Physical Properties of Boron Tribromide

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The triple point of boron tribromide has been found to be −45.84 ± 0.01° C. The density has been determined from −20° to 90° C. The viscosity and vapor pressures have been determined from 0° to 90° C.

BECAUSE BORON TRIBROMIDE is used as a source of ultra pure boron, there is a need for reliable physical property data for this compound. Much of the data in the literature were obtained from samples whose purity was not reported, and there is some disagreement in values of freezing point, boiling point, and density. Vapor pressure and viscosity data are sparse. To check and extend these reported data, the purity of a sample of boron tribromide was estimated from its triple point, and a systematic study made of its density, viscosity, and vapor pressure.

EXPERIMENTAL

Material. A sample of boron tribromide was twice fractionally distilled at 50 mm. of Hg pressure in a low temperature Podbielniak column. Mass spectrometric analysis indicated that the only impurity was a trace of hydrogen bromide.

Apparatus and Procedure. Boron tribromide (10 ml.) was distilled into a borosilicate glass vacuum-jacketed freezing point apparatus and sealed off under vacuum. A platinum resistance thermometer calibrated by the National Bureau of Standards was used to determine the cooling curve for the sample. The triple point was estimated by the graphical method of Taylor and Rossini (*5*).

The density was measured in a 3.6-ml. dilatometer, the neck of which was made from a 0.1-ml. graduated pipet. The dilatometer, closed at the top with a small stopcock, was calibrated with distilled water and filled with boron tribromide upon distillation in a vacuum system. Periodically, it was necessary to add or remove small amounts of sample . Boron tribromide readily attacks fluoro-carbon stopcock grease, and extreme care was required to avoid contaminating the sample while loading the dilatometer. A minimum of grease was used on all stopcocks and ground joints in the loading system.

The viscosity was measured in three size-25 Cannon-Zhukov capillary viscometers which were calibrated by the supplier or by the distilled water method. The sample was distilled in under vacuum, frozen at −196° C., and sealed off.

The vapor pressure was measured in a modified Smith and Menzies isoteniscope. The boron tribromide was distilled in under vacuum and pumped for two hours at −45° C. to remove any trace of hydrogen bromide. The mercury levels in the two arms of the U-tube were equalized at each temperature by admitting air to the outer side. The pressure was indicated on a mercury manometer and measured with a cathetometer.

Temperatures were measured with calibrated mercury thermometers. Temperatures above room temperature were controlled to ±0.05° C. with a mineral oil bath; temperatures below room temperature were controlled manually to ±0.1° C. by circulating cold methanol through coils of copper tubing in the bath.

The estimated precision of the density, viscosity, and vapor pressure measurements is ±0.1% of the observed values.

RESULTS AND DISCUSSION

The triple point of the purified sample of boron tribromide was −45.863° C. Its purity was 99.96 mole %. Measurements on two other samples of different purity indicated that the triple point of pure boron tribromide is −45.84 ± 0.01° C. This is higher than any freezing point reported previously, although it essentially confirms the −46.0° C. reported by Goubeau (*1*) and Stock (*4*).

The experimental density values over the range −20° to 90° C. fit the equation

$$\text{density (grams/ml.)} = 2.698 - 2.996 \times 10^{-3}\,{}^{\circ}\text{C.} \qquad (2)$$

with a standard deviation of ±0.0015 grams/ml. These results confirm three isolated values reported in the literature. However, Pohland's (*3*) value of 2.650 at 0° C., which appears in many handbooks and reference books, is apparently in error

The viscosity of boron tribromide over the range 0° to 90° C. fits the equation

$$\log_{10} \eta \text{ (millipoises)} = 333/{}^{\circ}\text{K.} - 0.257 \qquad (3)$$

with a standard deviation of ±0.02 millipoises. These viscosities were all 6 to 8% higher than values calculated from Hojendahl's (*2*) equation

$$\log_{10} \eta \text{ (poises)} = 346/{}^{\circ}\text{K.} - 3.33 \qquad (4)$$

No other viscosity data for boron tribromide have been found in the literature.

Table I. Vapor Pressure of Boron Tribromide

Temp., ° C.	Press. (Obsd.), Mm. of Hg	Dev. Mm. Obsd. − Calcd.
0.0	18.8	−0.2
10.0	33.0	+0.1
20.0	54.5	+0.1
25.0	69.0	+0.1
30.0	86.1	−0.4
35.0	107.8	+0.2
40.0	133.5	+0.6
45.0	162.9	0
50.0	199.6	+1.4
55.0	239.0	−0.4
60.0	286.7	−0.7
65.0	342.9	0
70.0	407.0	+0.4
75.0	480.0	+0.5
80.0	565.2	+2.6
87.4	705.1	−0.9
87.9	714.5	−2.1
88.8	738.0	+2.0
89.5	749.6	−1.8

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

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

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.

LITERATURE CITED

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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 $m\mu$, assumed due to the PIPSYL chloride. Upon standing, the 260 $m\mu$ peak decreased, and a new peak at 242 $m\mu$ made its appearance. The peak at 242 $m\mu$ 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 $m\mu$) and 1.6×10^4 (242 $m\mu$), respectively. However, because of the closeness