

Correlations for Prediction of Molecular Diffusivities in Liquids*

W. HAYDUK and B. S. MINHAS

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario K1N 9B4

New correlations have been developed for diffusivities in liquids at infinite dilution for normal paraffin solutions, for aqueous solutions, as well as generally for polar and non-polar solutions. The molar volume, parachor and radius of gyration for both solute and solvent were used as correlating parameters. The new correlations represent a significant improvement in accuracy for predicted diffusivities.

On a établi des corrélations nouvelles pour la diffusivité dans les liquides, à dilution infinie, pour les solutions de paraffines normales, les solutions aqueuses de même que de manière plus générale dans les solutions polaires ou non-polaires. On a employé, comme paramètres de corrélation, les volumes molaires, les parachors et les rayons de giration du soluté et du solvant. Les nouvelles corrélations représentent une amélioration importante de la précision avec laquelle les diffusivités peuvent être prédites.

Empirical correlations for the prediction of binary diffusion coefficients of non-electrolytes in liquids at infinite dilution have been reviewed by Ghai et al.⁽¹⁾ and Reid et al.⁽²⁾. The most general and best-known equation is that of Wilke and Chang⁽³⁾ which was intended for all solutes but contains a parameter to account for molecular association in water and other highly associated solvents:

$$D_{AB}^{\circ} = 7.4 (10^{-8}) (\phi M)^{0.5} T \mu_B^{-1} V_A^{-0.6} \dots \dots \dots (1)$$

Because of its generality and relative simplicity it cannot be used to predict diffusivities of high accuracy for all different types of molecular interactions, although the degree of success, even with associating solvents, is notable.

Another general correlation was developed by King et al.⁽⁴⁾ utilizing latent heats of vaporization as a measure of the intermolecular forces involved:

$$D_{AB}^{\circ} \mu_B T^{-1} = 4.4 (10^{-8}) (V_B/V_A)^{1/6} \cdot (\Delta H_B/\Delta H_A)^{0.5} \dots \dots \dots (2)$$

Of those tested, Equation (2) was shown by Reid et al.⁽²⁾ to give the smallest deviation from experimental results for a number of solutes in several selected organic solvents. It was found to give significantly smaller deviations than the Wilke-Change correlation.

A recent general correlation developed by Tyn and Calus⁽⁵⁾ utilized the parachor as a measure of molecular interaction. This correlation which was published recently enough to prevent its being discussed in the above-mentioned reviews is as follows:

$$D_{AB}^{\circ} = 8.93 (10^{-8}) T \mu_B^{-1} V_A^{1/6} V_B^{-1/3} (P_B/P_A)^{0.6} \dots (3)$$

Equation (3) was considered by the authors to be the best available general correlation for all solute-solvent systems and a significant improvement over both the Wilke-Change⁽³⁾ and King et al.⁽⁴⁾ equations. To be used in conjunction with Equation (3) were a number

of specific rules. The first was that water molecules should be treated as dimers in that the molar volume and parachor values should be doubled. Organic acid solutes should likewise be treated as dimers except when diffusing in water, methanol and butanol; then they should be treated as monomers. The final rule was that for diffusion of non-associating solutes in monohydroxy alcohols, a variable multiplying factor was to be used for the solvent molar volume and parachor which was related to the solvent viscosity:

$$n = 8 \mu_B \dots \dots \dots (4)$$

For use in Equation (3), parachor values were obtained from a compilation by Quayle⁽⁶⁾ or calculated by the addition method of Sugden⁽⁷⁾ also discussed by Reid et al.⁽²⁾. Since the parachor is related to the surface tension of liquids it was considered to be a more sensitive indicator of intermolecular forces than the latent heat of vaporization, particularly for polar compounds.

In addition to the parachor, yet another measure of molecular size and shape is the molecular radius of gyration as utilized by Passut and Danner for the correlation of vapor pressure⁽⁸⁾ and by Lyman and Danner for the correlation of heat capacity⁽⁹⁾. A compilation of radii of gyration for some 250 compounds is listed in Reid et al.⁽²⁾. It was considered useful to test whether the radius of gyration was a suitable parameter for describing the effect of molecular size and shape on the diffusion process in liquids.

Equations developed for predicting diffusivities at infinite dilution in specific solvents, such as water, and in particular solute-solvent solutions, such as normal paraffins would be expected to be of greater accuracy than the general equations. The correlation of Othmer and Thakar⁽¹⁰⁾ is one available for the prediction of diffusivities of dissolved substances in water:

$$D_{AB}^{\circ} = 14.0 (10^{-5}) \mu_B^{-1.1} V_A^{-0.6} \dots \dots \dots (5)$$

A modification of Equation (5) was considered to be a slight improvement⁽¹¹⁾:

$$D_{AB}^{\circ} = 13.26 (10^{-5}) \mu_B^{-1.14} V_A^{-0.589} \dots \dots \dots (6)$$

*Presented at the 30th Canadian Chemical Engineering Conference, Edmonton, Alberta, October 19-22, 1980.

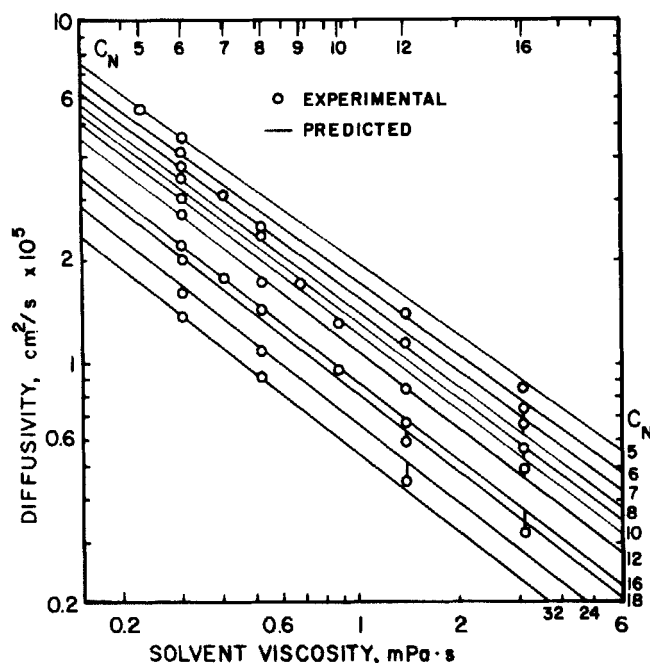


Figure 1 — Diffusivities at infinite dilution and at 25°C of normal paraffins from C_5 to C_{32} in normal paraffin solvents from C_5 to C_{16} .

An association parameter in the Wilke–Chang equation of $\phi = 2.26$ gave a comparable accuracy for the prediction of diffusivities in water⁽¹¹⁾ to that of Equations (5) and (6). Attention is drawn to the fact that Equation (6) was *incorrectly* reproduced in Reid et al.⁽²⁾ and a number of other reviews as well. The index for the viscosity term is -1.14 not -1.4 . Fortunately, calculations by Reid et al. were not significantly affected, because the viscosity of water at the temperatures under consideration was nearly unity when expressed in CP.

It has been shown by Hayduk and Buckley⁽¹²⁾ that diffusivities for straight-chained paraffins tend to be higher than those for essentially spherical molecules of the same molar volume. Because most molecules tend to be at least approximately spherical in shape, the difference in diffusion rate was attributable to the postulated mode of diffusion which has been termed 'segmental motion' of portions of the relatively long molecules. Hence, the use of a general correlation for predicting diffusivities in paraffin solutions is likely to have significant inherent error. A diffusivity-viscosity 'map' for normal paraffin solutes from C_5 to C_{32} in solvents from C_5 to C_{16} has been devised by Hayduk and Ioakimidis⁽¹³⁾ based on a number of very consistent data.

This work involves the development or improvement to four different correlations for diffusivities at infinite dilution: the first for non-polar solvents, the second specifically for normal paraffin solutions, the third for diffusivities in water, and the fourth a general correlation. A computational method which was essentially a non-linear regression analysis, (NONLIN), was utilized to evaluate the constants which best represented the experimental data available. For this purpose only the form of the relationship needed to be specified while the constants best representing the data were calculated. Various forms of correlating equations of increasing complex-

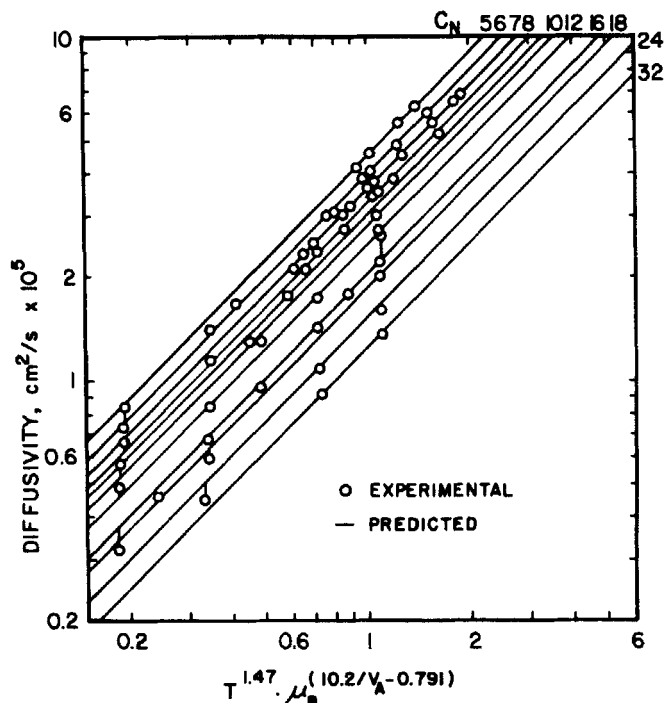


Figure 2 — Diffusivities at infinite dilution in normal paraffin solutions versus the factor $T^{1.47} \mu_B^{10.2/V_A^{0.791}}$ at temperatures ranging from 0 to 100°C.

ity were utilized in each case and resulting absolute errors between experimental and calculated diffusivities were evaluated.

DEVELOPMENT OF CORRELATIONS

The viscosity-diffusivity 'map'⁽¹³⁾ for paraffins which graphically indicates the relationship between diffusivity versus solvent viscosity at 25°C for solutes of different carbon content was used as a basis for correlating diffusivities in paraffin systems. Diffusivities were obtained from the graph corresponding to a particular viscosity, 1 mPa·s. It was found that diffusivities at one solvent viscosity could be correlated as a function of solute molar volume. The slopes of the lines were read and related again to the solute molar volume. Thus a basic form of the correlation was obtained. The effect of temperature was determined by considering the index of temperature to be variable. The final form of the equation for normal paraffin solutions was as follows:

$$D_{AB}^0 = 13.3 (10^{-8}) T^{1.47} \mu_B^{(10.2/V_A^{0.791})} V_A^{-0.71} \dots \dots \dots (7)$$

Equation (7) was developed utilizing some 58 data points for normal paraffin solutes from C_5 to C_{32} and for normal paraffin solvents from C_5 to C_{16} . Data utilized are from sources listed before⁽¹³⁾ and include those for self-diffusivities and those listed for different temperatures by Tyn and Calus⁽⁵⁾. After a number of trials using equations of different form, Equation (7) yielded the lowest average deviation from the experimental results of 3.4%. The low average error is considered exceptional since data were obtained by a number of workers using several different methods for which the inherent experimental error could easily have approached the average deviation in correlation. This good correlation would appear to con-

firm that the mechanism for diffusion is similar for all long-chained paraffin solutes in paraffin solutions. Furthermore there appears to be an interaction between the solute molar volume and the solvent viscosity since the effect of solvent viscosity on the diffusion rate is different depending on how large the diffusing molecules are. This latter observation may be made from an inspection of the complex index of the viscosity in Equation (7) or by inspecting the changing slope of the diffusivity — viscosity relationship shown in Figure 1, for solutes of various carbon number.

The revised diffusivity-solvent viscosity 'map' showing experimental data at 25°C and the resulting correlating equation are shown in Figure 1. The consistency of the data is also shown in Figure 2 where all the data are represented. Some minor deviations between experimental points and correlating equation may be observed for the low diffusivities in the high molecular weight solvents dodecane and hexadecane.

It was next determined whether further improvements to the predictive equations for diffusivity at infinite dilution in water were possible utilizing the non-linear regression technique. Eight different variations of Equation (6) and including Equation (6) itself were tested utilizing some 237 data points as referenced by Tyn and Calus⁽⁵⁾ and Hayduk and Laudie⁽¹¹⁾. The slightly more complex form of the equation giving the lowest average deviation from experimental data is as follows:

$$D_{AB}^{\circ} = (1.25 V_A^{-0.19} - 0.365) 10^{-8} \cdot \mu_B^{(9.58/V_A^{-1.12})} T^{1.52} \dots \dots \dots (8)$$

Equation (8) yielding an average deviation of 9.4% as compared with 10.3% for Equation (6), is considered a significant improvement for predicting diffusivities in water.

Further, based on all the data available, the general correlation of Tyn and Calus⁽⁵⁾ was tested for all types of non-electrolyte solute-solvent systems in several different ways. First it was determined whether a better fit of the data could be obtained by modifying the form of the equation or the constants involved using the non-linear regression method. Next a comparison between the Tyn-Calus⁽⁵⁾ and Wilke-Chang⁽³⁾ Equations was made to determine which best represented the same data. Finally, the general equations were tested for the specific two systems involving normal paraffin solutions and those involving water as solvent to see whether the correlations developed for the specific systems were significant improvements over the general correlations. The data source was chiefly that listed by Tyn and Calus⁽⁵⁾ although not all the data were used. Particularly when there was some question as to the method of evaluating the parachor of complex molecules, or of estimating the viscosity of certain solvents when not otherwise available, the data were omitted from the correlation. The new correlation based on the parachor values yielding the lowest average error for prediction purposes is as follows:

$$D_{AB}^{\circ} = 1.55 (10^{-8}) T^{1.29} \mu_B^{-0.92} V_B^{-0.23} P_B^{0.5} P_A^{-0.42} \dots (9)$$

Equation (9) yielded an average error for prediction

of 13.9% which can be compared with an equivalent average error for the Tyn and Calus⁽⁵⁾ Equation (Equation 3) of 14.2% and an average error of 16.1% for the Wilke-Chang⁽³⁾ Equation (Equation 1). It was further observed that the equations based on the parachor values had a significantly lower average error than those simply based on molar volumes. In fact, the effect of molar volume of solute was so small that this molar volume could be excluded entirely from the correlation as long as the corresponding parachor was included, as indicated by Equation (9). The same rules were applied in the development of Equation (9) as were originally specified for polar or associating substances by Tyn and Calus for their correlation. Of those available, 756 data points were selected as being the most recent or reliable (when several were available for one system) and to cover all types of solute-solvent interactions.

Finally, correlating equations were developed using the radius of gyration, first for all substances in both polar and non-polar solvents including water and subsequently in only non-polar solvents. Only those radius of gyration values for the most common substances which were readily available were utilized; hence not all the diffusivity data available could be utilized in the development of the correlations. Based on 436 data for diffusivities in both polar and non-polar solvents for which radii of gyration were available, the following correlation was obtained:

$$D_{AB}^{\circ} = 6.916 (10^{-10}) T^{1.7} \mu_B^{-0.80} R_B^{0.20} R_A^{-0.40} \dots (10)$$

Equation (10) was effective in correlating the data with an average error of 14.3% which can be compared with the average error for the Tyn and Calus⁽⁵⁾ Equation (Equation 3) of 14.2%. Based on 254 diffusivity data involving non-polar solvents for which radii of gyration were available the following correlation was obtained:

$$D_{AB}^{\circ} = 13.82 (10^{-10}) T^{1.6} \mu_B^{-0.78} R_B^{0.31} R_A^{-0.40} \dots (11)$$

The data were correlated by Equation (11) with an average error of 13.4%. When the general equation (10) was used with only the 254 data for non-polar solvents it resulted in an essentially identical average error of 13.4%. It may be concluded then that Equations (9) and (10) can be used just as effectively as Equation (11) for predicting diffusivities in non-polar solvents, thus making Equation (11) redundant.

Comparisons of the accuracy of the various equations are summarized in Table 1.

Discussion and Conclusion

Several new correlations for estimating diffusivities in dilute solutions have been developed which appear to be significantly more accurate than those currently in use. These new correlations were made possible by utilizing an optimization scheme termed NONLIN now part of the computational methods library at the University of Ottawa. The use of the parachor as a parameter for describing diffusion in liquids introduced by Tyn and Calus⁽⁵⁾ has increased the accuracy of the correlations. The radius of gyration appears to be equally useful for describing molecular size and shape as related to diffusion.

TABLE 1
Comparison of Correlations for Liquid Diffusivities at Infinite Dilution

	% Average Error	Number of Data
A General correlation for polar and non-polar substances:		
Wilke-Chang, Equation (1), for $\phi = 2.26$ for water solvent	16.1	756
Tyn-Calus, Equation (3)	14.2	756
New, Equation (9), using parachor	13.9	756
New, Equation (10), using radius of gyration	14.3	436
B Correlations tested with data for non-polar solvents only:		
Tyn-Calus	14.1	254
New, Equation (9), using parachor	13.4	254
New, Equation (10), using radius of gyration	13.4	254
New, Equation (11), using radius of gyration	13.4	254
C Correlations tested for normal paraffin solvents and solutes:		
Wilke-Chang, Equation (1)	13.3	58
New, Equation (9)	12.7	58
Tyn-Calus	12.5	58
New, Equation (7)	3.4	58
D Correlations tested for water as solvent:		
Tyn-Calus, Equation (3)	13.3	237
New, Equation (9)	12.8	237
Wilke-Chang with $\phi = 2.26$, Equation (1)	10.4	237
Hayduk-Laudie, Equation (6)	10.3	237
New, Equation (8)	9.4	237

It is noted that the correlations for normal paraffin solutions and for diffusivities in water have a lower average error than that for the general correlations. The very small error associated with the correlation for diffusivities in normal paraffin solutions of 3.4% is an indication of the high degree of consistency of the measurements made for these solutions. It may be possible to formulate equations utilizing the parachor or radius of gyration which would give average errors similar to those achieved by Equation (7), but the same degree of testing of different forms of equations was not performed for the latter two parameters. Equation (8), for diffusivities in water is slightly more complex than Equation (6); but it yields a useful reduction in average error of prediction. Diffusivities of many diverse compounds were considered in the development of the the correlations for water; until there is a major improvement in understanding of the diffusion process in water, further improvements in accuracy for correlations may be difficult.

The comparison of the general correlating equations confirms that the Tyn and Calus correlation⁽⁵⁾ Equation (3), is essentially the best of those currently used with an average error in predicted values of appreciably less than 16%. It is apparent that the other forms of correlating equations utilizing the parachor or radius of gyration give equivalent results. New variations of the general equations for *non-polar* substances, however, appear hardly justified since the improvement in accuracy is marginal.

It is of considerable interest to note the variation in temperature dependence of liquid diffusivities as described by the correlations obtained. The diffusivity depends on absolute temperature to a power ranging

from 1 (Wilke-Chang) to 1.7 (Equation 10) with an average value of approximately 1.5 when the Wilke-Chang index is excluded. A dependence of gas phase diffusivity on temperature as described by the Chapman-Enskog Equation (2) is also $D \propto T^{1.5}$. The suggestion is that diffusivities in liquids seem to have a similar dependence on temperature as those in gases. It is difficult to distinguish between the effects on diffusivity in liquids of changes in solute molecular activity as a result of temperature changes, and of changes in solvent viscosity, because these two variables cannot be independently varied. It usually follows that if the effect of temperature on diffusivity is described as a large index in a correlating equation, it is compensated for by a relatively large *negative* index for the solvent viscosity. Further study is required to elucidate these effects.

Acknowledgment

An operating grant from NSERC is gratefully acknowledged.

Nomenclature

C_N	= number of carbons in normal paraffins
D_{AB}^∞	= diffusivity at infinite dilution of A in B, $\text{cm}^2 \cdot \text{s}^{-1}$
M	= molar mass, $\text{g} \cdot \text{mol}^{-1}$ ($\text{kg} \cdot \text{kmol}^{-1}$)
n	= self-associating factor defined by Equation (4)
P_A, P_B	= parachor for solute, solvent, respectively, $\text{g}^{0.25} \cdot \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-0.5}$
R_A, R_B	= radius of gyration for solute, solvent, respectively, nm; Note: 1 Angstrom = 0.1 nm
T	= absolute temperature, $^\circ\text{K}$

V_A, V_B = molar volume at the normal boiling point of solute, solvent, respectively, $\text{cm}^3 \cdot \text{mol}^{-1}$
 μ_B = solvent viscosity, $\text{mPa} \cdot \text{s}$
 ϕ = Wilke–Chang association parameter, dimensionless
 $\Delta H_A, \Delta H_B$ = latent heat of vaporization at normal boiling point for solute, solvent, respectively, $\text{J} \cdot \text{mol}^{-1}$

References

- (1) Ghai, R. K., Ertl, H., and Dullien, F. A. L., *AIChE J.* **19** 881 (1973).
- (2) Reid, R., Prausnitz, J. M., and Sherwood, T. K., "The properties of Gases and Liquids, Third Ed.", McGraw-Hill, New York, N.Y., Chap. 11, 1977.
- (3) Wilke, C. R., and Chang, P., *AIChE J.* **1** 264 (1955).
- (4) King, C. J., Hsueh, L., and Mao, K.-W., *J. Chem. Eng. Data* **10**, 348 (1965).
- (5) Tyn, M. T., and Calus, W. F., *J. Chem. Eng. Data* **20**, 106 (1975).
- (6) Quayle, O. R., *Chem. Rev.* **53**, 439 (1953).
- (7) Sugden, S., "The Parachor and Valency", Routledge, London, England, 1930.
- (8) Passut, C. A., and Danner, R. P., *Chem. Eng. Prog. Symp. Ser. No. 140*, **70**, 30 (1974).
- (9) Lymann, T. J., and Danner, R. P., *AIChE J.* **22**, 759 (1976).
- (10) Othmer, D. F., and Thakar, M. S., *Ind. Eng. Chem.* **45**, 589 (1953).
- (11) Hayduk, W., and Laudie, H., *AIChE J.* **20**, 611 (1974).
- (12) Hayduk, W., and Buckley, W. D., *Chem. Eng. Sci.* **27**, 1997 (1972).
- (13) Hayduk, W., and Ioakimidis, S., *J. Chem. Eng. Data* **21**, 255 (1976).

Manuscript received February 16, 1981; accepted for publication October 8, 1981.