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The Solubility of Nicotine Silicotungstate in Solutions of Dilute Hydrochloric Acid

BY JOSEPH R. SPIES

In determining small quantities of nicotine by the silicotungstic acid method,[1] it was necessary to know the solubility of nicotine silicotungstate in dilute hydrochloric acid. No exact quantitative data on the solubility of this substance appear in the literature. Bertrand and Javillier[2] first determined the sensitivity of silicotungstic acid as a reagent for nicotine by noting the maximum dilutions at which turbidity could be obtained when solutions of the two substances containing different concentrations of hydrochloric acid were mixed. The maximum sensitivity was obtained in 1–1000 hydrochloric acid, and it decreased with increasing acid concentration. Chapin[3] later used silicotungstic acid for the precipitation of nicotine as the basis of the widely used gravimetric method for its determination. He found that the loss due to the solubility of nicotine silicotungstate was negligible in the macro method.

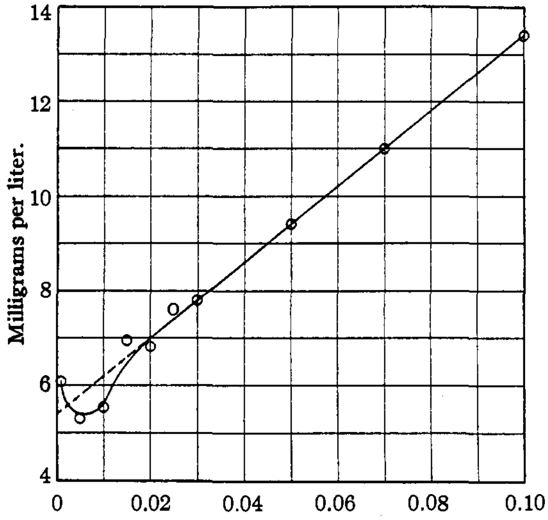

Fig. 1.—Effect of dilute hydrochloric acid on the solubility of nicotine silicotungstate.

The solubility of pure nicotine silicotungstate has been determined at 25 ± 0.02°[4] in distilled water (*p*H 6.5 as determined colorimetrically with brom thymol blue) and in 0.001 to 0.1 *N* hydrochloric acid solutions. The results are summarized in Table I and shown graphically in Fig. 1.

TABLE I

SOLUBILITY OF NICOTINE SILICOTUNGSTATE IN DILUTE SOLUTIONS OF HYDROCHLORIC ACID

Evaporations[a]	Concn. of acid, *N*	Soln. evaporated, ml.	Av. weight of residue, mg.	Av. soly.,[b] mg./liter	Av. deviation from mean ($\Sigma d/N$) mg./liter	Av. deviation from mean ($\Sigma d/N$) %
6	0.10	40	0.543	13.4	0.3	2.2
2	.070	40	.448	11.0	.0	0.0
6	.050	50	.481	9.41	.28	3.0
4	.030	50	.400	7.80	.08	1.0
2	.025	60	.466	7.59	.06	0.8
6	.020	60	.422	6.81	.36	5.3
2	.015	60	.427	6.96	.11	1.6
4	.010	60	.349	5.56	.04	0.7
2	.0050	60	.333	5.30	.00	.0
4	.0010	60	.373	6.08	.08	1.3
8	[c]	30	1.049	38.5	1.6	4.2

[a] Two evaporations were made from each saturated solution, and the average weights given in the fourth column are based on the total number of evaporations. [b] Calculated as $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2$. Factor = 1.127. The residue (column 4) was corrected for blank (dissolved glass) at the rate of 0.80 mg. per liter for water and 1.70 mg. per liter for 0.1 *N* acid. Intermediate acid concentrations were corrected proportionately. [c] Distilled water, *p*H of 6.5.

The maximum solubility, 38.5 mg. per liter, was found with water, and the minimum between 0.015 and 0.001 *N* acid. The lowest value obtained was 5.30 mg. per liter in 0.005 *N* acid. The results obtained for from 0.015 to 0.1 *N* acid fall on a straight line, the solubility increasing from 6.96 to 13.4 mg. per liter. It is probable that the break in the curve between 0.015 and 0.001 *N* acid is real and not due to experimental error, since the value obtained at 0.01 *N* is 14.5% lower than it would be if it fell on the straight line passing through the other points. The maxi-

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[1] While the results of the determinations reported in this paper express the "maximum solubility," or the solubility of pure nicotine silicotungstate in solutions of dilute hydrochloric acid, they also accurately represent the actual amount of nicotine lost in analytical determinations involving only nicotine. From analytical data presented by the author (paper accepted for publication in the *Analytical Edition* of *Industrial and Engineering Chemistry*) the excess (up to ten times) silicotungstic acid used apparently does not produce a detectable decrease in solubility of nicotine silicotungstate. The analytical results also indicate that the usual practice of permitting freshly precipitated nicotine silicotungstate to stand overnight (eighteen hours) to crystallize allows sufficient time for even unstirred solutions to attain equilibrium. The solubility values as determined in this paper, therefore, can be used in applying corrections for lost nicotine in analytical procedures where nicotine alone is present.

[2] G. Bertrand and M. Javillier, *Ann. chim. anal. Appl.*, **14**, 165 (1909).

[3] R. M. Chapin, U. S. Dept. Agr. Bur. Animal Ind., *Bull.*, **133**, 22 pp. (1911).

[4] The thermometer used, graduated in 0.1°, was checked against a National Bureau of Standards calibrated thermometer.

mum deviation from the mean found in all the other determinations is 5.3% while the average of the deviations is only 1.8%. No explanation is offered for the occurrence of this minimum solubility. It was more difficult to duplicate saturated solutions in water than when acid was present. This is shown in Table I by the greater deviation from the mean in this case.

At acid concentrations below 0.025 *N* the solid phase settled more slowly when stirring was interrupted. In a preliminary study some colloidal particles passed through the fritted-glass filter used to filter off the saturated solutions. These solutions showed a Tyndall cone when examined with a powerful light beam. At higher acid concentrations this difficulty did not occur, as settling was rapid and clear solutions readily were obtained. In the work reported in this paper a porcelain filterstick with a dense filtering surface was used, and the saturated solutions obtained even at concentrations below 0.025 *N* showed no distinct Tyndall cone.

Solutions saturated at 25° were prepared both by cooling solutions saturated at higher temperature and by stirring nicotine silicotungstate with the solvent at 25°. Where more than one saturated solution was prepared at a given acid concentration, both methods generally were used. The close agreement of the results indicates that true equilibrium was attained.

Experimental

Preparation of Nicotine Silicotungstate.—1.26 g. of nicotine[5] (n^{22}D 1.5241) was dissolved in 700 ml. of 0.086 *N* hydrochloric acid, and 14.2 g. (slight excess) of silicotungstic acid ($4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$) in 200 ml. of distilled water was added slowly with stirring. After standing twenty hours with occasional stirring, the precipitate was filtered off and washed with dilute hydrochloric acid on the filter. It was stirred up once with dilute hydrochloric acid, filtered, washed and dried by exposure to air at room temperature. The crystalline character of the precipitate was shown by the familiar scintillating effect produced when the solid was stirred with the dilute acid solution, and was verified by microscopic examination.

Anal. Calcd. for $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2 \cdot 5H_2O$: C, 7.29; H, 1.28; N, 1.70; $SiO_2 \cdot 12WO_3$, 86.32. Found: C, 7.29, 7.24; H, 1.28, 1.29; N, 1.75, 1.76;[6] $SiO_2 \cdot 12WO_3$, 86.48, 86.28.

Apparatus.—Pyrex glassware was used throughout. To minimize solution of glass each vessel was leached on the steam-bath with dilute hydrochloric acid for several hours before being used. All apparatus used for measurement of solutions was calibrated.

Preparation of Saturated Solutions.—One-tenth gram of nicotine silicotungstate was agitated with 250 ml. of distilled water on the steam-bath in a 1-liter three-necked Pyrex flask equipped with a glass mechanical stirrer. After about five minutes of warming the flask was placed in the constant-temperature bath at 25 ± 0.02° and the solution stirred until cooled to bath temperature. Sufficient constant-boiling hydrochloric acid was then added to give the desired acid concentration. The alternative procedure was to place the nicotine silicotungstate directly in the hydrochloric acid solution without warming. In either case the solutions were stirred for at least twenty hours, which experiment had shown to be ample for the attainment of equilibrium. A 9-cm. porcelain filterstick was used for withdrawal of the saturated solution so that filtration by suction could be made without removing the flask from the constant-temperature bath. The saturated solutions were stored in glass-stoppered Erlenmeyer flasks in the constant-temperature bath.

Evaporation of Saturated Solutions.—Accurately measured volumes, in 10-ml. portions, were pipetted from the flasks into 15-ml. platinum crucibles that had previously been ignited to constant weight at 650°. To protect the crucibles from dust the evaporations were carried out in an electrically heated (95–105°) glass cylinder of 50 mm. diameter to which two glass wells were sealed to hold the crucibles upright. Air was aspirated through the cylinder to remove the water vapor. To avoid contamination by dust the air was filtered through cotton and a fritted-glass plate, respectively, before it entered the evaporation chamber. With this apparatus 10 ml. of water could be evaporated from a crucible in five hours with no danger of spattering or contamination by dust.

Ignition and Weighing of Residue.—When evaporation of the solution was complete, the crucibles were ignited for fifteen minutes in an electric furnace at 646–652°. This procedure was chosen for the following reasons. It is well known that tungstic oxide is appreciably volatile at the temperature attainable with a Meker burner. Platinum also shows sufficient loss of weight to be detectable on the microchemical balance when ignited for ten minutes at this temperature. In view of these facts, and because of the small amounts of oxides of tungsten and silicon weighed, it was necessary to find a temperature at which small quantities of nicotine silicotungstate could be completely ignited without loss in weight of the residual oxides. Experiments in which weighed quantities of nicotine silicotungstate were ignited in platinum crucibles and weighed under conditions simulating those used in the solubility determinations showed 650° to be a suitable temperature.[7] The nicotine silicotungstate was weighed into the platinum crucibles, which contained residues from previous ignitions. After ignition the crucibles were cooled in air for thirty to forty minutes and then weighed. Table II gives the results of some of these experiments.

The residues were weighed on a Kuhlmann microchemi-

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(5) Purified by the method of Lowry and Lloyd, *J. Chem. Soc.*, 1381 (1929).

(6) The author is indebted to D. F. Houston for the micro Dumas determinations.

(7) C. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 538. The ignition of nicotine silicotungstate is more fully discussed in the paper referred to in footnote 1.

TABLE II

IGNITION OF NICOTINE SILICOTUNGSTATE AT 650°

Time of ignition, min.	Nicotine silicotungstate mg.	Residue, mg. Found	Residue, mg. Calcd.
15	2.737	2.366	2.363
15	3.172	2.741	2.738
45	2.107	1.818	1.819
45	2.146	1.869	1.852

cal balance the rider of which was checked against a 10-mg. weight calibrated by the National Bureau of Standards. The tares were adjusted so as to avoid the use of fractional weights. Since weighings were by difference and were sometimes made several days apart, it was necessary to use similar platinum crucibles for tares to eliminate errors due to change in pressure, temperature and humidity. The use of the usual glass lead-shot tares was found to introduce an appreciable error due to these causes. Throughout the experiments the crucibles were handled with platinum-tipped forceps.

The Distilled Water.—Stock distilled water was carefully redistilled into a leached 12-liter flask, with the use of a block-tin condenser. When about half the determinations had been made, blanks were run on the water alone and with 0.1 normal solutions of the hydrochloric acid used. The procedure and apparatus were the same as were used in the preparation of the saturated solutions. On the basis of three runs each, the values of the blanks were 0.80 ± 0.14 mg. per liter for the water and 1.70 ± 0.14 mg. per liter for the acid. The amount of the correction for dissolved glass was applied in proportion to the acid concentration of the solvent.

The author wishes to acknowledge the interest of Nathan L. Drake in this work.

Summary

The solubility of nicotine silicotungstate in water and in 0.001 to 0.1 *N* hydrochloric acid solutions has been determined. The maximum solubility, 38.5 mg. per liter, is found in water and a minimum of 5.30 mg. per liter in 0.005 *N* hydrochloric acid. The solubility increases from 6.96 mg. per liter in 0.015 *N* acid to 13.4 mg. per liter in 0.1 *N* hydrochloric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XXIII.[1] A Contribution to the Alkaline Hydrolysis of Oligosaccharides[1a]

BY HARRY GEHMAN, LEONARD C. KREIDER AND WM. LLOYD EVANS

After studying the action of aqueous potassium hydroxide on maltose (4-α-glucosidoglucose) to form lactic acid, Benoy[2] and one of us came to the conclusion that the hexose (reducing) portion of the molecule was first degraded by the alkali to form the following fragments: formaldehyde, glycolaldehyde and 2-glucosidoerythrose. Hydrolysis of the latter was then assumed to occur to produce glucose and erythrose. As it was quite certain from previous work[3] that formaldehyde, glycolaldehyde and erythrose would produce no lactic acid in alkaline solution, it was probable that when maltose was degraded by alkali the entire reducing half of the molecule was lost to lactic acid production. The hexosido-(non-reducing) portion, being released by hydrolysis as glucose, should then produce lactic acid as glucose was known to do. The fact that a solution of maltose (0.25 *M*) yielded approximately half as much lactic acid as was obtained under identical conditions from an equivalent amount of glucose (0.50 *M*) lent considerable weight to this argument.

Later in a similar study of the alkaline degradation of cellobiose (4-β-glucosidoglucose) and lactose (4-galactosidoglucose) Hockett[4] and one of us showed that these disaccharides also yielded only such amounts of lactic acid as would have been expected from their hexosido (non-reducing) portions alone.

The 6-hexosidohexoses, like gentiobiose (6-glucosido-glucose) and melibiose (6-galactosidoglucose), present a different type of behavior, for here the amount of lactic acid produced is considerably greater than that expected from the hexosido portion of the molecule alone. This was explained by pointing out that the reducing portion of these molecules contributed a part of the lactic acid. Simultaneous with the degradation

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(1) Number XXII of this Series, H. W. Arnold and W. L. Evans, THIS JOURNAL, **58**, 1950 (1936).

(1a) Presented before the Organic Section of the American Chemical Society, Pittsburgh Meeting, 1936.

(2) W. L. Evans and M. P. Benoy, *ibid.*, **52**, 294 (1930).

(3) J. U. Nef, *Ann.*, **376**, 40 (1910); J. E. Hutchman, Ph.D. Dissertation, O. S. U., 1927.

(4) W. L. Evans and R. C. Hockett, THIS JOURNAL, **53**, 4384 (1931).