with water whose viscosity was taken as 0.01005 poise. The measurements were checked repeatedly and the data given in the table represent the average of several observations.

TABLE I
At 20°

| Morpholine, % | Index of refraction | Viscosity in poises | Specific gravity | Surface tension, dynes/cm. |
|---|---|---|---|---|
| 8.558 | 1.3447 | 0.01327 | 1.0057 | 67.80 |
| 9.740 | 1.3460 | ..... | 1.0069 | 65.45 |
| 10.690 | 1.3472 | ..... | .... | ... |
| 19.394 | 1.3598 | .01963 | 1.0137 | 62.62 |
| 19.966 | 1.3608 | ..... | .... | 60.80 |
| 29.659 | 1.3750 | ..... | .... | ... |
| 30.405 | 1.3763 | .03082 | 1.0236 | 59.15 |
| 37.004 | 1.3863 | .04064 | 1.0305 | 58.00 |
| 50.449 | 1.4066 | .07227 | 1.0383 | 52.85 |
| 59.927 | 1.4201 | .10223 | 1.0432 | 49.65 |
| 65.479 | .... | .11613 | .... | ... |
| 67.646 | .... | .11865 | .... | ... |
| 69.925 | 1.4322 | .12168 | 1.0425 | 47.05 |
| 72.040 | .... | .12128 | .... | ... |
| 72.633 | .... | .12093 | .... | ... |
| 80.136 | 1.4428 | .10433 | 1.0357 | 43.62 |
| 91 | 1.4502 | .05954 | .... | 41.60 |
| 100.000 | 1.4540[a] | .02282 | 1.0007[a] | 38.72 |

[a] From "Beilstein," 4th ed., Vol. XXVII, p. 5.

We also confirmed Knorr's[4] observation of the evolution of heat when morpholine is mixed with water, finding the maximum effect to occur at about 70% morpholine, which corresponds approximately to the maximum viscosity. In the hope of finding whether a compound was formed in these solutions we attempted to measure their freezing points, but found this to be impossible except in the more dilute ones because of the slowness of adjustment of the freezing point equilibrium in solutions of such high viscosity. Seventy per cent. morpholine solution corresponds exactly to the composition of the possible dihydrate, *i. e.*, $C_4H_9ON \cdot 2H_2O$.

## Summary

The specific gravities, indices of refraction, viscosities, and surface tensions of morpholine–water mixtures have been determined at 20°

(4) Knorr, *Ann.*, **301**, 3 (1898).

ATLANTA, GA. RECEIVED APRIL 20, 1940

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

# The Solubility of Lead Iodate in Ammonium Acetate Solution

BY SYLVAN M. EDMONDS AND NATHAN BIRNBAUM

The fact that lead sulfate dissolves in ammonium acetate, of classic application in analytical chemistry, has been attributed to the formation of undissociated lead acetate[1] or of an acetoplumbite complex ion.[2] Sanved[3] in reviewing the more general investigations of the increased solubility of lead acetate and other lead salts in alkali acetate solution came to the conclusion that the ion formed is probably $PbC_2H_3O_2^+$, a result of the primary dissociation of lead acetate. Unfortunately, the experimental data have all been obtained for high and varying salt concentration, that is, under conditions where any application of the mass action law in terms of ionic concentrations would, at the very most, be qualitative in nature. In this investigation, the solubility of lead iodate has been determined at constant ionic strength, in the presence of varying acetate ion concentrations. From the data it should be possible to decide upon the reaction involved and to calculate the corresponding equilibrium constant.

## Experimental

**Materials.**—Lead iodate was prepared and aged as described by La Mer and Goldman.[4] A sample dried at 110° was analyzed for iodate by solution in excess potassium iodide and hydrochloric acid followed by titration of the liberated iodine with sodium thiosulfate solution. The latter was standardized against potassium iodate. The percentage of lead iodate thus calculated was 99.91%. The water solubility was determined after shaking at 25 ± 0.01° until constant values were obtained. Equilibrium usually required from three days to a week. The dissolved iodate was determined upon filtered aliquots by addition of potassium iodide and hydrochloric acid and titration of the liberated iodine with thiosulfate. The water solubility thus found was $3.58 \times 10^{-5}$ mole per liter (±0.3%). La Mer and Goldman reported the value $3.61 \times 10^{-5}$ mole per liter. La Mer and Goldman stated that they could not reproduce the solubility of lead iodate to 0.1%.

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(1) Noyes and Whitcomb, THIS JOURNAL, **27**, 747 (1905); Fox, *J. Chem. Soc.*, **95**, 878 (1909).

(2) White, *Am. Chem. J.*, **31**, 4 (1904); **35**, 218 (1906); Blomberg, *Chem. Weekblad*, **11**, 1030 (1914); *Z. Elektrochem.*, **21**, 438 (1915); Conrad, Diss., Göttingen, 1903; Labendzinski, Diss., Breslau, 1904.

(3) Sanved, *J. Chem. Soc.*, 2967 (1927).

(4) THIS JOURNAL, **52**, 2791 (1930).

Molar ammonium perchlorate solution was prepared from the reagent grade salt. It was standardized by addition of sodium hydroxide followed by distillation of the ammonia into standard acid and back titration with standard base.

Molar ammonium acetate solution, prepared from the reagent grade salt, was standardized by addition of phosphoric acid followed by distillation of the acetic acid into standard base and back titration with standard acid.

**Solubility Measurements.**—Solutions of unit ionic strength were prepared by proper dilution of ammonium acetate solution with ammonium perchlorate solution. The mixtures, to which a few grams of lead iodate had been added, were contained in 125-ml. glass-stoppered Pyrex flasks which were shaken at 25 ± 0.01° until constant solubility was obtained (±0.3%). Dissolved iodate was then determined upon filtered aliquots as described above.

## Results

The data are summarized in Table I.

TABLE I

| $m_{NH_4C_2H_3O_2}$ | $m_{NH_4ClO_4}$ | $m_{Pb(IO_3)_2} \times 10^4$ |
|---|---|---|
| 0.00 | 1.00 | 1.950 |
| .01 | 0.99 | 2.842 |
| .02 | .98 | 3.036 |
| .05 | .95 | 3.557 |
| .10 | .90 | 4.370 |
| .20 | .80 | 5.584 |
| .50 | .50 | 7.265 |
| 1.00 | .00 | 9.11 |

If we assume that the solution of lead iodate in ammonium acetate is the result of a single reaction, we may write the general equation

$$Pb(IO_3)_2 + nC_2H_3O_2^- \rightleftarrows Pb(C_2H_3O_2)_n^{(+2-n)} + 2IO_3^- \qquad (1)$$

The reaction will be controlled by the two equilibrium equations

$$a_{Pb^{++}} \times a^2_{IO_3^-} = K_{Pb(IO_3)_2} \qquad (2)$$

$$\frac{a_{Pb^{++}} \times a^n_{C_2H_3O_2^-}}{a_{Pb(C_2H_3O_2)_n^{(+2-n)}}} = K \qquad (3)$$

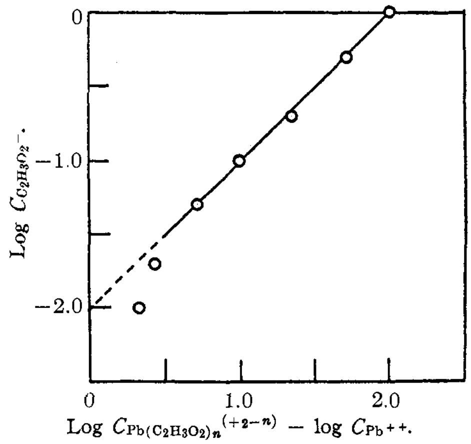

Fig. 1.—Solubility of lead iodate in ammonium acetate solution.

At constant ionic strength, the activity coefficients will all be assumed to remain constant as the concentration of acetate ion is varied. Upon this assumption, we may replace all activities in equations (2) and (3) by the corresponding molar concentrations. From the solubility of lead iodate at zero acetate ion concentration, although at the fixed ionic strength, the solubility product $K_{Pb(IO_3)_2}$ is calculated. The solubility of lead iodate in a solution of given acetate ion concentration supplies the term $C_{Pb^{++}}$, since from the solubility product relation

$$C_{Pb^{++}} = \frac{K_{Pb(IO_3)_2}}{C^2_{IO_3^-}} = \frac{4m^3_0}{4m^2} = \frac{m^3_0}{m^2}$$

where $m_0$ is the solubility at zero acetate ion concentration and $m$ the solubility at the given acetate ion concentration. The concentration of the lead acetate complex may then be calculated, *viz.*

$$C_{Pb(C_2H_3O_2)_n^{(+2-n)}} = m - C_{Pb^{++}}$$

The solubility data may be interpreted graphically by plotting log $C_{C_2H_3O_2^-}$ against log $C_{Pb(C_2H_3O_2)_n^{(+2-n)}}$ − log $C_{Pb^{++}}$, for from equation (3) we have

$$n \log C_{C_2H_3O_2^-} = \log C_{Pb(C_2H_3O_2)_n^{(+2-n)}} - \log C_{Pb^{++}} + \log K_c$$

The graph should then be a straight line of slope $1/n$ and intercept $(1/n) \log K_c$. The terms in equation (3) are tabulated in Table II and the proper logarithms plotted in Fig. 1.

Except for the two points corresponding to the most dilute acetate mixtures, all fit a straight line of slope equal to 1 and intercept equal to −2 ($K_c = 0.01$). Since the method is essentially a differential one (the term $C_{Pb(C_2H_3O_2)_n^{(+2-n)}} = m - C_{Pb^{++}}$ approaches zero as the acetate ion concentration is lowered), we might expect large deviations for the lowest acetate ion concentrations.

The fact that the slope, $1/n$, is 1 indicates that the lead acetate complex is the ion $PbC_2H_3O_2^+$ in accord with the reaction

$$Pb(IO_3)_2 + C_2H_3O_2^- \rightleftarrows PbC_2H_3O_2^+ + 2IO_3^-$$

Taking the value for $n$ of 1, $K_c$ may be calculated for each concentration of acetate. The results are given in Table II.

TABLE II

| $m_{NH_4C_2H_3O_2}$ | $C_{Pb^{++}} \times 10^4$ | $C_{PbC_2H_3O_2^+} \times 10^4$ | $K_c \times 10^3$ |
|---|---|---|---|
| 0.01 | 0.918 | 1.92 | 4.77 |
| .02 | .804 | 2.23 | 7.20 |
| .05 | .586 | 2.97 | 9.86 |
| .10 | .388 | 3.98 | 9.75 |
| .20 | .238 | 5.35 | 8.89 |
| .50 | .141 | 7.12 | 9.85 |
| 1.0 | .0894 | 9.02 | 9.92 |

The values of $K_c$ are as constant as one might expect considering the assumption of constancy of all activity coefficients in going from molar ammonium perchlorate to molar ammonium acetate. In addition, the calculation does not take into account the possible formation of undissociated lead acetate of higher complexes. It certainly seems, nevertheless, that the chief reaction involved in the increased solubility of an insoluble lead salt in acetate solution is the formation of the $PbC_2H_3O_2^+$ ion.

## Summary

1. Solubilities have been measured for lead iodate in mixtures of ammonium acetate and ammonium perchlorate of unit ionic strength.

2. The results are in agreement with the conclusion that the reaction involves the formation of the ion $PbC_2H_3O_2^+$.

NEW YORK, N. Y. RECEIVED JULY 13, 1940

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# The Fluorination of Thiophosphoryl Trichloride: The Thiophosphoryl Chlorofluorides[1]

BY HAROLD SIMMONS BOOTH AND MARY CATHERINE CASSIDY

Booth and Swinehart[1a] have shown that antimony trifluoride in the presence of a catalyst such as antimony pentachloride[2] causes the stepwise fluorination of various non-polar halides. It has been shown by Booth and Herrmann[3] that sulfuryl chloride, and by Booth and Mericola[4] that thionyl chloride, can be fluorinated by this reaction without reaction of the sulfur with the antimony fluoride. However, sulfur monochloride failed to be fluorinated by this reaction but instead the sulfur reacted with the antimony fluoride to give a mixture of reaction products.[5] This reaction has been applied by Booth and Dutton[6] to phosphoryl trichloride to yield three fluorination products.

In the light of these investigations it seemed of interest to determine whether thiophosphoryl chloride would react with antimony trifluoride in the presence of antimony pentachloride, in a manner similar to phosphoryl chloride or to sulfur monochloride.

In the former case three products would result; thiophosphoryl dichloromonofluoride, thiophosphoryl monochlorodifluoride and thiophosphoryl trifluoride. The last named was prepared by T. Thorpe and J. Rodgers[7,8] by four different methods: (1) by heating a mixture of phosphorus sulfide and lead fluoride in a current of dry nitrogen in a lead tube at not over 250°, (2) at a little higher temperature, by substituting bismuth fluoride as a fluorinating agent in place of lead fluoride in the above method, (3) by heating sulfur, phosphorus and lead fluoride, (4) by heating thiophosphoryl chloride and sulfur in a sealed tube at 150.

C. Poulenc[9] in 1891 obtained a gas of peculiar and disagreeable odor, that corresponded when analyzed to the formula $PSF_3$, by heating a mixture of phosphorus dichlorotrifluoride and sulfur at 115° and later in the same year by heating phosphorus dichlorotrifluoride with antimony trisulfide.[10]

More recently (1938) Willy Lange[11] prepared thiophosphoryl fluoride by the method recommended by Thorpe and Rodgers. Although he was chiefly interested in its hydrolysis products, he determined some other properties.

## Experimental

The fluorination of thiophosphoryl chloride was effected in a generator that has been described in detail by Booth and Bozarth.[12] When antimony pentachloride, the catalyst, was run into the thiophosphoryl chloride in the generator considerable heat was evolved and a heavy precipitate appeared which redissolved to some extent on stirring. After the temperature of the mixture in the generator had reached 75 to 80°, sublimed antimony trifluoride was slowly added.

Although all three fluorination products were formed

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[1] From a portion of a thesis submitted by Mary Catherine Cassidy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, May, 1939. [Original manuscript received November 13, 1939.]

[1a] Booth and Swinehart, THIS JOURNAL, **54**, 4751 (1932).

[2] F. Swarts, *Acad. roy. Belg.*, **24**, 309, 474 (1892).

[3] Booth and Herrmann, THIS JOURNAL, **58**, 62 (1936).

[4] Booth and Mericola, *ibid.*, **62**, 640 (1940).

[5] Unpublished investigation from this Laboratory by Charles Seabright.

[6] Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939).

[7] T. Thorpe and J. Rodgers, *J. Chem. Soc.*, **53**, 766 (1888).

[8] T. Thorpe and J. Rodgers, *ibid.*, **55**, 306 (1889).

[9] C. Poulenc, *Compt. rend.*, **113**, 75 (1891).

[10] C. Poulenc, *Ann. chim. phys.*, [6] **24**, 548 (1891).

[11] Willy Lange, *Ber.*, **71**, 801 (1938).

[12] Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939).