Summary

1. The adsorption of nitrogen, oxygen, hydrogen, argon, carbon dioxide and n-butane has been measured on porous glass and on partially dehydrated chabazite near the respective boiling points of the gases.

2. The surface area of porous glass can apparently be measured satisfactorily by the low temperature gas adsorption method; chabazite, on the other hand, when only 50% dehydrated adsorbs no nitrogen at −195° but will adsorb considerable hydrogen at −195° and carbon dioxide at −78°.

3. The occurrence of reproducible hysteresis loops in the adsorption–desorption curves on porous glass has been noted and discussed.

4. The average pore size of the porous glass has been calculated by various methods. The largest pores were about 60 Å. in radius as calculated by the Kelvin equation from the low temperature isotherms for argon, oxygen, nitrogen or butane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Molecular Surface Energy of Sulfur Dioxide Addition Compounds. II[1]

BY J. RUSSELL BRIGHT[2] AND JOSEPH J. JASPER

In a recent article[3] the effect of temperature on the molecular surface energy of the readily dissociated addition compound of sulfur dioxide with dimethylaniline, $C_6H_5(CH_3)_2N\cdot SO_2$, was presented. The purpose of this investigation was to extend the same physical measurements, over the temperature range 0 to 30°, to a more stable liquid addition compound of a tertiary amine with sulfur dioxide.

It was known[4] that gaseous sulfur dioxide reacts with triethylamine at room temperature to form a red, oily liquid, which by distillation under normal pressure gave a clear, light yellow to light green distillate; freezing point of product, −31.8°. Therefore, the triethylamine–sulfur dioxide complex was a logical one for study.[5] The density[6] and surface tension[7] of triethylamine at 20°, for example, are 0.7274 g./ml. and 20.9 dynes/cm., respectively; the Eötvös constant is 1.72.

Experimental

Preparation of the Liquid Molecular Addition Compound.—One mole of the best grade Eastman Kodak Company triethylamine, purified in the usual manner by distillation and drying over freshly cut sodium, was placed in a Florence flask. The index, $n^{20}D$ Abbe, of the sample was 1.4010. One mole of gaseous sulfur dioxide was purified and added as previously described.[3] During the reaction, noticeable heat was evolved and the product obtained had a deep red color. Distillation in an all-glass apparatus gave a nearly colorless product, b. p. 93.5° (751 mm.), f. p. −32°, $n^{20}D$ 1.4840. Freshly prepared material was analyzed for nitrogen by a modified Kjeldahl method: found N, 8.36%, 8.15%; calculated for $(C_2H_5)_3N\cdot SO_2$, N, 8.47%. The compound remains stable for an indefinite period as a white solid at the temperature of dry-ice. It is extremely hygroscopic and the liquid on exposure to moist air forms a voluminous white solid, which we have not yet investigated. Cryoscopic determination of the molecular weight, using purified benzene, f. p. 5.4°, gave 165.87, 164.65, 165.26; theoretical 165.19.

Procedure.—Since it was necessary to protect the compound from moisture, density measurements of the anhydrous substance were made in a manner somewhat different from that described in the first article of this series.[3] The 20-ml. pycnometer was fitted with a 10-cm. capillary tube of large bore (*ca.* 2.8 mm.) in which the liquid expanded as the temperature was raised. A stopcock and a standard ground-glass connector, sealed to the outer end, permitted evacuation of the pycnometer and facilitated transfer of the sample to it without exposure to the air. Increase in volume with temperature was readily followed and determined with the aid of a cathetometer. Water was used to calibrate the pycnometer. The precision of the temperature measurements was ±0.02°.

Surface tension measurements were made by the method already described,[3] using a capillary height apparatus with a capillary of 0.19168 mm. radius. The equation[8] sug-

$$\gamma = \frac{\left(h + \frac{r}{3}\right)(d_1 - d_v)gr}{2}$$

(1) Presented before the Division of Physical and Inorganic Chemistry at the Memphis meeting of the American Chemical Society, April, 1942.

(2) Present address: Gelatin Products Co., Detroit Mich.

(3) Bright and Jasper, THIS JOURNAL, **63**, 3486 (1941).

(4) Bright, Dissertation, The Ohio State University, June, 1940.

(5) It is recognized that Jander and Wickert, *Ber.*, **70**, 251 (1937), state that triethylamine dissolved in liquid sulfur dioxide forms a yellowish colored solution, which on evaporation of excess solvent gave a white, crystalline compound, melting point, 73°. These authors formulated this substance as $(Et_3NSO_2)_n$ or as a thionyl di-(triethylammonium)-sulfite, $[(Et_3N)_2S]SO_3$, and presented many chemical reactions to substantiate this peculiar formulation.

(6) Swift, THIS JOURNAL, **64**, 115 (1942).

(7) "Int. Crit. Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 435.

(8) N. E. Dorsey, "National Research Council Bull.," No. 69, p. 66.

gested by Dorsey was applied. In this equation, h is the capillary rise, r the capillary radius, and d_1 and d_a, respectively, the densities of the liquid and air during the experiment.

A modified Poiseuille viscosimeter was used for the viscosity measurements. The capillary tube of the viscosimeter was closed to the atmosphere with a ground-glass stopper carrying a stopcock. The reservoir and capillary tubes of the instrument were connected through a three-way stopcock, the third arm of which opened to the atmosphere. With this arrangement an enclosed system was maintained for all operations. Since a long capillary tube with a small radius was used, Poiseuille's correction[9] for the kinetic energy of the moving liquid was negligible.

Results

Experimental data are presented in Tables I, II, and III. It is evident that for the range 0 to 30° there is a straight line relation for both the density d and surface tension γ. These relations, as determined by least squares, are: $d = 1.0640 - 9.85 \times 10^{-4}t$, and $\gamma = 38.235 - 0.1376t$. The average deviation of the data from the d-curve and γ-curve is 0.01 and 0.084%, respectively. Both the density and surface tension of this compound are substantially greater than that of triethylamine. The average value of 3.27 for the Eötvös constant is greater than the average value of 2.12 for non-polar liquids but less than the average, 4.61, of the value reported[8] for the addition compound of dimethylaniline with sulfur dioxide.

TABLE I

DENSITY AND PARACHOR DATA FOR THE ADDITION COMPOUND OF SULFUR DIOXIDE WITH TRIETHYLAMINE

Temp., °C.	Density, g./ml.	Parachor[a]
0.0	1.0640	386.0
10.0	1.0543	386.1
17.0	1.0473	386.1
25.0	1.0395	386.0
33.4	1.0308	385.9

[a] Calculated from data of Tables I and II.

TABLE II

SURFACE TENSION DATA OF $(C_2H_5)_3N \cdot SO_2$

Temp., °C.	$\left(h + \frac{r}{3}\right)$, cm.	$(d_1 - d_a)$	Surface tension, dynes cm.$^{-1}$	Eötvös constant[a]
0.2	3.8244	1.0625	38.18	
10.0	3.7304	1.0531	36.91	3.10
21.0	3.6054	1.0421	35.30	3.36
25.0	3.5694	1.0383	34.82	3.28
29.0	3.5224	1.0343	34.23	3.34

[a] In the calculations the lower temperature was 0.2° in each case.

(9) Eugene C. Bingham, "Fluidity and Plasticity," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 18.

At room temperature the viscosity of this compound decreases about 2% for each degree rise in temperature. At 0° the decrease is much more marked. For the temperature range involved, the temperature–viscosity relations are satisfactorily expressed by the equation

$$\log \eta = 1240\ T^{-1} - 3.51171$$

The average deviation of the data from this curve is 0.6%.

TABLE III

VISCOSITY DATA OF $(C_2H_5)_3N \cdot SO_2$

Temperature, °C.	Viscosity (centipoises)
0.0	10.775
5.0	8.817
10.0	7.335
15.0	6.195
20.0	5.278
25.0	4.426
30.0	3.811

The data in Table IV indicate a molecular volume of 25 to 30 units less than values obtained by adding the molecular volumes of liquid sulfur dioxide and triethylamine. An observed value of 386.0 for the parachor of the addition compound is in perfect agreement with the value obtained from the sum of the atomic and structural parachors[10] for the structure

(R = C_2H_5)

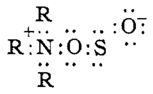

TABLE IV

MOLECULAR VOLUME OF $(C_2H_5)_3N \cdot SO_2$

Temp., °C.	Mol. vol. liq. SO_2[a]	Mol. vol. $(C_2H_5)_3N$[b]	Mol. vol. of addn. compd. Calcd.	Found
0.0	44.67	135.6	180.2	155.2
10.0	45.46	137.3	182.7	156.7
20.0	46.32	139.0	185.3	158.2
30.0	47.24	140.8	188.0	159.7

[a] See ref. 3, Table II. [b] Calculated with data obtained from Swift.[6]

Summary

The effect of temperature on the molecular surface energy of the relatively stable addition compound of sulfur dioxide with triethylamine, $(C_2H_5)_3N \cdot SO_2$, has been determined. Data are presented for density, surface tension, and viscosity over the temperature range 0 to 30°.

Parachor data furnish additional evidence for the existence of a nitrogen to oxygen to sulfur (N–O–S) linkage in this type of compound.

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(10) Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, N. Y., 1930, p. 38.