

- (8) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., pp. 528-30, Van Nostrand, New York, N.Y., 1947.
- (9) Guibe, L., Lucken, E. A. C., *Mol. Phys.*, **14**, 79 (1968).
- (10) Harrigan, E. T., Wong, T. C., Hirota, N., *Chem. Phys. Lett.*, **14**, 549 (1972).
- (11) Kempa, R., Lee, W. H., *J. Chem. Soc.*, **1958**, p 1936.
- (12) Kirkwood, J. G., *J. Chem. Phys.*, **7**, 911 (1939).
- (13) Lange, N. A., Ed., "Handbook of Chemistry," rev. 10th ed., pp 1201, 1864, McGraw-Hill, New York, N.Y., 1961.
- (14) Leader, G. R., *J. Amer. Chem. Soc.*, **73**, 856 (1951).
- (15) Malmberg, C. G., Maryott, A. A., *J. Res. Nat. Bur. Stand.*, **56**, 1 (1956).
- (16) Maryott, A. A., Smith, E. R., "Tables of Dielectric Constants of Pure Liquids," Nat. Bur. Stand. Circ., No. 514, pp 1, 10, 1951.
- (17) Mehrotra, N. K., Saxena, M. C., *Bull. Chem. Soc. Jap.*, **40**, 19 (1967).
- (18) Mertel, H. E., "Pyridine and Its Derivatives, Part Two," E. Klingsberg, Ed., p 299, Interscience, New York, N.Y., 1961.
- (19) Oliveto, E. P., "Pyridine and Its Derivatives, Part Three," E. Klingsberg, Ed., p 179, Interscience, New York, N.Y., 1961.
- (20) Schempp, E., Bray, P. J., *J. Chem. Phys.*, **49**, 3450 (1968).
- (21) Swindells, J. F., Coe, J. R., Godfrey, T. B., *J. Res. Nat. Bur. Stand.*, **48**, 1 (1952).
- (22) Vaughn, J. W., Sears, P. G., *J. Phys. Chem.*, **62**, 183 (1958).
- (23) Weast, R. C., "Handbook of Chemistry and Physics," 47th ed., pp C-153, C-154, C-159, C-161, C-518, C-519, C-520, Chemical Rubber Co., Cleveland, Ohio, 1966.
- (24) Wentworth, W. E., *J. Chem. Educ.*, **42**, 96, 162 (1965).

Received for review May 20, 1974. Accepted September 19, 1974. Work supported in major part by Themis Contract DAA B07-69-C-0366.

## Vapor Pressure of 2,4-Tolylene Diisocyanate

H. K. Frensdorff<sup>1</sup> and R. K. Adams

Elastomer Chemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. 19898

Vapor pressures of 2,4-tolylene diisocyanate between 20° and 40°C (determined by a gas saturation technique) and between 100° and 170°C (directly measured) are reported. They are well represented by the equation,  $\log_{10} p$  (torr) = 38.179 - 4821/T - 9.612 log<sub>10</sub> T, for the temperature range 20-170°C.

2,4-Tolylene diisocyanate (1-methyl-2,4-diisocyanatobenzene) is widely used, especially in the manufacture of polyurethanes. Because of its toxicity, its atmospheric concentration must be kept to a very low level, and accordingly, the vapor pressure above the pure liquid and above partially cured polyurethane is of considerable interest.

Three reports of vapor pressures above 100°C exist. Cole (1) reports vapor pressures of 2,4-tolylene diisocyanate and its 2,6-isomer from 100° to 180°C in the form of three-constant (Kirchhoff) equations. Molard's (4) data from 120° to 190°C, in the form of two-constant (Clausius) equations, are 3-11% lower than those of Cole, which represents quite good agreement. In contrast, Gol'dberg et al. (3) report vapor pressures of the 2,4-isomer at 100° to 155°C, which are two to three times higher than those of Cole and Molard. That the results of Gol'dberg et al. are erroneous, possibly owing to the presence of gaseous impurities during the static determination, is made manifest by the boiling point quoted by them (125° at 15 torr), which is much closer to the prediction of Cole's equation (130° at 15 torr) than to their own (103° at 15 torr).

Neither Cole (1) nor Molard (4) gives the data points used in deriving their correlating equations. Moreover, the literature contains no reports of room temperature vapor pressures, which are of special interest for health reasons. Hence, the purpose of this paper is twofold: to report the original data points between 100° and 170°C, on which the equation given by Cole (1) is based; and to report vapor pressures between 20° and 40°C obtained by a gas saturation method.

<sup>1</sup> To whom correspondence should be addressed.

### Health and Safety Considerations

Tolylene diisocyanates are highly irritating materials and have to be handled with great care. Their atmospheric concentration must be held to very low levels. The present threshold limiting value is 0.02 parts per million by volume (2), and an even lower standard (0.005 ppm) has been proposed (5).

These low standards should be kept in mind when handling these materials and, in addition, provide the rationale for the present measurements.

### Experimental

**Materials.** The 2,4-tolylene diisocyanate used in these measurements was a sample of commercial material specially selected for its purity. It contained 99.5% or more tolylene diisocyanate by titration, of which 98.9% was the 2,4-isomer by infrared analysis. The major expected impurity is the 2,6-isomer.

**High-temperature measurements.** Vapor pressures above 100°C were measured directly by means of an isoteniscope [as described by Weissberger (7)] connected to manometer, vacuum pump, 5-l. surge tank, and a controlled leak. The closed-end mercury manometer was made of 15-mm tubing and read to the nearest 0.1 mm with a cathetometer. Readings were corrected to 0°C (mercury vs. brass scale).

The isoteniscope was immersed in a vigorously stirred, baffled oil bath equipped with a bare-wire heater. A mercury thermometer, which had been calibrated against a platinum-resistance thermometer and could be read to the nearest 0.05°C, was located with its bulb near the reservoir of the isoteniscope.

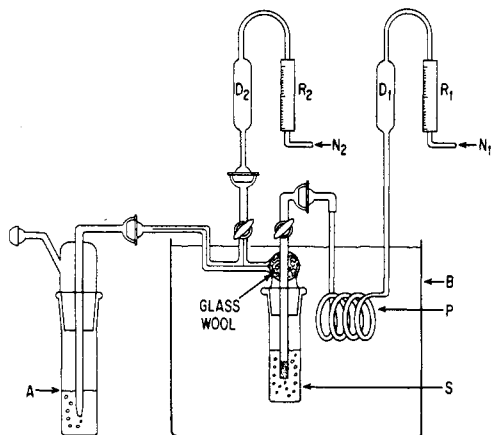
To initiate a series of measurements, freshly redistilled 2,4-tolylene diisocyanate was introduced into the isoteniscope and degassed. Measurements were started at the lowest pressure, which was then increased stepwise. At each pressure, equilibrium was obtained by adjusting the temperature until the liquid levels in the two legs of the isoteniscope were equal. Then the temperature was raised a few degrees to boil out any low-boiling impurities, and finally equilibrium was reestablished. This procedure took only a few minutes, and the two equilibrium temperatures never differed by more than 0.1°C.

When the isoteniscope was kept at 170°C for 30 min, the vapor pressure increased by 2.0 torr, i.e., 2.7%. Thus, the maximum error due to thermal decomposition during the 3 to 5 min elapsed between duplicate measurement would have been 0.5% without boil-out and correspondingly less with boil-out. A difference of 0.5% in the vapor pressure corresponds to a 0.15° difference in temperature, as estimated from the heat of vaporization, in agreement with the observed maximum temperature difference of 0.1°.

**Low-temperature measurements.** In the gas saturation apparatus (Figure 1), the metered main nitrogen stream passes through a fritted glass disperser into the saturator, which contains about 10 ml of 2,4-tolylene diisocyanate. After passing through a glass wool plug, it is joined by a second metered nitrogen stream, which dilutes it to prevent condensation whenever the bath temperature is above room temperature. The tolylene diisocyanate in the diluted stream is then absorbed in a midget impinger (30 ml with 1-mm opening and spherical joints) containing 10 ml of dimethylsulfoxide which had been dried over "Molecular Sieves." The underwater ground-glass joint was cemented with a thermoplastic polymer. Both nitrogen streams passed through copper tubing and were connected to the all-Pyrex glass system through 12/5 stainless-steel spherical joints. The connections from the saturator to the impinger were made of 2-mm Pyrex capillary tubing. The apparatus was submerged in a water bath controlled to within 0.05°C.

Water content of the nitrogen streams, determined by means of an electrolytic water analyzer, was less than 0.3 parts per million v/v (0.23 millitorr H<sub>2</sub>O partial pressure). Both nitrogen streams were kept running at all times to minimize contamination and to keep the interior glass surfaces conditioned. The rotameters were calibrated against soap bubble flow meters connected to the exit joint of the absorber. By occasionally using a second absorber in series, absorption efficiency was at least 97.5% in a single absorber, even at the highest nitrogen flow rate, and correspondingly greater at lower flow rates. The loss was taken into account when necessary.

The isocyanate collected in the absorber was determined by saponification to amine, diazotization, coupling to *N*-1-naphthylethylenediamine, and spectrophotometric determination of the resulting dye, as follows. Each absorber solution was acidified with 10-ml 1*N* HCl right after collection, and after a number of samples had been accumulated, the dye was developed by the procedure of

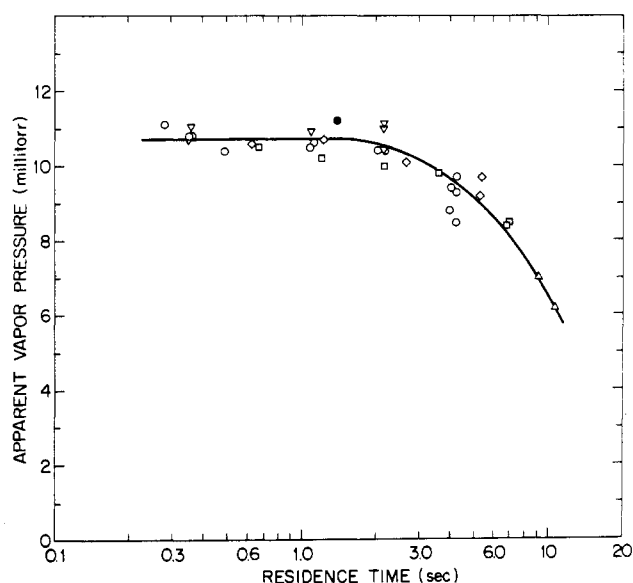


**Figure 1.** Schematic of gas saturation apparatus. N<sub>1</sub>, main nitrogen stream; N<sub>2</sub>, diluting nitrogen stream; R<sub>1</sub>, R<sub>2</sub>, flow meters; D<sub>1</sub>, D<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, driers; P, preheating coil; S, saturator; A, absorber; B, constant-temperature bath

Pilz (6). The molar extinction coefficient of the dye, determined by subjecting 10 different solutions of 2,4-diaminotoluene (assay 96.5% by titration) to the same procedure, was 40,800 cm<sup>-1</sup> (mol diisocyanate/l.)<sup>-1</sup> at 550 nm, with a standard deviation of 1%.

The vapor pressure was taken to be the pressure in the saturator multiplied by the partial volume, i.e., the volume of diisocyanate vapor, based on the ideal gas law, divided by the nitrogen volume, as given by time and flow rate through the saturator.

**Sources of error.** The principal source of error in the high-temperature measurements lies in the presence of low-boiling contaminants, especially those formed by thermal decomposition during the measurement, e.g., carbon dioxide. The method of operation of the isoteniscope tends to minimize this error. As described above, it should contribute well below 0.5% to the uncertainty of the vapor pressures. Thermometer reading errors of 0.1° should contribute no more than 0.5% to this uncertainty, as estimated from the heat of vaporization, while the ma-



**Figure 2.** Effect of flow rate on apparent vapor pressure at 20°C. Plotting symbols represent different mainstream flow rates (ml/sec):  $\Delta$ , 0.45;  $\square$ , 0.65;  $\diamond$ , 0.85;  $\circ$ , 1.1;  $\nabla$ , 2.05;  $\bullet$ , 3.15. Residence time is volume of capillary from glass-wool plug plus volume of absorber inlet tube (4.4 ml), divided by sum of nitrogen flow rates

**Table I. Vapor Pressure of 2,4-Tolylene Diisocyanate**

Temp, °C	Vapor pressure, torr	
	Obsd <sup>a</sup>	Calcd, Equation 1
20.0	0.0105 ± 0.0005	0.0105
30.0	0.025 ± 0.0005	0.0265
40.0	0.062 ± 0.0015	0.0624
103.3	4.2 ± 0.08	4.12
123.5	11.25 ± 0.10	11.20
128.2	14.0 ± 0.12	13.88
137.9	21.15 ± 0.16	21.19
144.1	27.3 ± 0.19	27.41
150.5	35.35 ± 0.23	35.40
159.8	50.2 ± 0.30	50.44
170.1	72.8 ± 0.42	73.07

<sup>a</sup> Uncertainty: 20–40°, range of scatter on flat portion of plots like Figure 1; 103–170°, range estimated from experimental parameters as 1% plus 0.1 torr.

nometer reading error is about 0.1 torr. Thus, the overall uncertainty of the high-temperature vapor pressures is estimated to be 1% plus 0.1 torr.

The specificity of the analytical method obviates spuriously high low-temperature vapor pressures owing to low-boiling contaminants. This, together with the high purity of the compound, tends to keep errors from impurities to at most 1 or 2%. Errors owing to the spectrophotometric analysis are expected to be of similar magnitude. Deviations from ideal gas behavior are negligible at the low partial pressures. Errors in the nitrogen volume, as judged by fluctuations in the rotameter calibrations, might be as high as 2–4%. Thus, the uncertainty of the low-temperature vapor pressures should be well under 10%.

## Results

In gas saturation measurements, one expects a decrease in apparent vapor pressure as the nitrogen flow rate is increased beyond the point where the residence time in the saturator is sufficient for vapor-liquid equilibrium. But on the contrary, the apparent vapor pressure rose to a limiting value as the nitrogen flow rates, whether of the main stream or of the diluting stream, were increased (Figure 2). In spite of the many precautions taken, such as rigorous water removal, installation of the glass-wool plug, and long-term conditioning of the apparatus, this effect persisted. As shown in Figure 2, the same limiting value is obtained over a decade of residence times (or flow rates), and this was taken to be the true vapor pressure. The attainment of such a limiting value also demonstrates that saturation was complete and that entrained droplets, if any, were effectively removed by the glass-wool plug.

The low apparent vapor pressure at residence times above two seconds points to an isocyanate-consuming chemical reaction. The most obvious possibility is the reaction with water to form amine and/or urea. However, 1 mole of water reacts with at most 1 mole of diisocyanate,

so that the water present (0.25 millitorr or less) can account for at most a 2.5% decrease in the vapor pressure, while a decrease of about 40% was observed for the longest residence time (Figure 2). Some other isocyanate-consuming reaction must, therefore, be involved. One might conjecture that dimerization or trimerization, both known reactions under base catalysis, might occur, possibly on the glass surface. However, the identification of this reaction is not essential for the present purpose, since its effects were circumvented by keeping the residence time short enough.

Vapor pressures obtained by both methods are given in Table I. They were fitted by regression to a single Kirchhoff equation, valid from 20° to 170°C:

$$\log_{10} p = 38.179 - 4821/T - 9.612 \log_{10} T \quad (1)$$

where  $p$  is the vapor pressure in torr, and  $T$  the absolute temperature in kelvins. Equation 1 predicts the vapor pressures from 120° to 170° to within less than 1% of the observed values and the others to within 6% or less, as shown in the last column of Table I.

Differentiation of Equation 1 gives the enthalpy of vaporization ( $\Delta H_v$ , in cal/mol) for the same temperature range:

$$\Delta H_v = 22060 - 19.10 T \quad (2)$$

## Literature Cited

- (1) Cole, H. N., *Ind. Eng. Chem., C&E Data Ser.*, **3**, 213 (1958).
- (2) *Fed. Reg.*, **37**, 22 141 (October 18, 1972).
- (3) Gol'dberg, N. A., Kucheryavii, V. I., Zinov'ev, G. N., *J. Appl. Chem. USSR*, **32**, 2898 (1959).
- (4) Molard, L., *Mem. Poudres*, **46–47**, 7 (1964–5).
- (5) National Institute for Occupational Safety and Health, Public Health Service, U.S. Department of Health, Education, and Welfare, "Occupational Exposure to Toluene Diisocyanate: Criteria for a Recommended Standard," 1973.
- (6) Pilz, W., *Mikrochim. Acta*, 504 (1970).
- (7) Weissberger, A., Ed., "Physical Methods of Organic Chemistry," 2nd ed., p 173, Interscience, New York, N.Y., 1949.

Received for review May 28, 1974. Accepted October 8, 1974. Contribution No. 319 from the Elastomer Chemicals Department.

# Solubility and Diffusivity of Hexamethylene Tetramine in Ethanol

John R. Bourne<sup>1</sup> and Roger J. Davey

Technisch-Chemisches Laboratorium ETH, CH-8006 Zurich, Switzerland

**The solubility and diffusivity of hexamethylene tetramine (HMT) in ethyl alcohol were accurately measured in the range 10–40°C. No accurate data were previously available for HMT in nonaqueous solvents.**

During studies on the growth of hexamethylene tetramine [(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>] (HMT) crystals from solution, reliable data were required for the solubility and diffusivity of HMT in ethanol. Despite previous reports of the growth of HMT from alcoholic solution (2, 4), no data were available on the diffusion of HMT in ethanol, and only one value [2.89 g/100 ml ethanol at room temperature (6)] could be found for its solubility. Fairly extensive data are, however, available for aqueous HMT solutions (1, 8).

<sup>1</sup>To whom correspondence should be addressed.

## Experimental

**Starting materials.** All solutions were prepared from pharmaceutical grade HMT (subsequently doubly recrystallized from methanol) and 99.8 vol % ethanol as supplied by Fluka AG (Switzerland). Contamination of the HMT by water vapor was prevented by storage over silica

**Table I. Solubility of HMT in Ethanol (Water Content, 0.04 Vol %)**

Temp, °C ± 0.02	Solubility, g HMT/100 g solution
15.04	2.606 ± 0.008
20.34	2.941 ± 0.003
25.28	3.298 ± 0.008
30.25	3.696 ± 0.005
39.76	4.569 ± 0.005