as $r_c = 2D$ as they are in bulk. (3) The open pore theory appears to be in most cases a satisfactory explanation of hysteresis. However, departure of experimental values from predicted values in a few instances indicates that the presence of other factors must also be considered.

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Summary

1. Several predictions based on the capillary theory of adsorption and the open pore theory of hysteresis have been shown to agree reasonably well with experimental data.

2. The agreement between theory and experiments indicates that the capillary theory of adsorption which postulates the formation of a monomolecular layer followed by capillary condensation is a fairly good first approximation for the adsorption mechanism in the systems considered.

3. The surface tension and molal volume of a liquid confined in a capillary of radius only twice the diameter of the liquid molecule appear to be about the same as for the liquid in bulk.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

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

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

The effect of temperature on the molecular surface energy of several liquid addition compounds of tertiary aliphatic amines with sulfur dioxide has been described in earlier articles.[3]

A more complete interpretation of the temperature effects described necessarily involves the extension of this series of studies to tertiary amine–sulfur dioxide addition compounds of still greater molecular weight. The purpose of this investigation, therefore, was to determine, for comparison with those preceding, the same physico-chemical constants for the respective equi-molecular mixtures of tripropylamine and tributylamine with sulfur dioxide.

Preparation of the Liquid Molecular Addition Compounds

The methods for purifying the materials were similar to those previously described.[3] Pure anhydrous sulfur dioxide was bubbled slowly through a known quantity of the best grade of Eastman Kodak Company tripropylamine ($n^{25}D$ 1.4151) until equi-molar quantities of the reactants were present. Since considerable heat was evolved during the reaction, the temperature was maintained at about 18° to prevent decomposition of the product. Upon further cooling, the product crystallized into light yellow needles, which melted at 15.3°. Distillation, even under reduced pressure, was impossible. The freshly prepared addition compound ($n^{25}D$ 1.4740) was analyzed for nitrogen by a modified Kjeldahl method; calculated for $(C_3H_7)_3N:SO_2$, N, 6.76. Found: N, 6.35, 6.46.

This compound is stable for an indefinite period as a light yellow solid at ice-box temperatures. It is very hygroscopic, changing to a red-brown liquid upon exposure to moist air. At temperatures above 45°, it changed to a black liquid whose density and surface tension deviated considerably from the linear relations given in a following paragraph.

Cryoscopic determination of the molecular weight, using purified benzene (f. p. 5.4°) as the solvent, gave 207.7, 208.4, 207.6 in 0.0327 weight molal solutions; theoretical 207.27. Increasing concentrations gave the molecular weights; 0.163 M, 2115.5; 0.327 M, 318.3; 0.411 M, 322.5. Similar association was observed by Bright and Fernelius[4] with the addition compound dimethylaniline–sulfur dioxide in the solvent dimethylaniline. Since the addition products are very hygroscopic, special precautions were used in their transfer to the various apparatus employed. Density and surface tension measurements were made, using the same apparatus and technique previously described.[3b] The viscosimeter used was constructed according to the design and specifications of Jones and Fornwalt.[5]

Experimental data are presented in Tables I and II. From these it is evident that the density d and surface tension γ are linear functions of the temperature for the compound tripropylamine-sulfur dioxide over the range 18 to 45°. These relations are given by the following equations

$$d = 1.0174 - 1.069 \times 10^{-3}t$$
$$\gamma = 32.72 - 0.125t$$

The average deviation of the data from the d-curve and γ-curve is, respectively, 0.02 and 0.08%. The Eötvös constant is −3.77 and, therefore, is less than the average value of −2.12, which is commonly assigned to non-polar liquids. This would seem to indicate considerable association, according to the criteria of Walden and Swinne.[6]

An observed value of 488.7 for the parachor of the $(C_3H_7)_3N:SO_2$ compound is in good agreement with the value of 503 obtained from the sum of

(1) Abstracted in part from material presented before the Symposium on Molecular Addition Compounds of the Division of Physical and Inorganic Chemistry at the Pittsburgh meeting of the American Chemical Society, September 6, 1943.

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

(3) Bright and Jasper, THIS JOURNAL, (a) **63**, 3486 (1941); (b) **65**, 1262 (1943).

(4) Bright and Fernelius, THIS JOURNAL, **65**, 637 (1943).

(5) Jones and Fornwalt, *ibid.*, **60**, 1683 (1938).

(6) Walden and Swinne, *Z. physik. Chem.*, **82**, 271 (1913).

TABLE I

DENSITY DATA FOR THE ADDITION COMPOUND $(C_3H_7)_3N:SO_2$

Temp., °C.[a]	Density, g./ml.
18.8	0.99716
22.1	.99369
23.8	.99158
24.9	.99065
27.3	.98818
30.5	.98465
33.5	.98139
36.0	.97869
40.0	.97406
45.0	.96919

[a] Precision of all temperature measurements reported in this paper is ±0.02°.

TABLE II

SURFACE TENSION AND PARACHOR DATA FOR $(C_3H_7)_3N:SO_2$

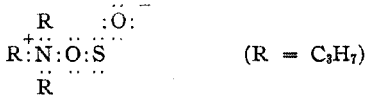
Temp., °C.	$(h + r/3)$, cm.	$(d_1 - d_a)$	Surface[a] tension, dynes, cm.$^{-1}$	Parachor
17.0	3.257	0.9980	30.542	488.3
21.7	3.211	.9930	29.959	488.4
25.0	3.187	.9895	29.631	488.8
30.0	3.132	.9841	28.961	488.7
35.0	3.088	.9788	28.411	488.9
40.0	3.033	.9730	27.729	488.8
45.0	2.979	.9679	27.093	488.6

[a] Values for surface tension were calculated from the equation

$$\gamma = \frac{(h + r/3)(d_1 - d_a)\, gr}{2}$$

where h is the capillary rise, r is the capillary radius, and d_1 and d_a, respectively, are the densities of the liquid and air during the experiment.

the atomic and structural parachors[7] for the structure



$(R = C_3H_7)$

At room temperature the viscosity of this compound decreases approximately 3% for each degree rise in temperature. The temperature–viscosity relations are satisfactorily expressed by the following equation, from which the average deviation of the data is 1.6%

$$\log \eta = 1797.75T^{-1} - 4.96534$$

TABLE III

VISCOSITY DATA OF THE ADDITION COMPOUND $(C_3H_7)_3N:SO_2$

Temp., °C.	Viscosity, centipoises
19.1	15.16
25.0	11.78
30.0	9.50
38.0	6.57
44.0	4.98

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

Similarly, an equi-molar mixture was prepared from tributylamine and sulfur dioxide. The liquid was orange in color; a slight excess of sulfur dioxide changed it to deep red, while a correspondingly small additional quantity of tributylamine restored the orange color. The product was very viscous. It was found impossible to distil this equi-molar mixture, even at very low pressures, and attempts to crystallize it resulted in the formation of a glass. Efforts to crystallize it from benzene solution were likewise unsuccessful.

The following linear relationships exist for the temperature range 0 to 40° for the equi-molecular mixture of tributylamine and sulfur dioxide, *viz.*

$$d = 0.9915 - 9.562 \times 10^{-4}t$$
$$\gamma = 33.25 - 0.1317t$$

Average deviations from the data of the d-curve and γ-curve are, respectively, 0.03 and 0.11%. The Eötvös constant −4.24 is less than any of the preceding lower molecular weight addition compounds studied. The observed parachor, 602.8, agrees satisfactorily with the theoretical 620.

TABLE IV

DENSITY AND SURFACE TENSION DATA FOR THE EQUIMOLECULAR MIXTURE $(C_4H_9)_3N$ AND SO_2

Temp., °C.	Density, g./ml.	Surface tension, dynes, cm.$^{-1}$
0	0.99084	33.232
5	.98659	32.647
10	.98205	31.914
15	.97745	31.299
20	.97293	30.592
25	.96792	29.947
30	.96247	29.246
35	.95803	....
40	.95308	28.032

Summary

The effect of temperature on the molecular surface energy of the addition compounds, $(C_3H_7)_3N:SO_2$, and the equi-molar mixture of $(C_4H_9)_3N$ and SO_2 has been determined. Data are presented for the density, surface tension and viscosity over the temperature range of 17 to 45° for the former and 0 to 40° for the latter.

The Eötvös constants were calculated and found to be less than any of the lower molecular weight addition compounds studied. Thus, the temperature coefficient of the molecular surface energy seems to decrease with increasing molecular weights of the addition compounds, and the tendency to associate increases.

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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