The System Cadmium Acetate, Acetic Acid, Water at 25°[1]

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This investigation was undertaken to determine the solubility of cadmium acetate in mixtures of acetic acid and water and to identify the solvates formed. No quantitative data seem to be available for the solubility of cadmium acetate in either water or acetic acid. Davidson[2] lists it among the salts readily soluble in acetic acid. The hydrates reported are a trihydrate and a dihydrate.[3]

Cadmium acetate was recrystallized by allowing a hot concentrated solution containing a little acetic acid to cool, seeding and shaking vigorously. To prepare the anhydrous salt, this material was heated to constant weight at 90 to 95°.

Acetic acid was purified by distilling from chromium trioxide.[4]

The saturated solutions were best prepared by mixing acetic acid, water and cadmium acetate (either the dihydrate or the anhydrous salt) in the desired proportions, warming to dissolve the cadmium acetate completely, and then cooling, seeding and shaking while crystallization took place. This method could not be used when the percentage of water was small, because of the limited solubility of the cadmium acetate. In this case the anhydrous salt was merely added to the mixture of acetic acid and water. The mixtures were sealed in test tubes and the tubes rotated for at least two days at 25 ± 0.02°, or in a few cases at 30 ± 0.02°. Duplicate mixtures rotated for different lengths of time showed that two days was sufficient time for the attainment of equilibrium. A few of the mixtures were rotated for a month or more. The method of sampling and the methods of analysis have been described in previous papers.[5] The results are given in Table I and graphically in Fig. 1.

In the first three columns of Table I are given the results for solutions in equilibrium with cadmium acetate dihydrate. The percentages of water in the dry solid phase were calculated by algebraic extrapolation[6] from the analytical results for the wet solids. The calculated percentage of water for the formula $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ is 13.52. The left-hand portion of the curve of Fig. 1 represents solutions in equilibrium with the dihydrate.

Most of the results in the last three columns of Table I are for solutions in equilibrium with a compound of cadmium acetate and both acetic acid and water. The algebraic extrapolation in this case was made on the assumption that the water and acetic acid were present in equimolecular quantities, graphic extrapolation having shown that this assumption is in agreement with experiment. The composition found for the dry solid is best expressed by the formula $3Cd(C_2H_3O_2)_2 \cdot 4HC_2H_3O_2 \cdot 4H_2O$, for which the theoretical composition is 68.91% cadmium acetate, 23.92% acetic acid and 7.18% water. The middle portion of the curve represents solutions in equilibrium with this compound.

TABLE I

SOLUBILITY OF CADMIUM ACETATE IN MIXTURES OF ACETIC ACID AND WATER AT 25.0°

Solution, % HC₂H₃O₂	Cd-(C₂H₃O₂)₂	Dry solid H₂O, %	Solution, % HC₂H₃O₂	Cd-(C₂H₃O₂)₂	Dry solid Cd-(C₂H₃O₂)₃, %
1.88	61.07	a	28.68	52.78	69.88
2.15	61.55	...	30.17	51.84	68.54
3.52	60.72	...	37.43	45.23	68.73
3.59	60.71	a	38.53	44.03	70.68
7.28	59.74	a	43.29	39.99	71.46
9.76	58.99	a	48.59	35.98	a
11.99	58.77	13.82	52.85	32.52	a
13.55	57.98	13.88	54.12	31.89	a
17.99	56.84	13.62	65.86	23.69	67.67
18.13	56.74	13.64	67.83	22.89	65.53
23.35	55.50	13.59	69.42	21.09	67.97
23.96	55.29	13.36	79.35	17.57	b
25.43	55.31	13.28	79.55	16.75	b
27.09	54.98	13.74	79.73	16.94	b
27.45	55.05	13.51	90.22	7.87	a
27.55	55.06	13.53	92.73	5.43	...
27.34	55.26	b	95.04	4.20	...
28.95	55.51	13.77	96.87	2.29	...
			97.44	1.68	...
			97.65	1.72	...

a The algebraic extrapolation is omitted in the least favorable cases.   *b* Transition mixture.

As a check on the composition of the dry solid as shown in Table II some samples of this solid were separated from the saturated solution by means of a centrifuge and dried in air until the crystals fell apart easily. Analysis gave the following results: cadmium acetate, 68.91, 68.92 and 67.37%; acetic acid, 23.52, 23.78 and 23.52%; and water (by difference), 7.57, 7.30 and 9.11%.

(1) Part of the thesis submitted by William C. Cagle in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Davidson, THIS JOURNAL, 50, 1892 (1928).

(3) (a) Gmelin-Kraut, "Handbuch der anorganischen Chemie," Heidelberg, 1911, Vol. IV, Part I, p. 151; (b) Schroeder, Ber., 14, 1610 (1881); (c) Guareschi, Chem. Abstr., 10, 565 (1916).

(4) Orton and Bradfield, J. Chem. Soc., 125, 960 (1924); 983 (1927).

(5) (a) Tarbutton and Vosburgh, THIS JOURNAL, 54, 4539 (1932); (b) Cagle, Tarbutton and Vosburgh, ibid., 56, 2331 (1934).

(6) Hill and Ricci, ibid., 53, 4306 (1931).

It would be expected that exposure to the air would tend to make the acetic acid content low and the water content high, the dihydrate being stable in air under ordinary conditions.

The third portion of the curve represents solutions in equilibrium with a compound that seems to be an acetic acid solvate. Conditions for extrapolation to the composition of the dry solid were so unfavorable that it was attempted in only one case, and no conclusion can be drawn. However, the solid phase was separated from two of the solutions in a Gooch crucible and kept in a desiccator over anhydrous cadmium acetate until the weight was constant. The material so prepared appeared dry. Analysis gave an average of 90.33% cadmium acetate in one, and 89.47% cadmium acetate and 9.40% acetic acid in the other. A third sample which was separated from the mother liquor in a centrifuge and analyzed without drying gave 10.83% acetic acid. This is doubtless an upper limit. The calculated value for $2Cd(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ is 11.55% acetic acid and for $3Cd(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ is 7.99%.

The third portion of the curve approaches the acetic acid apex rapidly as the percentage of water approaches zero. Attempts to prepare a mixture containing no water were not successful, probably because the cadmium acetate was either incompletely dehydrated or slightly hydrolyzed during the dehydration. However, there can be little doubt that the solubility of cadmium acetate in pure acetic acid is very small.[7]

Summary

The solubility of cadmium acetate in mixtures of acetic acid and water has been determined.

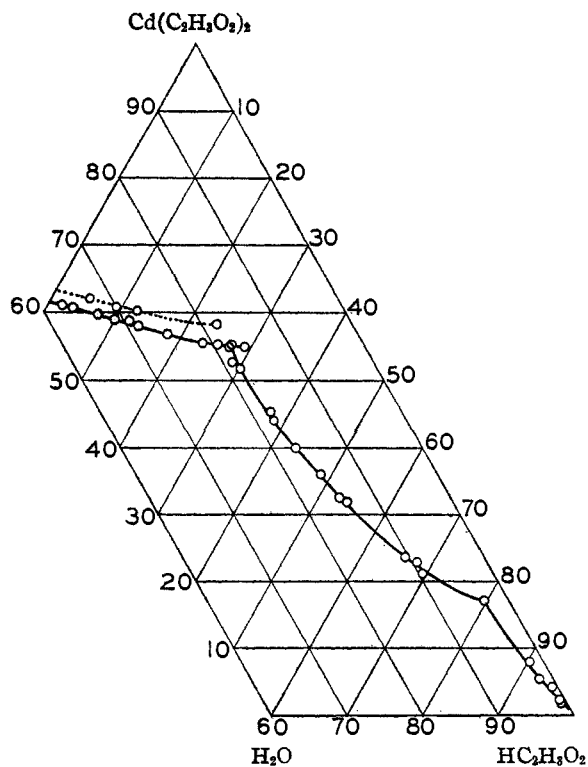(7) See Davidson, *Chem. Reviews*, **8**, 180 (1931).

Fig. 1.—Solubility of cadmium acetate in mixtures of acetic acid and water at 25° (full line) and 30° (dotted line). The compositions are given in weight percentage.

Cadmium acetate dihydrate can exist in stable equilibrium with saturated solutions in which the ratio of acetic acid to water by weight is less than 1.57. When the ratio is between 1.57 and 22.6, the solid phase is the compound $3Cd(C_2H_3O_2)_2 \cdot 4HC_2H_3O_2 \cdot 4H_2O$. For still larger ratios the solid phase is a compound of cadmium acetate and acetic acid the formula for which was not determined.