

Summary

The interpretation of electron diffraction photographs of thionyl bromide yields the following values for the structural parameters in the gas phase.

$$\begin{aligned} \text{S-Br} &= 2.27 \pm 0.02 \text{ \AA.} \\ \text{Br-S-Br} &= 96 \pm 2^\circ \\ \text{Br-O} &= 3.05 \pm 0.03 \text{ \AA.} \\ \text{S-O} &= 1.45 \text{ \AA. (assumed)} \end{aligned}$$

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Surface Tension in the System Hydrazine-Water at 25^o

BY NED B. BAKER AND E. C. GILBERT

No measurements of the surface tension of aqueous solutions of hydrazine are recorded in the literature, although the surface tension of pure hydrazine at 35° has been reported.²

Values for the surface tension of solutions over the entire concentration range at 25° have therefore been determined using the method of maximum bubble pressure.

Apparatus.—An all-glass apparatus similar in principle to that of Sugden³ was placed in a constant temperature bath at 25.00 ± 0.02°. To determine the surface tension of a liquid by this method it is necessary to measure the difference in maximum pressure required to force bubbles alternately from two tubes of different diameter submerged to the same level in the liquid. Certain limitations as to dimensions have been established under which a considerable simplification of the calculations is made possible.⁴

According to Sugden, if the diameter of the large tube is not greater than 4 mm. and that of the small one not above 0.2 mm., surface tension is given by the formula

$$\gamma = AP[1 + (0.69rgD)/P]$$

where A is a constant determinable by measurements on a liquid of known surface tension; P is the difference in pressure (dynes) necessary to form bubbles from the large and small tube; r is radius of large tube in cm.; g is acceleration due to gravity; and D is density of liquid. Examination of the equation reveals that a high degree of exactness is not necessary in determining the radius r .

Because of the extremely reactive nature of hydrazine it was necessary to alter the arrangement of the apparatus so that no oxygen or air ever came in contact with the liquid. Inert gas (hydrogen) was forced through the two tubes from a reservoir in the constant temperature bath by allow-

ing a fine stream of mercury to flow into the reservoir, whereas Sugden used a slight suction at the exit to draw air through the system.

The surface tensions thus obtained are therefore for the interface solution-hydrogen rather than solution-air. Examination of the data in the "International Critical Tables" reveals no significant difference between similar sets of data for liquids previously examined.

The manometer liquid was butyl phthalate and pressure differences were read to 0.01 mm. by means of a traveling microscope.

Procedure.—The apparatus was calibrated by the use of highly purified benzene, giving a constant $A = 0.007530$ cm. using a large tube of radius 0.180 cm. This in turn gave the surface tension for water at 25° as 71.96 dynes/cm. The calibration was repeated at times during the remainder of the work. When hydrazine was to be used, the system, including the manometer, was flushed out with dry hydrogen, and anhydrous hydrazine, prepared by Raschig's method,⁵ was distilled directly into the apparatus in a stream of hydrogen. When the bubble pressure difference for this liquid had been read, a sample was withdrawn into a glass ampoule for analysis and the hydrazine estimated by Kolthoff's bromate method.⁶

De-aerated water which had been distilled in an all-glass still was then added to lower the concentration and another pressure reading taken.

The density of three hydrazine solutions taken at random was found to agree with the results of Semishin,⁷ whose density data were therefore used in the remaining calculations.

Results

The results are shown in Table I and Fig. 1.

The values for the surface tension show a definite maximum at a concentration of 30–33 mole per cent. hydrazine. This was quite unexpected as other common physical properties of hydrazine such as density, viscosity, etc., show a maximum or minimum value in the region of 50 mole per cent. corresponding to the compound N₂H₄·H₂O whose presence has been demonstrated by the phase diagram study of Semishin. A composition

(1) Taken from a thesis submitted by Ned B. Baker toward the M.S. degree, Oregon State College, June, 1940. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research paper No. 34, School of Science, Department of Chemistry.

(2) Barrick, Drake and Lochte, *THIS JOURNAL*, **58**, 160 (1936).

(3) Sugden, *J. Chem. Soc.*, **121**, 853 (1922).

(4) Sugden, *ibid.*, **125**, 27 (1924).

(5) Raschig, *Ber.*, **43**, 1927 (1910).

(6) Kolthoff, *THIS JOURNAL*, **51**, 2009 (1929).

(7) Semishin, *J. Gen. Chem. U. S. S. R.*, **8**, 654 (1938).

TABLE I
SURFACE TENSION AND PARACHOR OF AQUEOUS HYDRAZINE
SOLUTION AT 25°

Mole % N ₂ H ₄	d^{25}_4 ^a	γ	Parachor of soln.	Parachor of hydrazine
0.0	0.9971	71.96	52.6	
6.7	1.0046	73.11	55.1	91.1
10.5	1.0087	73.68	56.6	90.5
20.5	1.0184	75.10	60.3	90.4
26.5	1.0228	75.41	62.5	90.4
28.7	1.0241	75.47	63.3	90.0
33.9	1.0274	75.47	65.3	90.2
40.1	1.0294	75.28	67.7	90.3
48.8	1.0317	74.18	70.6	89.5
49.1	1.0318	74.24	70.8	90.2
63.6	1.0298	72.38	76.3	90.0
69.7	1.0267	71.88	78.8	90.3
83.1	1.0161	69.97	84.5	91.0
84.9	1.0146	69.81	85.3	91.3
96.9	1.0051	67.57	90.2	91.4
100.0	1.0024	66.67	91.5	91.5

^a Densities taken from Semishin, ref. 7.

of 33 mole per cent. corresponds to the compound N₂H₄·2H₂O whose salts are known. It seems doubtful that the curve can be taken as indication of the presence of this compound as no trace of it is to be found in the work of Semishin.

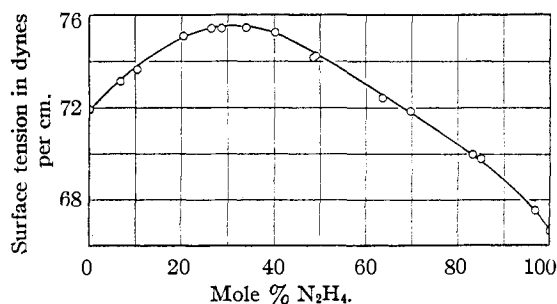


Fig. 1.—Surface tension in the system hydrazine-water at 25°.

The parachor of the solution was also calculated by the method of Hammick.⁸

According to this investigator the parachor of a binary solution is additive for both non-associated and associated solutes in any miscible

liquid. From the values for the parachor of the solution the parachor of hydrazine as solute may be calculated as shown in the last column of Table I. It is obvious that there is some deviation from linearity in both parachors but the maximum deviation does not agree with the maximum of the surface tension curve, occurring instead at approximately 50 mole per cent. This may be explained by the fact that there is a decided maximum in the density curve at this concentration, whereas the surface tension enters into the parachor only as the fourth root.

The parachor of hydrazine calculated from the atomic parachors of Sugden⁹ is 93.4 whereas the experimental value found either by extrapolation or by direct measurement on the pure hydrazine is 91.5.

The parachor of anhydrous hydrazine at 35° has been reported by Lochte, *et al.*,² whose measurements were also made by a modified bubble pressure method. Their parachor, 90.7, would indicate a proportionately lower surface tension in comparison to the results given here since the parachor does not change much with temperature. They do not mention the use of an inert gas, which may offer an explanation for the difference since in our work accidental exposure of hydrazine to air or oxygen always resulted in lower surface tension measurements.

Summary

1. The surface tension of aqueous hydrazine solutions at 25° has been measured over the entire concentration range.
2. A maximum surface tension is shown by this system at a concentration of 30–35 mole per cent. of hydrazine.
3. The parachor of hydrazine has been calculated from the surface tension to be 91.5 at 25°.

CORVALLIS, OREGON

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(8) Hammick and Andrew, *J. Chem. Soc.*, 754 (1929).

(9) Sugden, *ibid.*, 125, 1177 (1924).