ject to a certain amount of uncertainty. A 5% error in the slope of a plot of the major axis dimension versus the equivalent spherical diameter would result in a 50% error in the amplitude of oscillation. This magnitude of uncertainty would account for most of the system to system variation seen in Figure 1. Brunson and Wellek (1970) reviewed several theories for physical mass transfer in drops whose surface area could be described by Equation (1). For the reviewed theories, the percent error in the mass transfer coefficient is one-fourth as large as the percent error in the amplitude of oscillation. Thus, a 50% error in the amplitude of oscillation would lead to less than a 13% error in the calculated mass transfer coefficient. It must be kept in mind, however, that the data in Table 1 is based on chemically pure systems. Impurities could cause even greater deviation in the amplitude of oscillation and the rate of mass transfer.

LITERATURE CITED

Angelo, J. B., E. N. Lightfoot, and D. W. Howard, "Generalization of the Penetration Theory for Surface Stretch: Application to Forming and Oscillating Drops," *AIChE J.*, **12**, 751 (1966).

Brunson, R. J., and R. M. Wellek, "Mass Transfer Within Oscillating Liquid Droplets," *Can. J. Chem. Eng.*, **48**, 267 (1970).

Harmathy, T. Z., "Velocity of Large Drops and Bubbles in Media of Infinite or Restricted Extent," *AIChE J.*, **6**, 281 (1960).

Klee, A. J. and R. E. Treybal, "Rate of Rise or Fall of Liquid Drops," *ibid.*, **2**, 444 (1956).

Rose, P. M., "Mass Transfer from Single Oscillating Drops," Ph.D. thesis, Ill. Institute of Technology (1965).

Schroeder, R. R., and R. C. Kintner, "Oscillations of Drops Falling in a Liquid Field," *AIChE J.*, **11**, 5 (1965).

Shah, Y. T., "Simultaneous Mass Transfer and Chemical Reaction in a Case of Time-Dependent Interfacial Area," *ibid.*, **18**, 1070 (1972).

Wellek, R. M., W. V. Andoe, and R. J. Brunson, "Mass Transfer with Chemical Reaction Inside Single Droplets and Gas Bubbles: Mathematical Mechanisms," *Can. J. Chem. Eng.*, **48**, 645 (1970).

Manuscript received February 6, 1973; revision received April 10 and accepted April 12, 1973.

Diffusivities of Propane in Normal Paraffin, Chlorobenzene, and Butanol Solvents

WALTER HAYDUK, RICARDO CASTAÑEDA
HOWARD BROMFIELD and RAY R. PERRAS

Department of Chemical Engineering
University of Ottawa, Ottawa, Canada K1N 6N5.

Liquid phase diffusion coefficients for dilute solutes are commonly related to some parameter describing the solute molecular size, solvent viscosity, and solvent molar volume as well as many other parameters, but almost without exception including the system temperature. The relationship between these variables has been investigated based on hydrodynamic considerations, absolute rate theory, and by assuming similarity between diffusion processes in gases and liquids. In all cases, however, it would be desirable to test the functional dependence of diffusivity on each different variable by actual experiment. Such a procedure was alluded to by Hildebrand (1971) in his discussion concerning studies of liquid phase diffusion. Unfortunately, solute and solvent properties cannot be independently changed since all fluid properties vary with temperature, for example. Nonetheless, it is noted that although most empirical correlations contain the system temperature as a separate variable, strong support for its inclusion in correlations appears to be lacking, particularly for simple (nonaqueous) liquid solutions. The temperature range for diffusivity measurements is often small and experiments are seldom chosen to separate the effect of temperature.

It has been previously shown by Hayduk and Cheng (1971) that for many systems the diffusivity is simply related to the solvent (or solution) viscosity and apparently not dependent on temperature as a primary variable. This was expressed as

$$D = A\,\mu^{B} \tag{1}$$

EXPERIMENT

Experiments were performed using the steady state capillary cell method described earlier by Malik and Hayduk (1968). Each cell was constructed of a 0.1080 ± 0.0005 cm precision bore capillary, sealed into a glass tube equipped with two vacuum stopcocks for charging and purging the cell with deaerated solvent. The top portion of the capillary was joined to a second capillary stem, which was at least 10 cm in length, also of the same size precision bore for some experiments, and of smaller bore (0.0504 ± 0.0005 cm) for others. Both types of cells were found to be equally satisfactory. The cells were completely filled with deaerated liquid up to a level of at least 2 cm in the lower capillary, and immersed in a constant temperature bath controlled to ± 0.01°C. The stem of the capillary was continually exposed to a small flow of propane gas while a steady state concentration profile was allowed to develop in the solution, a procedure requiring about 10 to 24 hours. The absorption rate was subsequently measured by introducing a bead of propane-saturated solvent into the top of the capillary stem by means of a syringe. An accurate measurement by cathetometer of the rate of descent of the bead and the length of the diffusion path, along with the barometric pressure, solubility data corrected to the prevailing partial pressure, permitted calculation of the diffusion coefficient.

Beginning with Fick's law the equations for evaluating the diffusivities from experimental measurements as derived by Malik and Hayduk (1968) are as follows:

$$D = \frac{n_A\, L}{\rho_{AE} \ln (1 + \rho_{A0})/(1 + \rho_{AL})} \tag{2}$$

$$D = \frac{N_A\, L}{C_{AE} \ln (1 + C_{A0})/(1 + C_{AL})} \tag{3}$$

Equation (2) was expected to apply where the total mass concentration along the diffusion path remained nearly constant and Equation (3) for a nearly constant total molar concentration. Due consideration was given to the continuous, albeit small, volumetric expansion of the enclosed solvent resulting from the actual volume in solution of absorbed propane. An effective density for dissolved propane of 565 kg/m^3 at 25°C as obtained by Sage et al. (1934) in solutions of petroleum fractions was used. This density is considerably greater than that for liquid propane at 25°C and its saturation pressure, of 496 kg/m^3. That the apparent density of dissolved gases in solution is greater than for liquified gases at their saturation pressures was observed as early as 1931 by Horiuti. The effective density of dissolved propane was considered to have the same temperature coefficient as that for liquid propane. Because the densities of the paraffin solvents were closer to those of propane than the corresponding molar volumes, Equation (2) was used in evaluating diffusivities in the paraffin solvents. On the other hand, the molar volumes of chlorobenzene and butanol were similar to those of dissolved propane so that Equation (3) was used for those solvents. Using the inappropriate equation resulted in differences in diffusivity of up to 2.7%.

The effective solute diffusivity was considered to remain constant along the diffusion path. Hence the diffusivities as calculated from the experimental results represented integral average diffusivities corresponding to the average concentration along the diffusion path. The solute concentration varied from the saturated solubility at the gas-liquid interface to essentially zero in the bulk of the diffusion cell. Because of the relatively low average concentration employed (less than 7%) the results can be considered to approximate diffusivities at infinite dilution.

The propane used in these experiments was Instrument grade having a specified minimum purity of 99.5 mole % purchased from the Matheson Company. The solvents were all purchased from the Fisher Chemical Company, having specified minimum purities of 99.0 mole %. The densities, viscosities and propane solubilities obtained from literature sources are given in Table 1.

RESULTS AND DISCUSSION

The diffusivities at 25°C for propane in hexane, heptane, octane, hexadecane, *n*-butanol, and chlorobenzene, and at 0°C and 50°C in the last two solvents as well, are listed in Table 1. These data are also shown in Figure 1 as the logarithm diffusivity versus logarithm solvent viscosity. Diffusivities at 25°C of propane in 95% *n*-heptanol and *n*-octanol as measured by Dim et al. (1971), also shown in Figure 1, are slightly lower than those in the purer, essentially water-free solvents but lie within 10% of the log D-log μ relation obtained in this work. Diffusivities in water (or its solutions) are usually lower than those in other solvents of similar viscosity. The equation of the line describing the propane diffusivity-solvent viscosity relation was obtained as follows:

$$D = 0.591\ (10^{-10})\ \mu^{-0.545} \tag{4}$$

This equation is expected to apply at any temperature in the range at least from 0°C to 50°C, and in any solvent with the exception of solvents in which molecular interactions are extreme such as in water.

Hayduk and Cheng (1971) found that the self-diffusivity of a substance was expressed by the same diffusivity-viscosity relation as that obtained in other solvents. The self-diffusivity of liquid propane should therefore cor-

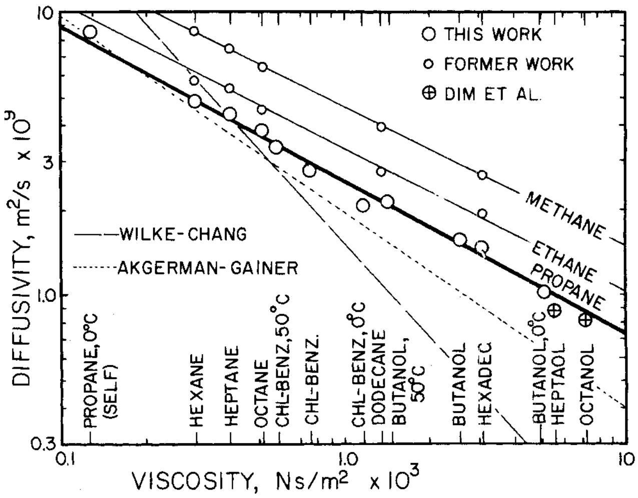

Fig. 1. Diffusivities of dissolved propane in liquid solutions.

TABLE 1. SOLVENT PROPERTIES AND PROPANE DIFFUSIVITIES

Solvent	Temp., °C	Density (a), kg/m^3 × 10^{-3}	Viscosity, Ns/m^2 × 10^3	x	Solubility L	Ref.	Diffusivity, m^2/s × 10^9
Hexane	25	0.6548	0.2985 (a)	0.1166	24.0	(d)	4.87 ± 0.20 (g)
Heptane	25	0.6795	0.3967 (a)	0.117	21.65	(e)	4.40 ± 0.08
Octane	25	0.6985	0.5151 (a)	0.120	—	(f)	3.83 ± 0.17
Hexadecane	25	0.7700	3.095 (a)	0.137	12.93	(d)	1.48 ± 0.02
Chlorobenz.	25	1.1016	0.755 (c)	0.0570	14.16	(d)	2.77 ± 0.09
Butanol	25	0.8060	2.605 (b)	0.0367	10.07	(d)	1.57 ± 0.04
Chlorobenz.	0	1.1280	1.180 (b)	0.1034	25.4	(d)	2.08 ± 0.01
Butanol	0	0.8242	5.186 (b)	0.0706	18.60	(d)	1.02 ± 0.01
Chlorobenz.	50	1.0746	0.576 (b)	0.0353	9.12	(d)	3.35 ± 0.10
Butanol	50	0.7867	1.411 (b)	0.0226	6.43	(d)	2.17 ± 0.08

(a) Rossini et al. (1953)
(b) Weast, editor (1968); extrapolated
(c) Caldwell and Babb (1956)
(d) Hayduk and Castaneda (1973)
(e) Hayduk et al. (1972)
(f) Thomsen and Gjaldbaek (1963)
(g) ± standard deviation of results from mean

respond to the viscosity of liquid propane as if it were a solvent. While the self-diffusivity of propane has not (to the authors' knowledge) been determined, a correlation by Dullien (1972) is available for estimation:

$$\frac{\mu V D}{RT} = 0.129 \times 10^{-16} \sigma^2 (\Omega_D \Omega_V)^{1/2} T_C \qquad (5)$$

Based on collision integrals for diffusion and viscosity and Lennard-Jones parameters as tabulated by Bird et al. (1960) the self-diffusivity of propane at 0°C was calculated using Equation (5) as 8.60 nm^2/s. The viscosity of liquid propane was reported by Huang et al. (1966) as 0.126 mN s/m^2 at 0°C and the saturation pressure. Assuming that the self-diffusivity at the saturation pressure can be compared with that at atmospheric pressure, the calculated self-diffusivity is shown in Figure 1. Considering that propane diffusivities are presented in solvents for viscosities which change by a factor of over 50, the simple linear relation between log D-log μ, including that for the self-diffusivity, is considered most significant.

Diffusivities in n-paraffin solvents of methane as reported by Hayduk and Buckley (1972) and of ethane as reported by Hayduk and Cheng (1970) are also shown in Figure 1. The diffusivities of small molecules have been considered by Hildebrand and co-workers (1964, 1965) to be related to the cross-sectional or collision area of the diffusing molecule (σ^2). As a result, in any single solvent at constant temperature the product $D\sigma^2$ would be expected to be constant. These factors for methane, ethane, and propane for diffusivities in the common solvents, hexane, heptane, octane, and hexadecane are indeed found to be at least approximately constant. It should be pointed out that while $D\sigma^2$ may remain constant for small or essentially spherical diffusing molecules, it would be expected to increase for elongated molecules such as n-paraffins, which have been shown by Hayduk and Buckley (1972) to have diffusivities greater by as much as 30% when compared with other essentially spherical molecules of the same molar volume.

In Figure 1 are shown the propane diffusivities as predicted by the Wilke-Chang correlation (1955) and more recent Akgerman and Gainer correlation (1972). While the latter correlation is apparently somewhat more successful, neither predicts propane diffusivities accurately, particularly in viscous solvents. In summary, it appears that the influence of temperature on propane diffusivities in chlorobenzene and butanol is only indirect by virtue of its effect on solvent viscosity. To provide an even better test as to whether diffusivity is completely independent of temperature as a separate variable, measurements over an even greater range in temperature are required. Furthermore, diffusivities should be preferably measured in nonassociating solutions so that the extent of association should not be variable with temperature.

ACKNOWLEDGMENT

The authors gratefully acknowledge an operating grant from the National Research Council of Canada.

NOTATION

A, B = constants based on relation between diffusivity and solvent viscosity
C_{AE} = apparent molar concentration dissolved propane kg moles/m^3
C_{A0} = molar concentration propane at interface, kg moles propane/m^3
C_{AL} = molar concentration propane in bulk of cell, kg moles propane/m^3
D = diffusion coefficient of dilute solute, m^2/s
L = Ostwald coefficient of solubility (Table 1)
L = diffusion path length, m [Equations (2), (3)]
n_A = mass flux, kg/m^{2}s
N_A = molar flux, kg moles/m^{2}s
R = gas constant
T = absolute temperature, °K
x = solubility in mole fraction propane
μ = dynamic viscosity, Ns/m^2
σ = Lennard-Jones distance parameter
Ω_D, Ω_V = collision integrals for diffusion, and for viscosity
ρ_{AE} = apparent mass concentration dissolved propane, kg/m^3
ρ_{A0} = mass concentration propane at interface, kg propane/m^3
ρ_{AL} = mass concentration propane in bulk of cell, kg propane/m^3

LITERATURE CITED

Akgerman, A., and J. L. Gainer, "Predicting Gas-Liquid Diffusivities," *J. Chem. Eng. Data*, **17**, 372 (1972).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, pp. 744-746, Wiley, New York (1960).

Caldwell, C. S., and A. L. Babb, "Diffusion in Ideal Binary Liquid Mixtures," *J. Phys. Chem.*, **60**, 51 (1956).

Dim, A., G. R. Gardner, A. B. Ponter and T. Wood, "Diffusion of Carbon Dioxide into Primary Alcohols and Methyl Cellulose Ether Solutions," *J. Chem. Eng.* (Japan), **4**, 92 (1971).

Dullien, F. A. L., "Predictive Equations for Self-Diffusion in Liquids: a Different Approach," *AIChE J.*, **18**, 62 (1972).

Hayduk, W., and S. C. Cheng, "Review of Relation Between Diffusivity and Solvent Viscosity in Dilute Liquid Solutions," *Chem. Eng. Sci.*, **26**, 635 (1971).

———., and W. D. Buckley, "Effect of Molecular Size and Shape on Diffusivity in Dilute Liquid Solutions," *ibid.*, **27**, 1997 (1972).

———., E. B. Walter, and P. Simpson, "Solubility of Propane and Carbon Dioxide in Heptane, Dodecane, and Hexadecane," *J. Chem. Eng. Data*, **17**, 59 (1972).

———., and R. Castañeda, "Solubilities of the Highly Soluble Gases, Propane and Butane, in Normal Paraffin and Polar Solvents," *Can. J. Chem. Eng.*, **50**, (1973).

Hildebrand, J. H., "Motions of Molecules in Liquids: Viscosity and Diffusivity," *Science*, **174**, 490 (1971).

Horiuti, J., "On the Solubility of Gas and Coefficient of Dilation by Absorption," *Sci. Papers, Inst. Phys. Chem. Res.* (Tokyo), **17**, 125 (1931).

Huang, E. T. S., G. W. Swift, and F. Kurata, "Viscosities of Methane and Propane at Low Temperature and High Pressures," *AIChE J.*, **12**, 932 (1966).

Malik, V., and W. Hayduk, "A Steady-State Capillary Cell Method for Measuring Gas-Liquid Diffusion Coefficients," *Can. J. Chem. Eng.*, **46**, 462 (1968).

Nakanishi, K., E. M. Voigt, and J. H. Hildebrand, "Quantum Effects in the Diffusion of Gases in Liquids at 25°C," *J. Chem. Phys.*, **42**, 1860 (1965).

Ross, M., and J. H. Hildebrand, "Diffusion of Hydrogen, Deuterium, Nitrogen, Argon, Methane, and Carbon, Tetrafluoride in Carbon Tetrachloride," *ibid.*, **40**, 2397 (1964).

Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Properties of Hydrocarbons and Related Compounds," A.P.I. Project 44, Am. Petrol. Inst., New York (1953).

Sage, B. H., W. N. Lacey, and J. G. Schaaftsma, "Solubility of Propane in Two Different Oils," *Ind. Eng. Chem.*, **26**, 874 (1934).

Thompsen, E. S., and J. C. Gjaldbaek, "The Solubility of Propane in Non-polar Solvents," *Acta Chem. Scand.*, **17**, 134 (1963).

Weast, R. C., (ed.), *Handbook of Chemistry and Physics*, **48**, F-36, Chemical Rubber, Cleveland, Ohio (1967-68).

Wilke, C. R., and Pin Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.*, **1**, 264 (1955).

Manuscript received February 13, 1973; revision received March 30 and accepted April 5, 1973.