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

Solubility Relations in the System Lead Acetate–Sodium Acetate–Acetic Acid at 30°

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The investigations of Davidson and his co-workers[1] have shown that certain metal acetates of low solubility in acetic acid, such as zinc acetate and cupric acetate, possess amphoteric properties in that they can be dissolved by alkali metal acetates or ammonium acetate, which are strong bases in this solvent. Lead acetate in acetic acid is formally analogous to amphoteric lead hydroxide in water. Partly for this reason, but more especially because of the anomalous behavior of lead acetate both in water and in acetic acid, it was thought of interest to investigate the solubility relations of lead acetate and sodium acetate in acetic acid at some one temperature. The results of such a study are given in the present paper.

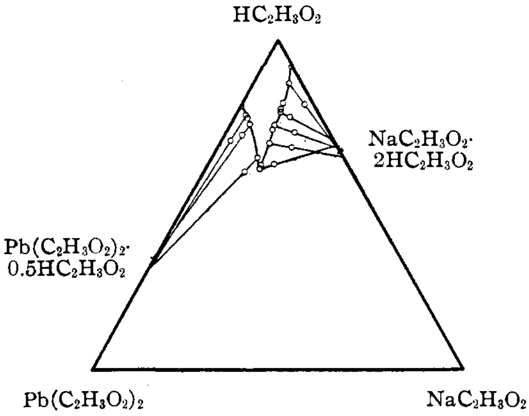

Fig. 1.—Solubility isotherm at 30° for the system lead acetate–sodium acetate–acetic acid.

Method.—Anhydrous acetic acid was prepared according to the method of Kendall and Gross,[2] except that a final distillation was carried out through a 5-foot (1.5-meter) fractionating column equipped with a spot condenser. The acid used melted at 16.6° or higher.

The lead acetate was prepared by essentially the same procedure as that given by Davidson and Chappell.[3] Analyses of the final product gave 63.72% lead (calcd., 63.70).

Sodium acetate was prepared according to the method described by Davidson and McAllister.[4] Analyses gave 28.01% sodium (calcd., 28.03).

Mixtures of the pure materials were made up with an excess of one of the salts, sealed in glass containers, and tumbled in a bath for two weeks or longer. Some of the mixtures were first heated and then allowed to approach equilibrium from supersaturation. The temperature of the bath was maintained at 30.0° as determined by a calibrated thermometer.

After attainment of equilibrium was reasonably assured, portions of the saturated solutions were filtered through glass wool at the temperature of the bath, moisture being excluded. Weighed samples were diluted and evaporated with sulfuric acid until fuming began, cooled, and taken up with 50% alcohol solution. The lead could thus be separated and determined as lead sulfate. The sodium in the filtrate was then converted to sulfate and weighed. Samples of the wet solid were analyzed by the same general procedure. In all cases the percentage of acetic acid was calculated by difference. The composition of the saturating phase was determined by Schreinemakers' method.

Results and Discussion

Compositions of the various saturated solutions and wet solids are given in Table I, and are represented graphically in Fig. 1. Only two solid phases were obtained at this temperature, as the diagram shows. With sodium acetate in excess the solid phase is $NaC_2H_3O_2 \cdot 2HC_2H_3O_2$, previously reported by Kendall and Adler[5] to be stable over a temperature range which includes 30°. Our

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND WET SOLIDS FROM THE SYSTEM LEAD ACETATE–SODIUM ACETATE–ACETIC ACID AT 30°

Solutions			Wet Solids			Solid phase[a]
$Pb(C_2H_3O_2)_2$ mole, %	$NaC_2H_3O_2$ mole, %	$HC_2H_3O_2$ mole, %	$Pb(C_2H_3O_2)_2$ mole, %	$NaC_2H_3O_2$ mole, %	$HC_2H_3O_2$ mole, %	
19.72	0.00	80.28				I
19.81	2.29	77.90	27.92	2.03	70.05	I
19.83	3.18	76.99				I
20.16	4.84	75.00	27.72	4.37	71.91	I
23.11	12.19	64.70	28.34	11.06	60.60	I
24.33	13.93	61.74	19.81	17.37	62.82	II
23.58	13.96	62.46				II
17.92	12.48	69.60	12.21	19.73	68.06	II
14.78	11.64	73.58				II
13.46	11.68	74.86	9.24	18.34	72.43	II
9.66	10.97	79.37	8.07	14.52	77.41	II
9.43	10.98	79.59				II
7.88	10.58	81.54				II
3.01	9.44	87.55	2.12	16.99	80.89	II
0.00	7.70	92.30				II

[a] Solid phases: I, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$; II, $NaC_2H_3O_2 \cdot 2HC_2H_3O_2$.

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(1) (a) Davidson and McAllister, THIS JOURNAL, **52**, 519 (1930); (b) Davidson and Griswold, *ibid.*, **53**, 1341 (1931); (c) Davidson and Griswold, *ibid.*, **57**, 423 (1935).

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

(3) Davidson and Chappell, *ibid.*, **55**, 4524 (1933).

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

(5) Kendall and Adler, *ibid.*, **43**, 1470 (1921).

value of 7.70 mole per cent. for the solubility of sodium acetate in acetic acid alone agrees fairly well with the value 7.84 interpolated from their data, which were obtained by the synthetic method.

Extrapolation of the tie-lines from the other branch of the solubility isotherm is somewhat uncertain, but there can be little doubt that the stable solid phase here is the hemi-solvate, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$, first reported by Tarbutton and Vosburgh,[6] and later shown by Davidson and Chappell[3] to be stable in contact with saturated acetic acid solutions between about 13 and 56°. Interpolation from the data of Davidson and Chappell gives a value of about 19.0 mole per cent. for the solubility of lead acetate in acetic acid alone, which is somewhat lower than the 19.72 mole per cent. found in the present investigation. As had been the experience of these other investigators, it was found necessary to seed the mixtures from which the hemi-solvate might reasonably be expected to separate with a small crystal of this compound, prepared by the method of Tarbutton and Vosburgh, whereupon complete transition of the anhydrous lead acetate to the solvate occurred within the period allowed for the attainment of equilibrium. If the seeding was omitted an extremely viscous solution resulted and none of the solid solvate appeared. On the other hand, transition of the anhydrous sodium acetate to the solvate occurred spontaneously.

The solvent effects mutually exerted by the two acetates are, perhaps, more clearly shown in terms of another mode of expressing composition. The data show that not only is the solubility of lead acetate increased from 4.09 to 6.63 moles per 1000 g. of acetic acid as the concentration of sodium acetate varied from zero to 3.79 moles per 1000 g. of solvent, but that, likewise, the solubility of sodium acetate increased from 1.389 to 3.79 molal as the concentration of lead acetate ranged from zero to 6.63 molal. In neither case is there any direct evidence of a common-ion effect.

Although these increased solubilities very likely may result from the formation of complexes in the solution, as has been suggested by Sandved[7] to explain the increased solubility of lead acetate in aqueous solutions of sodium acetate, it must be noted that no addition compound involving these two acetates has as yet been obtained as a solid phase. This is in distinct contrast to such systems as zinc acetate-sodium or ammonium acetate-acetic acid and cupric acetate-potassium or ammonium acetate-acetic acid, from all of which have been isolated solid ternary addition compounds, stable over certain ranges of composition and temperature. It is, of course, possible that even in the present case a similar compound might appear at lower temperatures.

Summary

1. The solubility relations of lead acetate and sodium acetate in acetic acid at 30° have been determined.

2. The solubility of lead acetate at this temperature in acetic acid alone is 19.72 mole per cent., the solid phase being $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$. The solubility of sodium acetate is 7.70 mole per cent., the saturating phase being $NaC_2H_3O_2 \cdot 2HC_2H_3O_2$. No other solid phase was obtained.

3. The solubility of each acetate is increased with progressively increased concentrations of the other in solution. The composition of the solution in equilibrium with both solid phases is about 24.5 mole per cent. lead acetate and 14.0 mole per cent. sodium acetate.

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[6] Tarbutton and Vosburgh, THIS JOURNAL, **54**, 4537 (1932).

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