that produced by the other acetates. For example, isotherms at 40°, not reproduced in this paper, have been drawn, and yield values of about 0.29 and 0.28 molal for the solubility of zinc acetate in 1 molal solutions of lithium acetate and ammonium acetate, respectively.

It seems reasonable to suppose that all of these cases are manifestations of the amphoteric behavior of zinc acetate in the acetic acid system.[6] The ternary compound described in this paper might then perhaps be appropriately termed a solvated lithium acetozincate, and formulated as $Li_2Zn(C_2H_3O_2)_4 \cdot 4HC_2H_3O_2$, which emphasizes its resemblance to such crystalline hydroxo compounds as $Na_2Zn(OH)_4$ and $NaZn(OH)_3 \cdot 3H_2O$ obtained by Scholder[7] and his co-workers from the system zinc oxide–sodium oxide–water.

Comparison of the results in this paper with those previously reported from this Laboratory on the solvent action of lithium nitrate show a pronounced difference in magnitude to exist. Thus at 40° the solubility of zinc acetate in 1 molal lithium nitrate is only 0.08 molal. There is no direct evidence of chemical interaction in this case, and it may very well be an example of salt effect. It seems safe to conclude, therefore, that the solvent effects of these two lithium salts upon zinc acetate are quite different in character, as well as in magnitude.

Summary

1. The solubility of zinc acetate in solutions of lithium acetate in acetic acid has been determined over a rather wide range of temperatures and concentrations. Its solubility has been found to increase with progressively increased concentrations of lithium acetate, so long as the solid phase is unsolvated zinc acetate.

2. A new ternary addition compound, $Zn(C_2H_3O_2)_2 \cdot 2LiC_2H_3O_2 \cdot 4HC_2H_3O_2$, has been isolated and analyzed.

3. Similarities in the effects of lithium acetate and of sodium and ammonium acetates upon zinc acetate have been discussed. Differences in the behavior of lithium acetate and lithium nitrate have been pointed out.

4. The pronounced solvent effect observed is ascribed mainly to specific chemical reaction, analogous to the effect of strong bases in aqueous solution upon amphoteric zinc hydroxide.

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(5) Lehrman and Skell, THIS JOURNAL, **61**, 3340 (1939).

(6) See refs. 2 and 5 for a more extended discussion of this point.

(7) Scholder and Weber, *Z. anorg. allgem. Chem.*, **215**, 355 (1933); Scholder and Hendrich, *ibid.*, **241**, 76 (1939).