

This is shown by the relative flattening of the curve as the melting point of the hydrate is approached from higher and lower concentrations, indicating that considerable change in the water content of the hydrate is necessary to change the melting point to any great extent. Since the addition of an impurity (in this case one of the decomposition products) tends to cause lowering of the melting point of a given compound, and since the lowering is greater with greater compound stability, the relative instability of this hydrate is indicated. The decomposition of the other amine hydrates is evidence of their instability.

The fibrous, curd-like, metastable compound formed only in the dodecylamine system suggests the behavior of dodecylamine hydrochloride in water.⁵ In the latter system, also, a similar fibrous, curd-like, metastable compound was found on rapid cooling of systems containing large amounts of water. This behavior is not observed in the case of the octadecylamine hydrochloride-water system, and likewise it is absent in the present case of octadecylamine-water.

In each of the three diagrams presented the dotted lines at the left of the figures show the existence of a small region of solid solution of amine and amine hydrate. While these areas were indicated, their exact location was not verified by direct measurement.

With the interpretations and limitations which

(5) Ralston, Hoffman, Hoerr and Selby, *THIS JOURNAL*, **63**, 1598 (1941).

have been placed upon the mesomorphic states, and since equilibrium conditions have been evidenced by the agreement of the transition temperatures obtained by several different experimental methods, the applicability of the phase rule to these colloidal systems has been demonstrated. The equilibria between the amines and their respective hydrates are similar to phase diagrams for ordinary crystalloidal compounds. In the case of the higher amine hydrates, their insolubility and their mesomorphic changes account for the numerous isothermals which are present in their diagrams.

The authors are indebted to Drs. J. A. Wilkinson and H. A. Wilhelm of Iowa State College for their assistance and helpful suggestions during the course of this investigation.

Summary

1. The systems octylamine-water, dodecylamine-water and octadecylamine-water have been investigated.

2. The phase rule has been applied to these systems.

3. The following hydrates have been found: $(C_8H_{17}NH_2)_2 \cdot 3H_2O$ (dec. -5.0°); $C_8H_{17}NH_2 \cdot 6H_2O$ (m. p. 35.6°); $(C_{12}H_{25}NH_2)_3 \cdot 2H_2O$ (dec. 24.4°); $C_{12}H_{25}NH_2 \cdot 2H_2O$ (m. p. 36.5°); $C_{12}H_{25}NH_2 \cdot 4H_2O$ (dec. 48.0°); $(C_{18}H_{37}NH_2)_3 \cdot H_2O$ (dec. 50.5°); and $C_{18}H_{37}NH_2 \cdot 2H_2O$ (dec. 64.0°).

CHICAGO, ILLINOIS

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

Plumbic Acetate-Anhydrous Acetic Acid Solutions

BY ARTHUR W. DAVIDSON, W. CLARENCE LANNING AND SR. M. MAXINE ZELLER

It is well known that whenever a comparison is made between two hydroxides of the same metal, the one in which the metal is in the lower state of oxidation is the more basic and the more soluble in water. A partial qualitative explanation of this fact may be based upon the distribution of electrons about the metal atom.¹ Evidence of an analogous relationship in non-aqueous systems has hitherto been limited to observations on the solubilities of sulfates in sulfuric acid.²

(1) See, for example, O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 428-9.

(2) Kendall and Davidson, *THIS JOURNAL*, **43**, 979 (1921).

The fact that plumbic acetate (lead tetraacetate), unlike most plumbic salts, is stable at ordinary temperatures and may, in fact, be prepared rather readily, affords an opportunity for a comparison of the solubilities of the two acetates of lead in anhydrous acetic acid, solutions of plumbous acetate in this medium having already been studied.³ Hutchinson and Pollard,⁴ who were the first to make an extensive study of the properties of plumbic acetate, reported that it is

(3) (a) Davidson and McAllister, *ibid.*, **52**, 507 (1930); (b) Davidson and Chappell, *ibid.*, **55**, 4524 (1933).

(4) Hutchinson and Pollard, (a) *J. Chem. Soc.*, **63**, 1136 (1893); (b) *ibid.*, **69**, 212 (1896).

not acted upon at ordinary temperatures by concentrated sulfuric acid, and it was confirmed in this Laboratory that plumbic acetate in acetic acid solution, unlike the plumbous salt, does not take part in rapid metathetic reactions (except with water); the compound behaves in this respect like a non-electrolyte. It seemed of interest, therefore, to compare the electrical conductivities of the two solutions.^{5,6} Another property of the acetates which might be expected to vary greatly with the valence state of the lead is the tendency to form addition compounds with alkali acetates. Griswold and Olson⁷ found the solubility of plumbous acetate in acetic acid to be increased in the presence of sodium acetate, although they were unable to obtain an addition compound of the two acetates in the solid state; Lehrman and Leifer,⁸ however, showed the existence of potassium acetatoplumbites analogous to the hydroxoplumbites of the aqueous system.

In the present work, the solubility of plumbic acetate in acetic acid over a range of temperatures has been determined, the conductances at 30° of both plumbous and plumbic acetates have been measured, and the effect of sodium acetate upon the solubility of the plumbic compound has been studied. The results, in every case, were in accord with the hypothesis that plumbic acetate is an extremely weak electrolyte in this solvent.

Method

Preparation of Materials.—Anhydrous acetic acid, and sodium and plumbous acetates, were prepared as described in previous papers from this Laboratory. Plumbic acetate was prepared by crystallization from a solution made by adding red lead to hot glacial acetic acid, as described by Hutchinson and Pollard^{4b}; their method was slightly modified, however, in that the product was recrystallized from anhydrous acetic acid and was dried over phosphorus pentoxide in a current of dry air. The product was analyzed by treatment with water to give lead dioxide and acetic acid; the precipitate was filtered off and weighed, while the filtrate was titrated with sodium hydroxide solution. A typical analysis gave: PbO₂, 54.00%; (CH₃CO)₂O, 46.07% (calculated for Pb(C₂H₃O₂)₄: PbO₂, 53.95; (CH₃CO)₂O, 46.05%).⁹

(5) Conductance data for solutions of plumbous acetate in 99.4% acetic acid are given by Schall and Meltzer, *Z. Elektrochem.*, **28**, 474 (1922). Molar conductances observed by them for this medium, however, are very much higher than for the anhydrous acid.

(6) A determination of the conductance of plumbous acetate in pure acetic acid at a single concentration is reported by Kolthoff and Willman, *THIS JOURNAL*, **56**, 1014 (1934).

(7) Griswold and Olson, *ibid.*, **59**, 1894 (1937).

(8) Lehrman and Leifer, *ibid.*, **60**, 142 (1938).

(9) Since the completion of the experimental work here described, an improved method of preparation of lead tetraacetate, similar to the above, has been described by Bailar, in "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 47.

Solubility of Plumbic Acetate in Acetic Acid.—The solubility at various temperatures was determined both by synthetic and by analytic methods. In the former method, equilibrium temperatures were determined for samples of known composition as described in previous papers. The chief source of error in these determinations lay in the difficulty of preventing hydrolysis of the plumbic acetate by atmospheric moisture. Because of the extraordinary sensitiveness of the dry salt to hydrolysis, samples which had been moistened with acetic acid and subsequently analyzed were used in many of the determinations. It may be of interest to mention that the atmospheric humidity was an important factor in determining whether or not the dry salt could be handled successfully. When the humidity was high, even the briefest exposure to the atmosphere brought about appreciable discoloration, whereas at low humidity several samples could be removed successively from the same weighing bottle without discoloration of the residue. At several temperatures, also, mixtures containing an excess of solid salt were allowed to come to equilibrium, from both higher and lower temperatures, in a constant temperature bath. Samples of the liquid phase were drawn off, weighed, and analyzed for plumbic acetate content. Points obtained by both methods fall upon the same smooth curve.

Conductance Measurements.—These were all made at 30°, by means of a Leeds and Northrup bridge, an audio oscillator as a source of alternating current, and a type A Washburn cell; the conventional method was suitably modified for the measurement of low conductances. The specific conductivity of the acetic acid used was 3.8×10^{-8} reciprocal ohm, which is within the range of variation of the values given in the literature.

Solutions were made up by weight in stoppered 50-ml. flasks; each such solution was diluted several times with known weights of acetic acid, and the conductance measured after each dilution. In the case of plumbic acetate, the conductivity of the solutions differed so little from that of pure solvent that only specific conductivities have been reported. For plumbous acetate, which was found to approximate a weak binary electrolyte in behavior, the molar conductances were calculated.¹⁰ Since the conductance of the solvent would probably be greatly decreased in acetate solutions, because of the common ion effect,¹¹ no solvent correction was applied.

Solubility of Plumbic Acetate in Sodium Acetate Solutions.—The method used for these determinations was the same as that described in a previous paper¹² for a similar study on zinc acetate. Acetic acid solutions were prepared containing six different concentrations of sodium acetate, and the solubility of plumbic acetate in each of these solutions, over a limited range of temperature (22 to 46°), was determined just as in the binary solutions. From these solubility curves data were obtained, by interpolation, to show the isothermal variation of solubility of plumbic acetate with sodium acetate concentration.

(10) In this calculation, the molar concentration was taken as the molality multiplied by 1.039, the density of acetic acid at 30°. Since the highest concentration used was less than 0.1 molar, no significant error was introduced by this simplification.

(11) Kolthoff and Willman, *THIS JOURNAL*, **56**, 1007 (1934).

(12) Davidson and McAllister, *ibid.*, **52**, 519 (1930).

Results

1. **Solubility of Plumbic Acetate in Acetic Acid.**—In the following table, S denotes the mole percentage of plumbic acetate, and T the corresponding equilibrium temperature. The synthetic method was used except as otherwise noted. The data are presented graphically in Fig. 1.

| S | T | S | T |
|---|-------|---|------|
| Solid phase $\text{HC}_2\text{H}_3\text{O}_2$ | | Solid phase | |
| 0 | 16.60 | $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ | |
| 0.088 | 16.52 | (cont.) | |
| .193 | 16.45 | 0.638 ^a | 37.0 |
| .280 | 16.40 | .798 ^a | 45.0 |
| | | 1.03 | 53.0 |
| Solid phase | | 1.29 | 59.8 |
| $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ | | 1.64 | 68.4 |
| 0.354 | 18.2 | 1.96 | 74.6 |
| .427 | 25.2 | 2.55 | 82.3 |
| .512 ^a | 29.9 | 3.31 | 90.7 |
| .582 | 33.5 | 3.74 | 94.4 |

^a These data were obtained by the analysis of solutions saturated at the given temperature.

Since analysis by the method already described had already shown that crystallization from acetic acid at ordinary temperatures yielded pure unsolvated plumbic acetate, and since there was no indication of a break in the curve except at the eutectic point, no further analysis of solid phases was necessary.

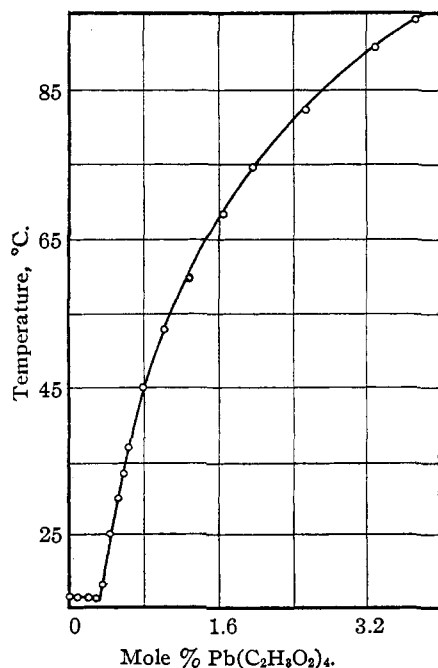


Fig. 1.—Solubility of plumbic acetate in acetic acid.

The solubility of plumbic acetate in anhydrous acetic acid at 25° is found by interpolation to be 0.43 mole %, or 0.072 molal; this is in marked contrast to the solubility of the plumbous salt (hemisolvate) at the same temperature, 16.75 mole %, or 3.35 molal. By a very short extrapolation, the solubility of the plumbic compound at 17° is found to be 0.34 mole %, or 0.057 molal; the latter figure may be compared with Hutchinson and Pollard's^{4b} value of 0.062 molal, which, however, applies to the solubility in "glacial" (not anhydrous) acetic acid.

2. **Conductance Data.**—Specific conductivities, κ , of solutions of plumbic acetate of molality m are shown in Table II, and of plumbous acetate in Table III. Here c is the concentration in moles of solute per liter of solution, Δ the molar conductance. The data for plumbous acetate are shown in a $\log c$ - $\log \Delta$ plot in Fig. 2.

TABLE II
CONDUCTANCE OF PLUMBIC ACETATE SOLUTIONS AT 30°

| m | $\kappa \times 10^8$ |
|---------|----------------------|
| 0 | 3.80 |
| 0.00593 | 3.80 |
| .0186 | 4.05 |
| .0262 | 4.82 |
| .0616 | 5.56 |

TABLE III
CONDUCTANCE OF PLUMBOUS ACETATE SOLUTIONS AT 30°

| c | $\kappa \times 10^7$ | Δ |
|---------|----------------------|----------|
| 0.00195 | 0.556 | 0.0286 |
| .00626 | .880 | .0141 |
| .00705 | .937 | .0133 |
| .0181 | 1.76 | .00973 |
| .0284 | 2.62 | .00921 |
| .0432 | 3.83 | .00887 |
| .0822 | 8.03 | .00977 |
| .0866 | 8.80 | .0102 |

It is evident from the data of Table II that the specific conductivities of plumbic acetate solutions differ so little from that of the pure solvent that any attempt to calculate molar conductances

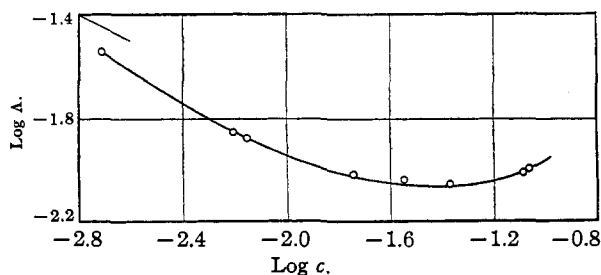


Fig. 2.—Molar conductance of solutions of plumbous acetate in acetic acid.

would have been meaningless. In Table III, the value of Λ is found to go through a minimum (at about 0.04 molar), as is usual in this solvent¹³ and in others of low dielectric constant. The molar conductance of a 0.02 molar solution obtained from these data by interpolation is 0.00942; Kolthoff and Willman¹¹ found the value of 0.00855 for a similar solution at 25°.

3. Solubility of Plumbic Acetate in Sodium Acetate Solutions.—In Table IV, the mole fraction of sodium acetate in the binary solvent is represented by R , while S denotes the mole percentage of plumbic acetate in the ternary solution in equilibrium with solid plumbic acetate at the temperature T .

TABLE IV
SOLUBILITY OF PLUMBIC ACETATE IN SODIUM ACETATE SOLUTIONS

| S | T | S | T | S | T |
|-------------|------|-------------|------|--------------|------|
| $R = 0.003$ | | $R = 0.007$ | | $R = 0.015$ | |
| 0.390 | 24.1 | 0.404 | 25.2 | 0.394 | 25.7 |
| .417 | 26.2 | .425 | 27.3 | .445 | 28.3 |
| .460 | 28.3 | .523 | 34.5 | .457 | 30.2 |
| .501 | 31.7 | .589 | 38.3 | .489 | 31.6 |
| .525 | 32.8 | .654 | 40.8 | .524 | 34.7 |
| .560 | 34.7 | .688 | 42.6 | .586 | 38.1 |
| .638 | 38.8 | .772 | 46.0 | .607 | 39.3 |
| $R = 0.025$ | | $R = 0.050$ | | $R = 0.07^a$ | |
| 0.321 | 22.5 | 0.266 | 23.1 | 0.339 | 32.1 |
| .446 | 32.7 | .294 | 26.3 | .368 | 34.3 |
| .507 | 36.2 | .356 | 31.9 | .379 | 36.3 |
| .597 | 41.3 | .451 | 37.8 | .429 | 40.5 |
| .634 | 43.2 | .471 | 39.0 | .461 | 42.8 |

^a This mole fraction is barely below the solubility of sodium acetate (7.06%) in acetic acid at 25°. Hence, in the ternary solutions, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$ appeared as solid phase at temperatures in the neighborhood of 25°.

Samples of the solid phase from several different solutions were filtered off, dried between porous tiles, and analyzed. The percentages of lead dioxide were found to vary only between 53.6 and 53.9%; hence the solid phase was undoubtedly unsolvated plumbic acetate.

The data of Table IV were plotted in a series of curves, not reproduced here, none of which showed any discontinuity of slope. From these curves were obtained, by interpolation, the isothermal data shown in Table V, where R and S have the same significance as in Table IV.

Thus, contrary to the statement of Schall and Meltzer,⁵ the solubility of plumbic acetate is not increased by the presence of sodium acetate, but

(13) Weidner, Hutchison and Chandler, *THIS JOURNAL*, **60**, 2877 (1938).

TABLE V

SOLUBILITY OF PLUMBIC ACETATE IN SODIUM ACETATE-ACETIC ACID SOLUTIONS AT 30°

| R | S |
|-------|------|
| 0 | 0.51 |
| 0.003 | .48 |
| .007 | .46 |
| .015 | .45 |
| .025 | .41 |
| .050 | .33 |
| .070 | .31 |

decreases markedly with increasing concentration of the sodium salt.

Discussion

A comparison of the behavior of plumbous and plumbic acetates in acetic acid brings out the following differences.

1. The plumbic compound forms no solvate, and its solubility is little more than one-fortieth as great as that of the plumbous salt. This variation corresponds to the difference between plumbous and plumbic oxides in water; the solubility of the former, at 25°, is about 0.0002 mole per 1000 g. of water,¹⁴ while that of the latter is so small (less than 1×10^{-6} mole per 1000 g.)¹⁵ that it has never been accurately determined.

2. As was pointed out by Kolthoff and Willman,⁶ plumbous acetate is a much poorer conductor in acetic acid than are the acetates of the alkali metals; the lead salt must be regarded as being but very slightly dissociated. The course of the $\log \Lambda - \log c$ curve, with its slope of $-1/2$ at the lowest concentrations measured (as indicated by the straight line in Fig. 2), is characteristic of the behavior of electrolytes in solutions of low dielectric constant,^{13,16} while the minimum molar conductance at a concentration of 0.04 molar, and the increase in Λ with increasing concentration beyond this point, may be attributed to the formation of triple ions.¹⁷ In the case of plumbic acetate, however, the increase in specific conductance brought about by its addition to acetic acid is so small that this solute appears to be altogether non-ionic in character.

3. Although no compound of sodium and plumbous acetates has as yet been isolated from acetic acid solutions, it has been shown⁷ that the solubility of plumbous acetate increases with in-

(14) Garrett, Vellenga and Fontana, *ibid.*, **61**, 367 (1939).

(15) Topleman, *J. prakt. Chem.*, **229**, 320 (1929).

(16) Kraus and Fuoss, *THIS JOURNAL*, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 476 (1933).

(17) Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

creasing concentration of sodium acetate. In the case of plumbic acetate, the solubility is *decreased* by the addition of the sodium salt. There is no evidence for the existence of compounds corresponding to the plumbates of the aqueous system. The absence of amphoteric properties of plumbic acetate would, by itself, be difficult to reconcile with the generally analogous behavior of corresponding compounds of the water and the acetic acid systems. In view of the other facts here presented, however, the decrease in solubility of plumbic acetate in the presence of sodium acetate appears merely as an instance of the "salting out" of a non-electrolyte.

Summary

1. The solubility of plumbic acetate in acetic acid over a wide range of temperature was determined. No solvate was isolated.

2. The conductivities of solutions of plumbous and plumbic acetates in acetic acid at 30°, over a range of concentrations, were measured. The former was found to behave as a typical weak base, the latter as a non-electrolyte.

3. The solubility of plumbic acetate was found to decrease with increasing concentration of sodium acetate. There was no evidence of amphoteric behavior.

LAWRENCE, KANSAS

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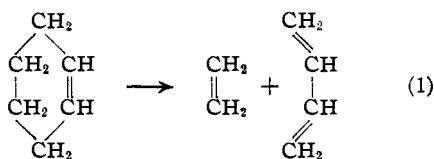
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY]

The Decomposition of Cyclohexene Oxide and 1,4-Cyclohexadiene from the Standpoint of the Principle of Least Motion¹

BY FRANCIS OWEN RICE AND ADRIAN L. STALLBAUMER

(I) **Cyclohexene Oxide.**—In this paper we propose to discuss the homogeneous thermal decomposition of organic compounds in the gaseous state, more particularly with reference to two compounds which we have investigated experimentally. The principle of least motion which we use to interpret our results has been discussed in a recent paper.^{2a}

Before taking up in detail the decomposition of cyclohexene oxide, we should like to point out that under certain conditions^{2b} cyclohexene decomposes according to the following equation, in which ethylene and butadiene are the sole products



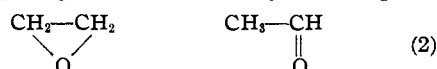
This decomposition illustrates the value of the principle of least motion because this reaction obviously requires less motion of the constituent atoms and involves less disturbance of the electronic system than any other thermodynamically possible reaction that can be written.

(1) This is taken from the dissertation presented by Adrian L. Stallbaumer for the Degree of Doctor of Philosophy in the Catholic University.

(2a) Rice and Teller, *J. Chem. Physics*, **6**, 489 (1938); **7**, 199 (1939).

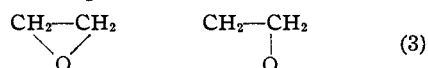
(2b) Rice, Ruoff and Rodowskas, *THIS JOURNAL*, **60**, 955 (1938).

A second reaction that we wish to discuss in this connection is the decomposition of ethylene oxide.³ The decomposition is obviously complicated yielding methane and carbon monoxide as the final products presumably produced from the decomposition of acetaldehyde which appears as an intermediate product. We exclude a direct migration of a hydrogen atom according to the equation



both from the principle of least motion (attack of a hydrogen atom on a shielded carbon atom) and also on the experimental basis that ethylene oxide produces free radicals (Paneth effect) under conditions⁴ where acetaldehyde is stable. Accordingly we are forced to assume that the change of ethylene oxide into acetaldehyde is not a single step reaction merely involving the migration of a hydrogen atom.

The first step of the decomposition of ethylene oxide may occur in two ways. The first way represented by the equation



seems unlikely because migration of a hydrogen atom to the exposed end carbon atom could read-

(3) Heckert and Mack, *ibid.*, **51**, 2706 (1929).

(4) Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 160.