pendence to a certain degree. This behavior could be due to the lack of information of μ_0, the gas phase viscosity data.

RECOMMENDED VALUES

Recommended values for viscosity of *n*-decane for temperatures from 100° to 460° F. and pressures from 200 to 8000 p.s.i.a. are presented in Table I, in which experimental data are also presented in parentheses. The density values were those of Sage and Lacey (*7*).

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LITERATURE CITED

(1) Brebach, W.J., Thodos, G., *Ind. Eng. Chem.* **50**, 1095–1100 (1958).
(2) Dolan, J.P., Starling, K.E., Lee, A.L., Eakin, B.E., Ellington, R.T., J. CHEM. ENG. DATA **8**, 396–9 (1963).
(3) Eakin, B.E., Ellington, R.T., *Trans. AIME* **216**, 85–91 (1959).
(4) Feldkirchner, H.L., Lee, A.L., Johnson, J.L., Eakin, B.E., "Novel Laboratory Equipment for Physical Property and Reaction Kinetic Studies," A.I.Ch.E. Meeting, Memphis, Tenn., February 2–5, 1964.
(5) Lee, A.L., Eakin, B.E., *Soc. Petrol. Engrs. J.* **4**, 274–9 (1964).
(6) Michels, A., Gibson, R.O., *Proc. Roy. Soc. London, Ser A* **134**, 288–307 (1931).
(7) Sage, B.H., Lacey, W.N., "Thermodynamic Properties of Lighter Paraffin Hydrocarbons and Nitrogen," Am. Petrol. Inst., New York, 1950.

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Liquid Phase Diffusion of Nonelectrolytes at High Dilution

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A correlation is presented for the prediction of diffusivities at high dilution in binary liquid solutions of nonelectrolytes. The correlation is based upon the empirical observation that $D\mu/T$ is nearly constant for self diffusion. The correlation is simple in nature, contains three constants and fits available data in the normal range of viscosities with a lower standard error than provided by other existing correlations.

THERE HAVE BEEN several recent significant theoretical contributions to the understanding of liquid phase diffusion. Despite this fact, empirical or semiempirical methods will likely continue to provide the most convenient and the most reliable estimation methods for liquid diffusivities for some time to come. The most widely used correlation for diffusion at high dilution is that of Wilke and Chang (*50, 51*); several others have put forward modifications or other equations (*17, 29, 39, 41*). All of these correlations have shortcomings when applied to the entire spectrum of available data; for example, difficulties have been encountered when the solute is highly polar (*10, 27*), when the solute has a low molecular weight, and when the solvent has a relatively large viscosity. The Wilke-Chang correlation also requires the estimation of an association parameter for polar solvents.

Despite the existence of several different theoretical approaches to liquid phase diffusion, it is possible to draw some general conclusions concerning the nature of independent variables which should affect the diffusion process. Diffusion rates are probably influenced by parameters reflecting molecular size and the strength of intermolecular forces. Although the necessary importance of solute-solvent interaction forces has been previously recognized (*28*), the only existing diffusivity correlation which allows for such effects is that of Sitamaran, Ibrahim, and Kuloor (*41*).

Several theoretical approaches (*2, 16, 35, 52*) suggest that the group $D\mu/T$ should be essentially constant with respect to temperature for a given solute-solvent pair. This prediction is borne out by available data with major exceptions occurring only at relatively high viscosities. The group $D\mu/T$ should then depend upon temperature-insensitive variables reflecting solute and solvent properties.

SELF DIFFUSION

Table I shows available data for self diffusion. Most theoretical approaches (*52*) indicate that for self diffusion the group $D\mu/T$ should be dependent upon variables reflecting molecular size, intermolecular forces, number of nearest neighbors, etc. However, the most striking feature of Table I is the relative constancy of $D\mu/T$ from one liquid to another. This conclusion is particularly apparent if water is treated as an exception along with substances such as liquid metals (*21*). The standard deviation of $D\mu/T$ in Table I is only 9%, without water. Obviously $D\mu/T$ (a nondimensionless group) will not have one and the same value for self-diffusion in all common liquids, but taking $D\mu/T$ to be empirically constant appears to be more in accord with the facts than taking $D\mu/T$ to vary inversely as $V^{1/3}$ (*35*) and /or inversely with the cohesive energy (*6*).

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Table I. Self-Diffusion Data

	T, ° K.	$10^5 D$, Sq. Cm./ Sec.	Ref.	$10^8 D\mu/T$, Cp. Sq. Cm./Sec. ° K.	V, Cu. Cm./ G. Mole	ΔH, Cal./ G. Mole
Methanol	298	2.21	*(15, 30)*	4.10	42	8491
Ethanol	298	1.01	*(11, 30)*	3.70	64	9400
n-Propanol	298	0.646	*(30)*	4.26	81	10030
Isopropanol	298	0.649	*(30)*	4.56	72	9729
n-Butanol	298	0.504	*(30)*	4.32	103	10460
tert-Butanol	308	0.497	*(30)*	4.4	103	9710
Cyclopentane	303	3.41	*(9)*	4.40	100	6529
Cyclohexane	298	1.38	*(23)*	4.18	117	7895
Benzene	298	2.14	*(14, 23)*	4.37	96	7353
Isopentane	298	5.30	*(23)*	3.91	118	5910
Neopentane	298	4.86	*(23)*	3.72	118	5430
n-Pentane	298	5.45	*(6)*	4.03	118	6120
n-Hexane	298	4.21	*(6)*	4.10	141	6896
n-Heptane	298	3.12	*(6)*	3.98	163	7575
n-Octane	298	2.00	*(6)*	3.43	185	8160
n-Nonane	298	1.70	*(6)*	3.83	207	8730
n-Decane	298	1.31	*(6)*	3.74	229	9400
n-Octadecane	323	0.46	*(6)*	3.33	...	...
n-Dicetyl	373	0.30	*(6)*	4.31	...	...
Water	298	2.10	*(11, 23)*	6.30	18.7	9708
Ethyl bromide	295.5	3.80	*(11)*	4.94	75	6550
CCl_4	298	1.41	*(48)*	4.29	102	7154
Nitromethane	298	2.11	*(23)*	4.40	56	6080
Acetone	298	4.77	*(23)*	4.92	74	6907

MUTUAL DIFFUSION

The empirical conclusion that $D\mu/T$ is essentially constant for self-diffusion can serve as a basis for a correlation of mutual diffusivities at high dilution. In comparison to self diffusion in the same solvent, mutual diffusion differs only through a change in the solute species. The ratio of $D\mu/T$ for mutual diffusion to $D\mu/T$ for self diffusion should be a function of parameters reflecting the ratio of solute size to solvent size and the ratio of solute-solvent interaction force to solvent-solvent interaction force. This conclusion follows since the solvent is the solute in the case of self diffusion. A logical form of correlation for mutual diffusion is therefore

$$\frac{D\mu}{T} = a \left(\frac{V_v}{V_u}\right)^b \left(\frac{\Delta H_v}{\Delta H_u}\right)^c \tag{1}$$

where a is the constant value of $D\mu/T$ for self diffusion. If the solute-solvent attractive forces are characterized to a first approximation by a pseudo latent heat, $\Delta H_{uv} = (\Delta H_v \, \Delta H_u)^{1/2}$, the term $(\Delta H_v/\Delta H_u)^{1/2}$ would represent the ratio of the solvent latent heat to this pseudo latent heat. This in turn is nearly equal to the ratio of the cohesive energy per mole for solvent-solvent interactions to that for solute-solvent interactions. The use of molar volume and latent heat of vaporization at the normal boiling point as temperature-insensitive variables reflecting the size and force effects appears to fulfill best the twin objectives of widespread applicability and a good fit to experimental data. Lennard-Jones parameters, for example, are not known for a wide enough range of substances.

In order to develop an equation of the form of Equation 1, 213 experimental mutual diffusivity measurements at high dilution were assembled from various sources (*1, 3–16, 19–26, 30–34, 37, 38, 40, 42–49*). No effort was made to include all available measurements; however, an attempt was made to cover a wide range of systems. Many of the measurements may have been subject to serious experimental error, but the use of a large number of points should serve to wash out any major directional errors in the set as a whole. Latent heats were obtained from the Giacalone equation and Riedel factor (*36*, Eq. 4–43) in cases where they were not available from standard sources. Molal volumes were estimated by the method of LeBas (*36*). Diffusivities were based on a concentration gradient driving force and a frame of reference giving no net volume flow.

As a check on the assumptions involved in Equation 1 a stepwise multiple regression was carried out with a digital computer to fit five constants with minimum standard deviation, giving

$$\frac{D\mu}{T} = 7.37 \times 10^{-9} \left[\frac{V_v^{0.174} \, \Delta H_v^{0.676}}{V_u^{0.221} \, \Delta H_u^{0.454}} \right] \tag{2}$$

which fits the combined data with a standard deviation of 19.2%. However, the combined data are fit with a standard deviation of only 19.5% by the following equation:

$$\frac{D\mu}{T} = 4.4 \times 10^{-8} \left(\frac{V_v}{V_u}\right)^{1/6} \left(\frac{\Delta H_v}{\Delta H_u}\right)^{1/2} \tag{3}$$

The exponents in Equation 3 are all within the 95% confidence limits of the exponents in Equation 2. Thus, the analysis behind Equation 1 seems to be borne out within the scatter of the data employed, and Equation 3 is, therefore, the recommended correlation for the prediction of diffusivities.

The variables employed in Equation 3 are similar to those employed by Sitamaran, Ibrahim, and Kuloor (*41*); however, the group $D\mu/T$ has been preserved in view of the self diffusion data and the apparent effect of temperature. Also, the variables ΔH_v and μ are not sufficiently independent of one another to warrant inclusion of both to a fitted power. V was a somewhat better correlating variable than molecular weight. The Sitamaran correlation gives a standard deviation of 26.3% for the assembled data while the Wilke-Chang correlation gives a standard deviation of 28.5%, with the multiplicative constant adjusted to the best value in both cases. Thus, in the present correlation the variance is reduced almost to half that attainable with previous empirical correlations. The standard deviation of the entire set of diffusivities when uncorrelated is 90%.

A simple interpretation may be placed on Equation 3. T represents the kinetic energy driving force for diffusion; μ represents the resistance to self diffusion in the particular solvent; and the terms on the right represent the adjustments to μ necessary to provide the resistance to mutual diffusion. These adjustments involve the first power of cohesive energies between solute and solvent and the square root of solute diameter. Logically the exponents should be positive, since large solute size and strong solute-solvent interaction forces should tend to hinder diffusion. There appears to be a slight tendency for the correlation to predict high for self-diffusion and for mutual diffusion when the solute and solvent are quite similar. This coincides with the probability that $(\Delta H_v \, \Delta H_u)^{1/2}$ overestimates the solute-solvent attraction when molecules are dissimilar.

The correlation seems to work satisfactorily when the solute is small or polar. Data for water as solvent or solute tend to be handled adequately despite the deviation of water self diffusion from the assumed constant value of $D\mu/T$. There are still difficulties for polar solvents of high viscosity as is illustrated by the fact that the correlation predicts a diffusivity 72% lower than experimental data for the diffusion of water in glycerol (*10, 18*). Thus it seems best to limit application of the correlation to cases where the resultant $D\mu/T$ should be less than 1.5×10^{-7} cp. sq. cm./° K. sec.

NOMENCLATURE

D = diffusivity at high dilution, sq. cm./sec.
ΔH = latent heat of vaporization at normal boiling point, cal./gram mole
T = absolute temperature, ° K.
V = molal volume at normal boiling point, cu. cm./gram mole
μ = viscosity of solvent, cp.

Subscripts

u = solute
v = solvent

LITERATURE CITED

(1) Anderson, D.K., Hall, J.R., Babb, A.L., *J. Phys. Chem.* **62**, 404 (1958).
(2) Bearman, R.J., *Ibid.*, **65**, 1961 (1961).
(3) Calderbank, P.H., *Trans. Inst. Chem. Engrs. (London)* **37**, 173 (1959).
(4) Caldwell, C.S., Babb, A.L., *J. Phys. Chem.* **59**, 1113 (1955); **60**, 51 (1956).
(5) Chang, Pin, Wilke, C.R., *Ibid.*, **59**, 592 (1955).
(6) Douglass, D.C., McCall, D.W., *Ibid.*, **62**, 1102 (1958).
(7) Dummer, E., *Z. Anorg. Allgem. Chem.* **109**, 49 (1919).
(8) Emanuel, A., Olander, D.R., J. CHEM. ENG. DATA **8**, 31 (1963).
(9) Fishman, E., Vassilades, T., *J. Phys. Chem.* **63**, 1217 (1959).
(10) Garner, F.H., Marchant, P.J.M., *Trans. Inst. Chem. Engrs. (London)* **39**, 397 (1961).
(11) Graupner, K., Winter, E.R.S., *J. Chem. Soc.* **1952**, p. 1145.
(12) Hammond, B.R., Stokes, R.H., *Trans. Faraday Soc.* **45**, 890 (1953).
(13) Herzog, R.O., Ilig, R., Kudar, H., *Z. Physik. Chem.* **A167**, 329, 343 (1933).
(14) Hiraoka, H., Izui, Y., Osugi, J., Jono, W., *Rev. Phys. Chem. Japan* **28**, 61 (1958).
(15) Hiraoka, H., Osugi, J., Jono, W., *Ibid.*, **28**, 52 (1958).
(16) Johnson, P.A., Babb, A.L., *Chem. Rev.* **56**, 387 (1956).
(17) Kamal, M.R., Canjar, L.N., *A.I.Ch.E. J.* **8**, 329 (1962).
(18) Lamm, O., Sjostedt, G., *Trans. Faraday Soc.* **34**, 1158 (1938).
(19) Lemonde, H., *Ann. phys.* **9**, 539 (1938).
(20) Lewis, J.B., *J. Appl. Chem. (London)* **5**, 228 (1955).
(21) Li, J.C.M., Chang, P., *J. Chem. Phys.* **23**, 518 (1955).
(22) Lyons, M.S., Sandquist, C.L., *J. Am. Chem. Soc.* **75**, 3896 (1953).
(23) McCall, D.W., Douglass, D.C., Anderson, E.W., *J. Chem. Phys.* **31**, 1555 (1959).
(24) Miller, C.C., *Proc. Roy. Soc. (London)* **A106**, 724 (1924).
(25) Mills, R., *J. Phys. Chem.* **67**, 600 (1963).
(26) Muchin, G.E., Faermann, G.P., *Z. Physik. Chem.* **121**, 180 (1926).
(27) Olander, D.R., *A.I.Ch.E. J.* **7**, 175 (1961).
(28) *Ibid.*, **9**, 207 (1963).
(29) Othmer, D.F., Thakar, M.S., *Ind. Eng. Chem.* **45**, 589 (1953).
(30) Partington, J.R., Hudson, R.F., Bagnall, K.W., *Nature* **169**, 583 (1952); *J. Chim. Phys.* **55**, 77 (1958).
(31) Randall, M., Longtin, B., Weber, J., *J. Phys. Chem.* **45**, 343 (1941).
(32) Reamer, H.H., Lower, J.H., Sage, B.H., J. CHEM. ENG. DATA **9**, 54 (1964).
(33) Reamer, H.H., Opfell, J.B., Sage, B.H., *Ind. Eng. Chem.* **48**, 275 (1955).
(34) Reamer, H.H., Sage, B.H., J. CHEM. ENG. DATA **4**, 296 (1959).
(35) Ree, F.M., Ree, T., Eyring, H., *Ind. Eng. Chem.* **50**, 1036 (1958).
(36) Reid, R.C., Sherwood, R.K., "Properties of Gases & Liquids," McGraw-Hill., New York, 1958.
(37) Ross, M., Hildebrand, J.H., *J. Chem. Phys.* **40**, 2397 (1964).
(38) Rossi, C., Bianchi, E., Rossi, A., *J. Chim. Phys.* **55**, 93 (1958).
(39) Scheibel, E.G., *Ind. Eng. Chem.* **46**, 2007 (1954).
(40) Scriven, L.E., Pigford, R.L., *A.I.Ch.E. J.* **4**, 439 (1958).
(41) Sitamaran, R., Ibrahim, S.H., Kuloor, N.R., J. CHEM. ENG. DATA **8**, 198 (1963).
(42) Stearn, A.E., Irish, E.M., Eyring, H., *J. Phys. Chem.* **44**, 981 (1940).
(43) Stokes, R.H., Dunlop, P.J., Hall, J.R., *Trans. Faraday Soc.* **49**, 886 (1953).
(44) Taylor, H.S., *J. Chem. Phys.* **6**, 331 (1938).
(45) Thomas, W.J., Furzer, I.A., *Chem. Eng. Sci.* **17**, 115 (1962).
(46) Thovert, J., *Ann. Chim. Phys.* (7), **26**, 366 (1902).
(47) Vivian, J.E., King, C.J., *A.I.Ch.E. J.* **10**, 220 (1964).
(48) Watts, H., Alder, B.J., Hildebrand, J.H., *J. Chem. Phys.* **23**, 659 (1955).
(49) White, J.R., *Ibid.*, **23**, 2247 (1955).
(50) Wilke, C.R., *Chem. Eng. Progr.* **45**, 218 (1949).
(51) Wilke, C.R., Chang, Pin, *A.I.Ch.E. J.* **1**, 264 (1955).
(52) Wilke, C.R., Prausnitz, J.M., Acrivos, Andreas, Petersen, E.E., Olander, D.R., *Ind. Eng. Chem.* **53**, 925 (1961).

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Size Measurement of Collected Drops

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MEASUREMENTS of drops in the size range from 5 to 250 microns can be performed using a number of techniques. The diversity of techniques and the technique chosen for any particular measurement can partially be attributed to various drop compositions, to the variety of collection methods and to the proposed sizing and counting techniques. In this study, the scope was limited to measurement with an optical microscope, and the liquids considered were water, dibutyl phthalate, and No. 2 heating oil. Six methods of sizing drops collected on slides or in cells were investi-