Table I lists the observed vapor pressure values and their deviations from values calculated from the equation

$$\log_{10} P(\text{mm. of Hg}) = 6.9792 - 1311/(^\circ\text{C.} + 230) \quad (5)$$

The standard deviation is ± 1.2 mm. of Hg. The vapor pressure values are slightly high compared with the data of Stock (*4*), particularly at the higher temperatures. Stock's data, reported to the nearest centimeter above 60° C., extrapolated to a normal boiling point of 91.5° C., while that calculated from equation (*5*) is 89.9° C. Observed boiling points reported in the literature range from 90.0° to 91.3° C.

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RECEIVED for review June 25, 1963. Accepted August 8, 1963. This work was supported by the Navy Department, Bureau of Aeronautics under contract NOa(s) **58-454-d.**

The Solubility of *p*-Iodobenzenesulfonyl Chloride

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The solubility of p-iodobenzenesulfonyl chloride was found by measuring the weight loss on passing water through a tube filled with the solid. Errors due to hydrolysis and incomplete saturation were avoided by finding a weight loss that was independent of flow rate. At temperatures of 25°, 35°, and 50° C., solubilities were 16.3, 26.6, and 49.8 mg./liter, respectively; standard deviations were about 0.3 mg./liter.

IN ATTEMPTING to put the isotope derivative procedure for aminoacid determination (*4*) on a continuous basis, it seemed feasible to mix a stream of *p*-iodobenzenesulfonyl chloride (PIPSYL chloride) with a stream of the aminoacid sample to form the *p*-iodobenzenesulfonamides (PIPSYL derivatives of the aminoacids). To design the continuous process, knowledge of the PIPSYL chloride solubility was necessary. Although the hydrolysis of acyl halides has been studied in water (*2*) and water-solvent mixtures (*3*), no value for the solubility of PIPSYL chloride could be found in the literature.

The low solubility of PIPSYL chloride and its fairly rapid rate of hydrolysis make conventional methods of solubility determination that require a long time for saturation unsuitable (*5*). It was therefore decided to estimate the solubility from the weight loss of a tube of PIPSYL chloride after passing a known volume of water through it. This technique has been used by Bronsted and LaMer (*1*) to ensure saturation for solubility measurements. The results of such measurements are described in this paper.

Preliminary Experiments. Upon passing CO_2-free water at room temperature through a tube containing PIPSYL chloride, the effluent solution ranged in pH from 6.5 to 7.5. The solution, after standing at room temperature for 40 minutes, or upon boiling for a few minutes, had a pH of 4.2–4.5. The change was postulated to be due to hydrolysis of the PIPSYL chloride to the sulfonic acid and HCl.

The change was confirmed by absorbance measurements. Typically, the fresh effluent showed an absorption spectrum with a peak at 260 mμ, assumed due to the PIPSYL chloride. Upon standing, the 260 mμ peak decreased, and a new peak at 242 mμ made its appearance. The peak at 242 mμ was presumed to be due to the sulfonic acid. Combination of absorbance and solubility measurements (vide infra) gave molar absorptivities for PIPSYL chloride and the sulfonic acid of 1.3×10^4 (260 mμ) and 1.6×10^4 (242 mμ), respectively. However, because of the closeness

of the peaks and the rapidity with which they change due to hydrolysis, these molar absorptivities should not be regarded as accurate.

Procedure for Solubility Measurements. PIPSYL chloride (Lot No. 26071, K and K Laboratories, Jamaica, N. Y.) was sieved to give a fraction passed by a 20-mesh sieve and retained by a 40-mesh sieve. The PIPSYL chloride was packed to a depth of 8 cm. in a 10 cm. × 4 mm. I.D. tube equipped with 12/4 borosilicate ground glass joints at each end. Tubes with inside diameters of 1 and 2 mm. were also prepared. The particles were retained by a 5-mm. plug of 140-mesh Microbeads (Microbeads, Inc., Jackson, Miss.) that had been sintered at 680° C. into the tube beforehand. The tube was then connected through ⅛-inch I.D. stainless steel tubing to a reservoir of CO_2-free distilled water, which was drawn through the tube with a peristaltic pump (New Brunswick Scientific Co., New Brunswick, N. J.) to control the flow rate. The stainless steel tubing and PIPSYL tube were immersed in a thermostatically controlled water bath, to assure a known temperature for the water passing through the PIPSYL tube.

Before taking any solubility measurements, about 500 ml. of water was passed through each new batch of PIPSYL chloride, in order to remove impurities (mostly the sulfonic acid) in the reagent PIPSYL chloride. After flushing it with water, the tube was removed from the thermostat, disconnected, carefully wiped dry on the outside, and then aspirated with air for two hours to dry the remaining PIPSYL chloride. (The air was dried by placing a drying tube containing Drierite before the PIPSYL chloride tube.) The tube was then carefully weighed, replaced in the thermostat, and a measured volume of water passed through it. Flow rates were measured by noting the time required to collect the measured volume of effluent solution. After cessation of flow, the tube was quickly removed from the thermostat, air-dried by aspirating again, and weighed. Adequacy of the two-hour drying period was checked. Also, losses of PIPSYL chloride due to sublimation during drying were reproducible (0.3 to 0.4 mg. for 2 hours at room temperature); a correction was applied to the observed weight loss to obtain the correct one in each case.

Weight losses were measured at various flow rates and temperatures, and on different columns, with results as given in Table I. In the measurements, each batch of PIPSYL chloride sufficed for 10 or more solubility determinations.

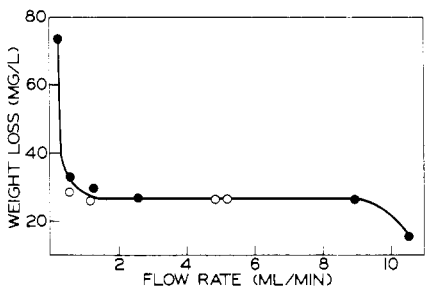

Figure 1. Dependence of weight loss upon flow rate at 35° C.
1-mm. I.D. tubes
2-mm. I.D. tubes

Table I. Weight Losses on Passing Water through PIPSYL Chloride Tubes at Various Temperatures and Flow Rates

Temp., °C.	Flow Rate, Ml./Min.	Water Passed, L.	Weight Loss, Mg. Obsd.	Weight Loss, Mg. Calcd./l.	Col. Diam., Mm.
25.0	0.31	0.525	10.7	20.4	2
25.0	0.56	0.650	12.2	18.8	2
25.3	1.37	1.350	21.9	16.2	2
25.2	2.59	0.755	12.2	16.2	2
25.0	3.20	0.640	10.6	16.6	4[a]
25.2	5.10	0.500	8.1	16.2	1
25.2	5.20	0.505	8.2	16.3	2
25.4	5.50	0.500	8.3	16.6	4[a]
25.3	6.78	0.650	9.2	14.2	1
25.3	10.5	0.630	8.2	13.0	2
35.0	0.23	0.235	17.3	73.5	2
35.0	0.52	1.360	44.6	32.8	2
35.0	0.52	1.180	33.5	28.4	1
35.0	1.25	1.125	33.4	29.7	2
35.0	1.22	1.325	34.7	26.2	1
35.0	2.56	1.085	29.5	27.0	2
35.0	4.86	0.500	13.2	26.4	1
35.0	5.20	0.625	16.5	26.4	1
35.0	8.72	0.890	23.8	26.7	2
35.0	10.5	1.020	15.9	15.6	2
50.2	5.35	0.500	25.1	50.2	4
50.2	7.15	0.500	25.0	50.0	4
50.0	9.10	0.500	24.7	49.4	4
50.0	9.60	0.500	24.9	49.8	4

[a] Solution was not pumped for this run, but flowed from a constant head at a constant rate.

RESULTS AND DISCUSSION

A plot of the weight loss against flow rate is shown in Figure 1, for data at 35° C. At low flow rates, the solution resides in the tube for so long that hydrolysis of the dissolved PIPSYL chloride is appreciable, leading to high weight losses. At high flow rates, the weight losses drop off, owing to incomplete saturation. The curve of Figure 1 appears to level out at a weight loss of 26.6 mg./liter, which may be taken to represent the true solubility. This weight loss is invariant over a sixfold range of flow rates, indicating that hydrolysis is negligible and that the solution is saturated. In the flow independent region, there are four points which are scattered from the smoothed curve with a standard deviation of 0.3 mg./liter, which may be taken to represent the standard deviation of the solubility measurement.

Data in the region where the weight loss is flow-dependent should not be given quantitative significance, for the weight loss depends upon variables that bear no relation to solubility. Thus, at flow rates of 0.5 and 1.2 ml./min., the weight loss is dependent upon the PIPSYL tube diameter. Estimates of the rate of hydrolysis should not be made from data in the region where the weight loss is flow-dependent.

The data in Table I for 25° C. give a plot that is similar in shape to Figure 1. The average solubility, calculated from the six points at flow rates ranging from 1.37 to 5.50 ml./min., is 16.3 mg./liter, with a standard deviation of 0.2 mg./liter. At 50° C., weight losses are given in Table I only for the flow invariant region. The average solubility is 49.8 mg./liter, with a standard deviation of 0.3 mg./liter.

ACKNOWLEDGMENT

Support of this work by a grant from the Atomic Energy Commission [Contract No. AT(11-1)-1082] is gratefully acknowledged.

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RECEIVED for review July 15, 1963. Accepted September 27, 1963.