

# Refractive Indexes of Dimethylsulfoxide, *n*-Hexane, and Octamethylcyclotetrasiloxane by Method of Minimum Deviation

H. LAWRENCE CLEVER<sup>1</sup> and MALCOLM L. TAYLOR, JR.  
Chemistry Department, Emory University, Atlanta, Ga. 30322

The refractive indexes of benzene, water, dimethylsulfoxide, *n*-hexane, and octamethylcyclotetrasiloxane were measured by the classical method of minimum deviation at three temperatures between 20° and 30° C and at the sodium-D (5893 Å), mercury *e* (5461 Å), and mercury *g* (4358 Å) wavelengths. The refractive index values of benzene and water check accepted values with a standard deviation of less than  $6 \times 10^{-5}$ .

The method of minimum deviation is potentially one of the most accurate methods for the measurement of refractive index. It has long been used by physicists, geologists, and mineralogists (1, 2, 7, 10, 23) to determine the refractive index of solids and occasionally liquids. It is a method whose general use by chemists for the measurement of the refractive index of pure liquids and solutions is overdue.

The precise application of the method was developed in a series of classical papers by Tilton (14-17). More recently, the precautions and tolerances necessary to obtain an accuracy of  $1 \times 10^{-6}$  refractive index unit for solids were summarized (8). Liquids present special problems, including purity and a high temperature coefficient of refractive index, so that the accuracy mentioned above is probably not attainable for liquids. However, it should be noted that the refractive indexes of 2,2,4-trimethylpentane, methylcyclohexane, and toluene determined by the method of minimum deviation (3) were used as the standard values for the refractive indexes of hydrocarbons in the well known API-NBS series (3-6, 13).

Our own interest in the method developed because of our plans to measure the refractive index of binary non-electrolyte solutions when one component was more volatile than the other. The difficulties in controlling temperature and composition when the solution is in a thin film and more or less open to the atmosphere as in either the Abbe or the Pulfrich refractometer, are obvious. In the method of minimum deviation, a relatively large sample is enclosed in a hollow prism in which variations of temperature and composition can be controlled [Tilton (17)]. Special cells for very small liquid samples have been described (1, 7, 10), and a commercial open hollow prism of good quality is available.

In the determination of refractive index by the method of minimum deviation, the liquid is enclosed in a 60° hollow prism. The total deviation of the light beam is measured on a divided circle spectrometer when the light beam through the prism of liquid is parallel to the prism base. The deviation is minimum when the light beam is parallel to the prism base. Under the condition of minimum deviation the refractive index, *n*, is given by the exact equation from classical optics (24)

$$n = \sin [(A + D)/2] / \sin (A/2)$$

where *A* is the prism angle, and *D* is the total deviation (Figure 1). Measurements were made of the refractive index of five pure liquids at three temperatures and three wavelengths by the method of minimum deviation. The values

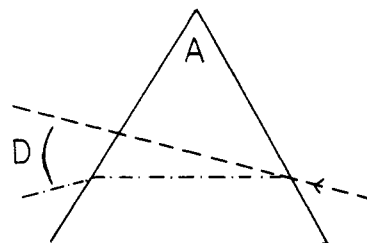


Figure 1. Light path in prism  
*A*, prism angle. *D*, total deviation angle

of refractive index of benzene and water were used to check our application of the method. Dimethylsulfoxide, *n*-hexane, and octamethylcyclotetrasiloxane refractive indexes are reported for the three wavelengths—sodium-D (5893 Å), and mercury *e* (5461 Å), and *g* (4358 Å). The mercury wavelength refractive indexes of these three liquids have not been reported before.

## EXPERIMENTAL

**Purification of Liquids.** Benzene, Mallinckrodt, was washed with concentrated sulfuric acid, until the acid layer was no longer colored, and with distilled water to remove all traces of acid, dried with CaSO<sub>4</sub>, and distilled over CaH<sub>2</sub> through a 2-ft column packed with stainless steel helices; bp 79.2° C at 740 mm Hg [literature value: 79.25° C (3, 13)]; density at 30° C, 0.86828 g/ml [literature value 0.86833 g/ml (3, 13)].

Water was distilled and demineralized, then distilled a second time from a basic potassium permanganate solution using a Yoe distillation apparatus.

Dimethylsulfoxide, (CH<sub>3</sub>)<sub>2</sub>SO, Baker Reagent Grade, distilled under reduced pressure; bp 49.0° C [literature values: 56.6° C at 5.11 mm Hg; 47.4° C at 282 mm Hg (12)]; density at 20° C, 1.09996 g/ml [literature value; 1.100 g/ml (12)]. After distillation, three fractional crystallizations were carried out.

*n*-Hexane, Phillips, 99 mole %, was washed with concentrated sulfuric acid until the acid layer was no longer colored and with distilled water to remove all traces of acid, dried with CaSO<sub>4</sub>, and distilled over CaH<sub>2</sub> through a 2-ft column packed with stainless steel helices; bp 68.0° C at 741 mm [literature value 67.95° C (5, 13)]; density at 30° C, 0.65021 g/ml [literature value 0.65027 g/ml (5, 13)].

Octamethylcyclotetrasiloxane (CH<sub>3</sub>)<sub>8</sub>Si<sub>4</sub>O<sub>4</sub> General Electric Silicone Products Division, distilled over CaH<sub>2</sub>; bp

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

173°C at 739 mm Hg [literature value 175°C at atmospheric pressure (11)]; density at 20°C, 0.95572 g/ml [literature value 0.9558 g/ml (11)]. After distillation three fractional crystallizations were carried out.

**Refractive Index Measurement.** The refractive indexes were measured by the method of minimum deviation using a Gaertner Model L114 divided circle spectrometer which could be read to 6 sec of arc, and a Gaertner Model L751A precision-type hollow prism. It is an equilateral prism with faces of high-quality parallel plate glass, 30 mm high and 57 mm long, cemented to a brass frame with an open top. The prism met published (8, 16, 17) criteria for an accuracy of refractive index of  $1 \times 10^{-5}$ . A prism-shaped piece of brass with a slit parallel to the base for the passage of light and drilled for the internal passage of thermostated water was constructed to fit inside the hollow prism. Figure 2 is a sketch of the hollow prism and brass insert with thermostated water connections (a), thermocouple well (b), and slit for light passage (c). The brass prism insert served three purposes. It decreased the sample volume of the hollow prism from about 60 to 25 ml, and it acted both as a conductor for thermostated water and as a cover for the hollow prism. The procedure was essentially that described by Tilton (17) with several readings made of the minimum deviation angle, from both up and back positions to cancel errors. In this work the hollow prism angle,  $A$ , was measured by the standard optical technique and found to be  $59^\circ 55' 7''$ .

The sample temperature was controlled by circulating thermostated water through the brass insert set in the liquid sample. At the same time the room temperature was usually brought to within  $1^\circ$  of the sample temperature. The sample temperature was constant to  $\pm 0.03^\circ$ . Temperatures were measured by a copper-constantan thermocouple calibrated by comparison with a National Bureau of Standards calibrated mercury in glass thermometer at the ice point, 25.00°C, and the water boiling point (pressure corrected).

Light sources were a sodium laboratory arc and a mercury laboratory arc with a combination green filter to isolate the 5461 Å light and a combination blue filter to isolate the 4358 Å light.

## RESULTS

The experimental refractive indexes and the temperatures of measurement are given in Table I. Also given are smoothed values of refractive index at 20.00, 25.00, and 30.00°C. The smoothed values were obtained from a linear

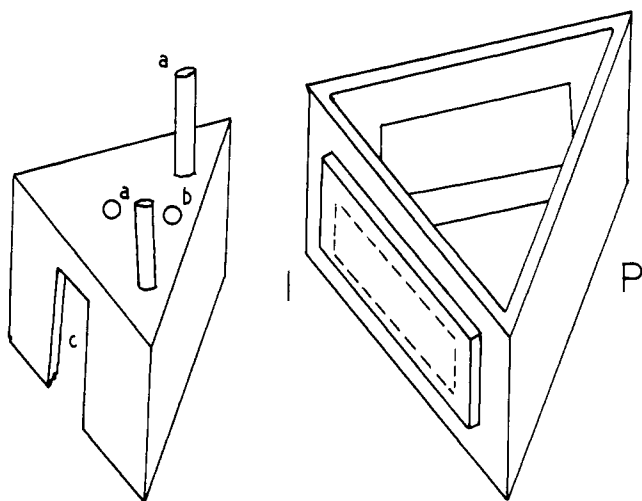


Figure 2. Hollow prism (P) and brass insert (I)

Table I. Refractive Index of Dimethylsulfoxide, *n*-Hexane, and Octamethylcyclotetrasiloxane at Three Wavelengths

	$t$	5893 Å	$t$	5461 Å	$t$	4358 Å
Dimethylsulfoxide						
20.00		1.47933		1.48171		1.49297
	20.45	1.47917	20.51	1.48152	20.67	1.49275
25.00		1.47754		1.47985		1.49132
	25.56	1.47734	25.58	1.7963	25.58	1.49113
<i>n</i> -Hexane						
20.00		1.37489		1.37680		1.38318
	20.25	1.37476	20.87	1.37635	22.18	1.38207
	23.60	1.37304	24.07	1.37467	23.69	1.38130
25.00		1.37231		1.37419		1.38062
	27.89	1.37081	28.96	1.37215	28.58	1.37876
30.00		1.36971		1.37161		1.37802
Octamethylcyclotetrasiloxane						
20.00		1.39675		1.39855		1.40607
	21.08	1.39624	21.11	1.39804	21.09	1.40557
25.00		1.39463		1.39668		1.40413
	25.21	1.39454	25.24	1.39648	25.26	1.40404
	29.95	1.39301	29.95	1.39503	29.82	1.40271
30.00		1.39300		1.39502		1.40264

Table II. Standard Deviation of Experimental Refractive Indexes from Linear Equation  $n = A + Bt$

Compound	Standard deviation $\times 10^5$		
	5893 Å	5461 Å	4358 Å
Benzene	1.5	0.5	0.3
Water	1.7	1.0	1.6
<i>n</i> -Hexane	0.3	0.6	0.9
Octamethylcyclotetrasiloxane	9.2	7.2	7.7

extrapolation of the experimentally measured values except in the case of octamethylcyclotetrasiloxane data which showed a slight curvature with temperature. Table II gives the standard deviations of the experimental refractive indexes from the linear equation  $n = A + Bt$  at each wavelength.

The benzene values at 20°, 25°, and 30° agree with accepted values (3) with a standard deviation of the nine values of  $5.4 \times 10^{-5}$ . The water values also agree with accepted values (18) with a standard deviation of  $3.9 \times 10^{-5}$ . For both benzene and water the agreement is best with the sodium-D line values and poorest with the mercury 4358 Å line values, which we assume is associated with a poorer eye sensitivity as the wavelength decreases.

Only refractive indexes at the sodium-D wavelength are reported in the literature for dimethylsulfoxide. The present value is considerably higher than one report (13) but is within  $2 \times 10^{-4}$  unit of a value reported at 25° (9) and 20° (19, 20). The most likely contaminator in the dimethylsulfoxide is water. Our 30° values for dimethylsulfoxide were considered invalid because of the high humidity following a rainstorm at the time of the measurement.

The *n*-hexane sodium-D refractive index at 20° and 25° agrees with accepted values (5, 12) with a standard deviation of  $4.1 \times 10^{-5}$ . Refractive indexes of *n*-hexane at four other wavelengths are in the literature (21, 22) but values at the two mercury wavelengths have not been reported before.

The sodium-D wavelength refractive index of octamethylcyclotetrasiloxane at 20° agrees well with the literature value (11) of 1.3968.

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## LITERATURE CITED

- (1) Butler, R. D., *Amer. Mineral.*, **18**, 386 (1933).
- (2) Fairbairn, H. W., *ibid.*, **37**, 37 (1952).
- (3) Forziati, A. F., *J. Res. Nat. Bur. Stand.*, **44**, 373 (1950).
- (4) Forziati, A. F., Camin, D. L., Rossini, F. D., *ibid.*, **45**, 406 (1950).
- (5) Forziati, A. F., Glasgo, A. R., Jr., Willingham, C. B., Rossini, F. D., *ibid.*, **36**, 129 (1946).
- (6) Forziati, A. F., Rossini, F. D., *ibid.*, **43**, 473 (1949).
- (7) Gogswell, R. F., *Amer. Mineral.*, **30**, 541 (1945).
- (8) Hafner, H. C., Rood, J. L., *Mater. Res. Bull.*, **2**, 303 (1967).
- (9) Kenttamaa, J., Lindberg, J., *Suom. Kemistilehti*, **33B**, 32 (1960).
- (10) Larsen, E. S., Berman, H., *U.S. Geol. Surv. Bull.*, 848, 2nd ed., 18-20 (1934).
- (11) Patnode, W., Wilcock, D. F., *J. Amer. Chem. Soc.*, **68**, 358 (1946).
- (12) Rossini, F. D., Pitzer, K. S., Taylor, W. J., Ebert, J. P., Kilpatrick, J. E., Beckett, C. W., Williams, M. G., Werner, H. G., *Selected Values of Properties of Hydrocarbons*, National Bureau of Standards Circ. C461, 1947.
- (13) Schlafer, H. L., Schaffernicht, W., *Angew. Chem.*, **72**, 618 (1960).
- (14) Tilton, L. W., *J. Res. Nat. Bur. Stand.*, **2**, 909 (1929).
- (15) Tilton, L. W., *ibid.*, **6**, 59 (1931).
- (16) Tilton, L. W., *ibid.*, **11**, 25 (1933).
- (17) Tilton, L. W., *ibid.*, **14**, 393 (1935).
- (18) Tilton, L. W., Taylor, J. K., *ibid.*, **20**, 419 (1938).
- (19) Traynelis, V. J., Hergenrother, W. L., Livingston, J. R., Valicenti, J. A., *J. Org. Chem.*, **27**, 2377 (1962).
- (20) Traynelis, V. J., Hegenrother, W. L., Hanson, H. T., Valicenti, J. A., *ibid.*, **29**, 123 (1964).
- (21) Wibaut, J. P., Hoog, H., Langedijk, S. L., Overhoff, J., Smit-tenberg, J., *Rec. Trav. Chim.*, **58**, 329 (1939).
- (22) Wibaut, J. P., Langedijk, S. L., *ibid.*, **59**, 1220 (1940).
- (23) Wolfe, C. W., Franklin, V., *Amer. Mineral.*, **34**, 893 (1949).
- (24) Wood, R. W., "Physical Optics," Dover Publications, New York, N. Y., 1967, pp 75-77.

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# Solubility of Cyclopropane in Alkyl Carboxylic Acids

JAMES R. BARTON<sup>1</sup> and CHENG C. HSU<sup>2</sup>

Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada

**The solubility of cyclopropane gas in acetic, propionic, *n*-butyric, *i*-butyric, and *n*-valeric acids has been measured over the temperature range of 0-40°C at a partial gas pressure of one atmosphere. The experimental error is estimated to be within 0.5%. The results show that the solubility increases with increasing chain length in the homologous series.**

Gas solubilities provide useful information for the study of highly nonideal liquids such as the carboxylic acids which tend to associate, by hydrogen bonding, to form dimers. The solubilities of several gases in acetic have been reported in the literature (2, 8). Very few solubility data exist, however, for nonpolar gases in the other carboxylic acids.

In this work, an experimental investigation of the solubilities of nonpolar gases in several carboxylic acids has been made, employing an apparatus based on the original design of Markam and Kobe (9). The solubility of cyclopropane gas in acetic, propionic, *n*-butyric, *i*-butyric, and *n*-valeric acids has been measured over the temperature range of 0-40°C at a partial gas pressure of 1 atm. Reliable density data for these acids are also presented for the same temperature range.

The reliability of the equipment was checked by determination of the solubilities of carbon dioxide in water and cyclopropane in aliphatic alcohols.

## EXPERIMENTAL

The Ostwald type of apparatus which was constructed for this study was based on the original design of Markam

and Kobe (9), but also included the modifications suggested by Yen and McKetta (14). The measurement of the solubility of a gas in a liquid using this type of apparatus involves four main steps. A sample of the liquid solvent must be measured at a gas partial pressure of 1 atm. The saturated gas and liquid solvent are then mixed until an equilibrium quantity of the gas has dissolved at the temperature of the experiment. Finally, the volume of the saturated gas remaining, at a partial gas pressure of 1 atm, is determined. In actual operation, at least two equilibrium positions are determined at different partial pressures of gas; one above 760 mm Hg and one below. The equilibrium position at a partial pressure of 1 atm is then obtained by linear interpolation. The total pressure corresponding to the partial pressure of the solute is calculated from vapor pressure data by assuming ideal gas mixture.

The difference in the gas volumes before and after dissolution permits the calculation of the gas solubility in terms of the Bunsen coefficient which is defined as: "the volume of gas, reduced to 0°C and 760 mm Hg, which is absorbed by a unit volume of solvent, at the temperature of the measurement, under a partial gas pressure of 760 mm Hg."

The solubility in terms of mole fraction is easily calculated from the Bunsen coefficient.

The volume of the liquid solvent was determined by isolating it in a previously calibrated Pyrex bulb. The

<sup>1</sup> Present address, Research Center, Du Pont of Canada Ltd., Kingston, Ont., Canada

<sup>2</sup> To whom correspondence should be addressed.