(12) Hammer, R. R. Ph.D. Thesis, University of Washington, Seattle, WA, 1963.
(13) Hammer, R. R.; Gregory, N. W. *J. Phys. Chem.* **1962**, *66*, 1705.
(14) Jellinek, K.; Koop, R. *Z. Phys. Chem., Abt. A* **1929**, *145*, 305.
(15) Ringwald, O. E. Doctoral Dissertation, Princton University, Princeton, NJ, 1949.
(16) Kangro, W.; Bernstorff, H. *Z. Anorg. Allg. Chem.* **1950**, *263*, 316.
(17) Schafer, H. *Z. Anorg. Allg. Chem.* **1949**, *259*, 53.
(18) Givan, A.; Loewenschuss, A. *J. Raman Spectrosc.* **1977**, *6*, 84.
(19) Loewenschuss, A.; Givan, A. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 74.
(20) Shannon, J. S.; Swan, J. M. *Chem. Commun.* **1965**, *3*, 33.
(21) Matsumoto, K.; Kiba, N.; Takeuchi, T. *Talanta* **1975**, *22*, 321.
(22) Naumova, T. N.; Zhevnina, L. S.; Poponova, R. V.; Chupakhin, M. S.; Stepin, B. D. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 13.
(23) Fowler, R. M.; Medford, S. S. *Inorg. Chem.* **1976**, *15*, 473.
(24) Rustad, D. S.; Gregory, N. W. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 521.
(25) Kangro, W.; Petersen, E. *Z. Anorg. Allg. Chem.* **1950**, *261*, 157.
(26) Schafer, H.; Oehler, E. *Z. Anorg. Allg. Chem.* **1953**, *271*, 206.
(27) "JANAF Thermochemical Tables"; Dow Chemical Co.: Midland, MI, revised Dec 31, 1970.
(28) "JANAF Thermochemical Tables"; Dow Chemical Co.: Midland, MI, revised Sept 30, 1979.
(29) Frey, R. A.; Werder, R. D.; Günthard, Hs. H. *J. Mol. Spectrosc.* **1970**, *35*, 260.
(30) Mapes, W. H.; Gregory, N. W. *J. Chem. Eng. Data* **1968**, *13*, 249.

Received for review August 31, 1982. Accepted January 21, 1983.

# Binary Gaseous Diffusion Coefficients. Air with Methylfuran Derivatives

**Ricardo Alvarez, Ignacio Medina, Julio L. Bueno, and José Coca***
*Department of Chemical Engineering, University of Oviedo, Oviedo, Spain*

**Binary gaseous diffusion coefficients at 1-atm pressure of air with methylfuran derivatives were measured at three temperatures by the capillary tube method of Stefan–Winkelmann: 2-methylfuran (49, 56.5, 61 °C), 2,5-dimethylfuran (49, 65, 80 °C), 2-methyltetrahydrofuran (49, 61, 71.7 °C), and 2,5-dimethyltetrahydrofuran (49, 65, 80 °C). Experimental results are compared with those predicted by the Chen–Othmer and Slattery–Bird equations. Some regularities in the behavior of furan and tetrahydrofuran homologous series are observed.**

Furan derivatives have been used as solvents and as starting materials for polymer compounds. An effective design of separation and reaction processes involving an organic compound in the gas phase requires reliable data on the gaseous diffusivities. There are equations and correlations available that predict diffusion coefficients with a reasonable accuracy but, under certain conditions or for complex molecules, experimental data are indispensable.

Using the Stefan–Winkelmann technique, we measured binary gaseous diffusion coefficients at 1 atm and three temperatures for the following systems: air-2-methylfuran, air-2,5-dimethylfuran, air-2-methyltetrahydrofuran, and air-2,5-dimethyltetrahydrofuran.

## Experimental Section

The experimental technique was identical with that described in previous works (*1*–*3*). There are several sources of error in any experimental measurement of diffusivities based on the Stefan–Winkelmann technique (*4*, *5*) which are worthy of consideration in relation to the apparatus used in this work.

1. Cooling effect at the liquid–gas interface. This effect is due to the evaporation of the liquid in the capillary tube. It may be considered negligible given the cell used (0.3-cm i.d. × 20-cm length), there being in all the experiments an initial diffusion length of at least 9 cm.

2. Turbulence at the cell top. Mixing effects at the cell top may disturb the concentration profile inside the capillary cell and, therefore, invalidate the stagnant-film assumption. It was shown experimentally that, by use of airflows between 100 and 450 $cm^3$/min, a good reproductivity of data was obtained. In all the experiments in this work an airflow of 250 $cm^3$/min was used.

3. Surface tension effect at the liquid–gas interface. The liquid meniscus may cause a decrease in the vapor pressure at the interface in accordance with Kelvin's equation. For the systems measured in this work this effect was negligible.

4. Free convection inside the cell. This effect can arise because of the difference in density between the vapors produced from the liquid inside the cell and the inert sweeping gas. In our case this effect is not relevant as the vapor density is higher than the air density at the operating conditions.

An important advantage of the apparatus used is that thermal gradients inside the diffusion cell are kept to a minimum. This is achieved by using condensing vapors as heat-transfer media.

Table I. Critical Constants and Boiling Temperatures Used in Calculations of Vapor Pressures To Determine Diffusion Coefficients

| substance | $T_c$, K | $P_c$, atm | $V_c$, $cm^3$ $g\text{-}mol^{-1}$ | $T_b$, °C | ref |
|---|---|---|---|---|---|
| air | 132 | 37.2 | 90.5 | | *8* |
| 2-methylfuran | 528 | 46.6 | 246 | 63.8 | *8* |
| 2-methyltetrahydrofuran | 537 | 37.1 | 267 | 80 | *8* |
| 2,5-dimethylfuran | 559 | 41.1 | 304 | 93 | *a* |
| 2,5-dimetiltetrahydrofuran | 552 | 36.1 | 339 | 91 | *a* |

[a] Estimated values.

Table II. Experimental and Calculated Diffusion Coefficients $D_{AB}$ ($cm^2$ $s^{-1}$) for Air-Methylfuran Derivatives at 760 mmHg

| $T$, °C | $D_{AB,exptl}$ | $D_{AB,calcd}$ (*10*) | $D_{AB,calcd}$ (*11*) | $n$ |
|---|---|---|---|---|
| | | Air-2-Methylfuran | | |
| 49 | 0.0981 | 0.1025 | 0.1061 | |
| 56.5 | 0.1027 | 0.1069 | 0.1106 | 1.99 |
| 61 | 0.1055 | 0.1096 | 0.1134 | |
| | | Air-2-Methyltetrahydrofuran | | |
| 49 | 0.0992 | 0.0977 | 0.0969 | |
| 61 | 0.1067 | 0.1044 | 0.1036 | 1.93 |
| 71.7 | 0.1131 | 0.1106 | 0.1097 | |
| | | Air-2,5-Dimethylfuran | | |
| 49 | 0.0825 | 0.0900 | 0.0970 | |
| 65 | 0.0912 | 0.0983 | 0.1060 | 1.93 |
| 80 | 0.0985 | 0.1063 | 0.1147 | |
| | | Air-2,5-Dimethyltetrahydrofuran | | |
| 49 | 0.0666 | 0.0850 | 0.0930 | |
| 65 | 0.0734 | 0.0928 | 0.1016 | 1.99 |
| 80 | 0.0800 | 0.1004 | 0.1100 | |

0021-9568/83/1728-0155$01.50/0 © 1983 American Chemical Society

Table III. Diffusion Coefficients at 15, 20, and 25 °C

| substance | 15 °C | $\Delta D$ | 20 °C | $\Delta D$ | 25 °C | $\Delta D$ |
|---|---|---|---|---|---|---|
| furan | 0.0997 | | 0.1044 | | 0.1107 | |
| 2-methylfuran | 0.0786 | 0.0211 | 0.0813 | 0.0231 | 0.0841 | 0.0266 |
| 2,5-dimethylfuran | 0.0666 | 0.0331 | 0.0689 | 0.0355 | 0.0712 | 0.0395 |
| tetrahydrofuran | 0.0935 | | 0.0967 | | 0.0998 | |
| 2-methyltetrahydrofuran | 0.0801 | 0.0134 | 0.0828 | 0.0139 | 0.0825 | 0.0143 |
| 2,5-dimethyltetrahydrofuran | 0.0533 | 0.0402 | 0.0552 | 0.0415 | 0.0571 | 0.0427 |

The following vaporizing liquids were used to obtain the desired temperatures: hexane-acetone (azeotropic mixture), 49 °C; acetone, 56.5 °C; chloroform, 61 °C; methanol, 65 °C; benzene-isopropyl alcohol (azeotropic mixture), 71.7 °C; benzene, 80 °C.

The solvents used were Merck synthesis grade (2-methylfuran and 2-methyltetrahydrofuran) and Aldrich pure grade (2,5-dimethylfuran and 2,5-dimethyltetrahydrofuran). They were distilled in a packed Oldershaw column with automatic control of the reflux ratio. The purity of the solvents after distillation was checked by gas chromatography using a dinonyl phthalate column, the liquid phase being supported on glass beads of 0.016-cm diameter.

## Results and Discussion

The binary diffusion coefficients were calculated from eq 1 based on a quasi-steady-state analysis of the evaporation process (*2*, *6*, *7*):

$$z_i = -2z_0 + D_{AB}K(t_i/z_i) \qquad (1)$$

where

$$K = \frac{2PM_A}{RT\rho_A}\ln(1 - p_A/P) \qquad (2)$$

To determine $p_A$, the vapor pressure of the solvent at the interfacial conditions, we used the Frost-Kalkwarf-Thodos (*8*) equation. Critical constants were estimated by the Riedel (*8*) and Lydersen (*9*) correlations, when experimental data were not available. A summary of the critical constants and boiling temperatures of the solvents is shown in Table I. Densities were measured experimentally with a 5-cm$^3$ pycnometer.

Each diffusion coefficient, $D_{AB}$, was determined by adjusting a set of 15-20 data points of $z_i$ vs. $t_i/z_i$ by the least-squares method, the linear regression index being about 0.9999 for all systems.

The high-temperature values of diffusion coefficients at several temperatures are given in Table II.

The temperature dependence of the diffusion coefficient is usually obtained by fitting the experimental data of ln $D_{AB}$ vs. ln $T$; the exponent $n$ for a correlation of the type $D_{AB} \sim T^n$ is given for each system in Table II. These values for the exponent $n$ are higher than the values suggested by prediction equations (*10*, *11*).

Calculated values of diffusion coefficients from Chen-Othmer (*10*) and Slattery-Bird (*11*) equations are also given in Table II. The Chen-Othmer equation gives values closer to the experimental ones than the Slattery-Bird equation, although deviations as high as 22% are observed for the air-2,5-dimethyltetrahydrofuran system.

A comparison of diffusivities of the systems studied in this work together with furan and tetrahydrofuran data, reported in a previous work (*2*), shows certain regularities, although the number of compounds in every homologous series is too small for general quantitative conclusions to be drawn. From the extrapolated diffusivity data shown in Table III the following features can be observed: (a) Diffusivities are higher for similar molecules when the heterocycle ring is aromatic (furan series) than when it is saturated (tetrahydrofuran series). (b) Diffusivities decrease in both series as the number of methyl groups increases. (c) Diffusivity ratios at different temperatures for two compounds, within every series, remain constant. The highest deviations are shown by 2,5-dimethyltetrahydrofuran; its behavior could be explained on the basis of the critical properties, which were estimated, and its molecular geometry. It was shown by NMR spectra that the 2,5-dimethyltetrahydrofuran used in this work was formed by an equimolecular mixture of cis and trans isomers.

## Glossary

| | |
|---|---|
| $D_{AB}$ | molecular diffusion coefficient, cm$^2$ s$^{-1}$ |
| $K$ | constant for each system defined by eq 2, dimensionless |
| $M$ | molecular weight |
| $n$ | temperature exponent |
| $P$ | total pressure, atm |
| $p_A$ | partial pressure at the interface, atm |
| $P_c$ | critical pressure, atm |
| $R$ | gas constant, atm cm$^3$ K$^{-1}$ g-mol$^{-1}$ |
| $t$ | time, s |
| $T$ | absolute temperature, K |
| $T_b$ | boiling point temperature, °C |
| $T_c$ | critical temperature, K |
| $V_c$ | critical volume, cm$^3$ g-mol$^{-1}$ |
| $\rho$ | density, g cm$^{-3}$ |
| $z_0$ | initial interface depth, cm |
| $z_i$ | drop of the interface depth, cm |
| $\Delta D$ | methyl-group contributions to the diffusivities of furan and tetrahydrofuran |

**Registry No.** 2-Methylfuran, 534-22-5; 2,5-dimethylfuran, 625-86-5; 2-methyltetrahydrofuran, 96-47-9; 2,5-dimethyltetrahydrofuran, 1003-38-9.

## Literature Cited

(1) Alvarez, R.; Bueno, J. L.; Coca, J. *J. Chem. Eng. Jpn.* **1981**, *14*, 239.
(2) Bueno, J. L.; Coca, J.; Alvarez, R.; Villanueva, A. F. *J. Chem. Eng. Data* **1980**, *25*, 27.
(3) Coca, J.; Bueno, J. L.; Alvarez, R. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 219.
(4) Altshuller, A. P.; Cohen, J. R. *Anal. Chem.* **1960**, *32*, 802.
(5) Pommershein, J. M. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 1.
(6) Coca, J.; Bueno, J. L.; Alvarez, R. *Polym. Bull.* **1979**, *1*, 459.
(7) Wilhem, E.; Battino, R. *J. Chem. Eng. Data*, **1975**, *20*, 399.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids"; McGraw-Hill: New York, 1977.
(9) Lydersen, A. L. *Univ. Wis., Eng. Exp. Stn., Rep.* **1955**, 3.
(10) Chen, N. H.; Othmer, D. F. *J. Chem. Eng. Data* **1962**, *7*, 37.
(11) Slattery, J. C.; Bird, R. B. *AIChE J.* **1958**, *4*, 137.

Received for review April 8, 1982. Accepted December 6, 1982.