[Contribution from the Chemical Laboratory, University of Maine]

THE TERNARY SYSTEM: SILVER PERCHLORATE, PYRIDINE AND WATER

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Received February 17, 1925 Published April 4, 1925

In a previous paper with a senior author[1] a ternary system was studied which consisted of silver perchlorate, aniline and water. It was shown that silver perchlorate forms a series of compounds with aniline and that these double compounds are extremely insoluble in water. From a phase-rule study of the system it was then found that under certain conditions aniline can be quantitatively removed from solution by addition of the silver salt; and that the silver salt can be precipitated quantitatively from solution by addition of aniline. The silver perchlorate-aniline compounds at 25° are even more insoluble than silver chloride.

The investigation has been pursued further with the intention of determining whether silver perchlorate may be used in the role of universal precipitant for aromatic amines. The action of silver perchlorate on solutions of various aromatic amines has been investigated, and it has been found that the formation of insoluble double compounds is the exception rather than the rule. In most cases the amines are quite rapidly oxidized, the salt being reduced to metallic silver. However, with pyridine which, although it is not strictly an amine, is often classed as a tertiary amine, it was found that a set of compounds is formed which are similar in properties to those formed with aniline. The data for the solubility of silver perchlorate in pyridine, and for the solubility in the ternary system with water at 25° are reported in this paper.

The silver perchlorate was made from silver nitrate by precipitation of the silver as silver oxide, and solution of the oxide in perchloric acid. The silver perchlorate was obtained from solution in practically quantitative yield by evaporation in an oven at 110°, and occasional stirring. Analyses showed that the purity of the salt was well over 99.9%. The analysis for silver perchlorate content of solutions was made by titration with standard ammonium thiocyanate solution by Volhard's method.

The pyridine came from two commercial sources, and the bearing of this fact on the solubility data obtained will be commented on later. The pyridine was purified by the method of Wilcox.[2] It was digested with potassium permanganate on a steam-bath for 48 hours, decanted into a flask containing freshly ignited barium oxide (from the peroxide), and refluxed for another 48 hours. After decanting from the sludge of barium oxide it was distilled with a Wurtz still-head, using a calibrated Anschütz thermometer. After this treatment about 300 cc. could be distilled within a range of 0.15° down to the last drop. The boiling points of three samples are as follows: (1)

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[1] Hill and Macy, This Journal, **46**, 1132 (1924).

[2] Wilcox, *J. Phys. Chem.*, **14**, 583 (1910).

(Merck), 114.8° at 768 mm.; (2) 114.9° at 766 mm.; (3) pyridine (Kahlbaum), 115.1° at 768 mm. The purified pyridine was stored over potassium hydroxide.

In solutions in the ternary system in which the concentrations of pyridine were small (from 1 to 6%) this substance was determined by titration with standard sulfuric acid using congo red as indicator.[3] When the concentrations were larger than this they were measured graphically on the 25° isotherm (Fig. 2) after determination of the silver perchlorate content.

In the solubility measurements at 25°, equilibria were obtained by rotating the complexes in stoppered flasks in a thermostat. At other temperatures the usual Beckmann freezing-point apparatus was employed, the apparatus being immersed in several liters of water at the required temperature. Low temperatures were obtained with a mixture of carbon dioxide and ether.

Binary System: Silver Perchlorate, Pyridine.—The solubility of silver perchlorate in pyridine has been measured from the eutectic at —43° to a temperature of 110°. In this range the double compounds which are successively in equilibrium with saturated solutions are $AgClO_4.4C_5H_5N$, $4AgClO_4.9C_5H_5N$, and $AgClO_4.2C_5H_5N$. The data are given in Table I and Fig. 1. These data are the solubilities of the salt in Merck's pyridine. The broken curve in the figure represents the data for a sample of Kahlbaum's pyridine which was also used, and in which the average solubility is 1.5% higher. (S and Py represent silver perchlorate and pyridine, respectively.)

Table I

Silver Perchlorate and Pyridine

Solid phases	Temp. °C.	% $AgClO_4$ by wt.	% C_5H_5N by wt.	Density	Point (Fig. 1)
Py	−40.3	...	100.00	...	p
Py	−41.5	4.0	96.0	...	
Py + S.4Py	−43	7.2	92.8	...	e
S.4Py	−35	8.3	91.7	...	
S.4Py	−11.5	12.23	87.77	1.118	
S.4Py	− 1.3	14.53	85.47	1.139	
S.4Py	25.0	20.90	79.10	1.201	
S.4Py	36.1	24.52	75.48	1.221	
S.4Py	49.2	29.4	70.6	1.278	
S.4Py	60.4	34.5	65.5	...	
S.4Py	66.8	41.1	58.9	...	
S.4Py + 4S.9Py	68.0	41.7	58.3	...	a
4S.9Py	71.0	42.4	57.6	...	
4S.9Py	75	43.0	57.0	...	
4S.9Py	86.3	45.8	54.2	...	
4S.9Py + S.2Py	95.6	47.8	52.2	...	b
S.2Py	110	50.0	50.0	...	
S.2Py + S	144–147	...	...	...	

The freezing point of pyridine given in the literature by a number of investigators varies widely, as shown by the following values: Pickering,[4]

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[3] Lazier and Adkins, This Journal, **46**, 746 (1924).

[4] Pickering, *J. Chem. Soc.*, **63**, 1018 (1893).

—49.8°; Kahlenberg and Brewer,[5] —48.5°; Baud,[6] —38°; and Pearce and Moore,[7] —48.2°. The value obtained in the present work, —40.3°, is in best agreement with that of Baud. Further work on the preparation and physical constants of pure pyridine is to be carried out in this Laboratory.

The composition of the double compound, $AgClO_4.4C_5H_5N$, was determined by direct analysis of large crystals obtained by slow evaporation of a saturated solution at room temperature. The dry compound loses its pyridine very rapidly so that the crystals had to be large and well-formed in order to be wiped dry easily and quickly, and give concordant results on analysis. Nearly perfect agreement between theoretical composition and analysis was obtained when smaller crystals were prepared pure by placing them together with mother liquid in a small desiccator over anhydrous silver perchlorate. It has been shown by the phase rule[8] that such a system dries up at equilibrium to the formation of the pure pyridine compound. The calculated salt content of the compound is 39.58%; the results of two analyses are 39.53% and 39.60% of silver perchlorate.

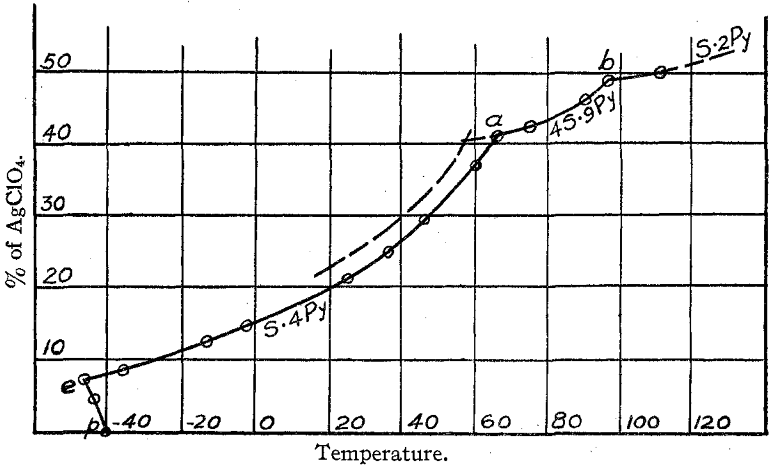

Fig. 1.—Solubility of silver perchlorate in pyridine.

A phenomenon that could not be explained in these solubility measurements is the fact that the composition of the solution at the transition temperature, 68°, is 2% higher in salt content than the solid phase which, as just mentioned, is 39.58% salt. This was thought to be due to the fact that $AgClO_4.4C_5H_5N$ melts congruently at some slightly higher temperature than 68°, but careful freezing-point measurements showed that

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[5] Kahlenberg and Brewer, *J. Phys. Chem.*, **12**, 283 (1908).

[6] Baud, *Bull. soc. chim.*, [4] **5**, 1022 (1909).

[7] Pearce and Moore, *Am. Chem. J.*, **50**, 218 (1913).

[8] Hill and Smith, THIS JOURNAL, **44**, 557 (1922).

the solubility curve rises quite sharply to the transition point and has no retroflex portion. The broken curve represents the solubility data obtained with a sample of Kahlbaum pyridine; the increased solubility is undoubtedly due to the presence of homologs of pyridine, but it is found that the curve parallels the lower one, and also shows no retroflex portion. It is possible that the compound melts congruently but that the temperature at which the phenomenon occurs is considerably altered by the presence of some impurity, such as traces of water, which it is very difficult to remove. The remarkable effect of traces of water on the boiling point of pyridine, for example, has been pointed out by Wilcox.[2]

Between 68° and 95.6° the solid phase is $4AgClO_4.9C_5H_5N$. The composition of this compound was determined indirectly by phase-rule methods from the 25° isotherm (Fig. 2), as will be explained later. At 95.6° it undergoes a transition to the compound $AgClO_4.2C_5H_5N$, the composition of which also was at first determined from the 25° isotherm. The composition was later checked by analysis of the powdery compound remaining when some $AgClO_4.4C_5H_5N$ was placed in a desiccator over concd. sulfuric acid. The latter compound slowly lost pyridine, and in the course of six months the substance gave on analysis a composition in good agreement with the theoretical value for $AgClO_4.2C_5H_5N$: calcd. 56.7% of $AgClO_4$; found, 56.1% and 56.5%. As indicated by its stability over sulfuric acid, the compound is quite stable at ordinary temperatures, and has practically no odor of free pyridine.

Table II

Solubility Curve AE at 25°

Solid phase	% $AgClO_4$ by wt.	% C_5H_5N by wt.	% H_2O by wt.	Density	Point (Fig. 2)
S.4Py	20.9	79.1	0.00	1.201	a
..	19.5	69.9	10.6	1.185	
..	17.8	65.9	16.3	1.170	
..	14.5	60.0	25.5	1.135	
..	9.8	51.0	39.2	1.093	
..	6.6	42.4	51.0	1.060	
..	1.3	20.6	78.1	1.014	
..	0.48	5.38	94.14	1.005	
S.4Py + 4S.9Py	.40	3.8	95.8	1.002	b
4S.9Py	7.0	trace	93.0	1.065	
..	10.76	..	89.24	...	
..	17.0	..	83.0	1.156	
..	17.4	..	82.6	...	
4S.9Py + S.2Py	20.0	..	80.0	1.186	c
S.2Py	20.2	..	79.8	...	
..	35.6	..	64.4	...	
..	54.6	..	45.4	...	
..	77.0	..	23.0	...	
S.2Py + S_H	84.3	..	15.7	...	d
S_H	84.5	0.00	15.5	2.806	e

Above 130° the saturated solution of silver perchlorate in pyridine undergoes a chemical reaction, with deposition of metallic silver, so that no solubility measurements were made at these temperatures. The melting point (whether congruent or incongruent is uncertain) of the compound $AgClO_4.2C_5H_5N$ was determined in the usual form of melting-point apparatus with a capillary tube. The substance clumps together at 144° and melts quite sharply at 147°. The same result was obtained with several different samples.

The Ternary System.—The solubility curve at 25° is made up of four parts, which give the solubilities of the four phases: S.4Py, 4S.9Py, S.2Py and S_H. The last of these abbreviated formulas is that of the hydrate of silver perchlorate, $AgClO_4.H_2O$. The data are contained in Table II and Fig. 2.

In the isotherm at 25° there is only one area of unsaturated solution (L), and there are four areas of invariant equilibria, marked by numbers. The solubility of silver perchlorate varies from 20% in pure pyridine down to less than 0.5% when much water is present (Curve ab). In this respect the system differs from the system containing water and aniline, in which there is a region of extreme insolubility of the salt. On the axis W-S the pyridine system is similar to the aniline system, the curves being practically coincident with the axis, indicating almost complete insolubility of pyridine. This is analogous to the insolubility of aniline in aqueous solutions of silver perchlorate. The presence of free pyridine in these solutions cannot be detected by indicators such as methyl orange or congo red. The curve de is very short and represents the solubility of the hydrate of silver perchlorate; the data for Point e have been taken from the literature.[9]

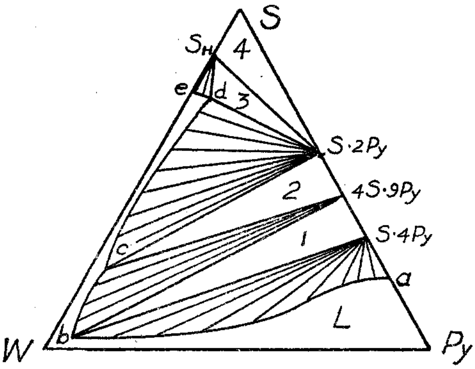

Fig. 2.—Silver perchlorate, pyridine, water at 25°.

The compositions of S.4Py and S.2Py were determined by direct analysis, as already explained. The composition of the intermediate compound, 4S.9Py, was obtained by a graphic method. If a ternary complex is made up in the saturated solution area between Areas 1 and 2, then a line joining the composition of the resulting solution on Curve bc with the composition of the complex will pass through a point representing the composition of the solid phase. Such lines in four different experiments intersected on the

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[9] Hill, This Journal, 44, 1165 (1922).

axis S-Py between 53% and 54% $AgClO_4$. It is evidently the compound, $4AgClO_4.9C_5H_5N$, which contains 53.81% of silver perchlorate.

At temperatures higher than 30° conjugate solutions appear in the ternary system, but the study of isotherms above 25° was not attempted, and these solutions were not studied.

Summary

It has been shown that the formation of water-insoluble compounds such as those of silver perchlorate with aniline is not general for silver perchlorate with other aromatic amines. Pyridine, however, is precipitated quantitatively by silver perchlorate.

The solubility of silver perchlorate in pyridine has been measured from —40.3° to a temperature of 110°. The 25° isotherm of the system, silver perchlorate, water, pyridine, has also been determined. Three compounds isolated are $AgClO_4.4C_5H_5N$, unstable, m. p. 68°; $4AgClO_4.9C_5H_5N$, unstable, m. p. 95.6°; and $AgClO_4.2C_5H_5N$, stable, m. p. 144–147°. The composition of the intermediate compound was established by a phase-rule method; of the others, by direct analysis.

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THE ENTROPIES OF THE VAPORS OF ZINC AND LEAD

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RECEIVED MARCH 23, 1925 PUBLISHED APRIL 4, 1925

In a recent publication[2] a description was given of the measurement of the vapor pressure of cadmium by a direct method. In this method the cadmium was boiled under reduced pressure in an inert atmosphere and the temperature read by a platinum-platinrhodium thermocouple. This method with some modifications has been used in the measurements of the vapor pressures of zinc and lead.

On account of the higher temperature it was impossible to use Pyrex glass either for a container for the metal or to enclose the thermocouple. The metals were boiled in a porcelain test-tube and the thermocouple was enclosed in a quartz tube. For zinc the porcelain test-tube was mounted as described in the previous article in a large Pyrex tube. The porcelain test-tube was heated electrically and the walls of the enclosing Pyrex tube were shielded from radiation by silver foil. Since the temperature of the zinc vapor is just high enough to heat the walls of the containing tube to a visible red it was possible to see the exact height to which the zinc vapor rose.

In the measurements on lead it was not feasible to provide sufficient

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[1] Research Fellow of the Chas. A. Coffin Foundation.

[2] Fogler and Rodebush, THIS JOURNAL, **45**, 2080 (1923).