Molecular Gaseous Diffusion Coefficients of Long Chain Alkanes, Alcohols, Esters and Acids

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Molecular gaseous diffusion coefficients are required in many areas of science and chemical engineering process design (Lyman et al., 1982; Reid et al., 1977; Sherwood et al., 1975; Treybal, 1980). Modeling mass-transfer rates in the environment has placed increased emphasis on better values for gaseous diffusion coefficients of high molecular weight compounds. Although many diffusion coefficient measurement results have been published for large molecules, experimental data is rather sparse.

A number of theoretical models for mutual gaseous diffusion coefficients have been suggested (Chapman et al., 1970; Hirschfelder et al., 1964; Marrero and Mason, 1973). However, these predictions are often inaccurate for process design and environmental evaluations dealing with high molecular weight compounds. Typically, process engineers and environmental scientists use semi-empirical equations that correlate available gaseous diffusion coefficient data and extrapolate it to other mixtures. One of the most accepted semi-empirical equations for correlation of experimental gaseous diffusivity data was published 30 years ago (Fuller et al., 1966). This equation is based on the Chapman-Enskog first-approximation solution to the Boltzmann equation, and the rigid elastic-sphere model (Chapman et al., 1970).

Fuller et al. (1966) developed a practical correlation (the FSG correlation) for the prediction of gaseous diffusion coefficients

$$D_{12} = \frac{1.00\times 10^{-3} T^{1.75} (1/m_1 + 1/m_2)^{1/2}}{p\left[(\Sigma_1 \upsilon_i)^{1/3} + (\Sigma_2 \upsilon_i)^{1/3}\right]^2} \tag{1}$$

where p = pressure, atm; T = temperature, K; υ_i = diffusion volumes, cm^3/mol; m_1, m_2 = molecular mass, g; D_{12} = binary gaseous diffusion coefficient, cm^2/s.

The υ_is have the same dimensions as atomic volumes, but are not true atomic volumes. Diffusion volumes are the sum of group contributions of the atoms in a compound. For several common simple molecules with many data measurements, total equivalent diffusion volumes were calculated by nonlinear least-squares analyses of published diffusion coefficients. The FSG correlation was based on 340 actual data points in 153 different binary systems. Only 68 of these diffusion measurements included large, nonspherical molecules.

The purpose of the present note is to modify the FSG correlation to account for certain functional groups, namely: (1) methylene group, $-CH_2-$; (2) carboxy linkage $-COO-$; and (3) the hydroxyl group, $-OH$. The portions of the υ_i's that are contributed by these three functional groups in Eq. 1 are modified by empirically determined multiplying factors to reflect the fact that the diffusion cross-section of these groups is greater than the sum of its diffusion volumes.

Data Sources

The modification to the prediction (Eq. 1) of the diffusivities of various compounds containing straight aliphatic chains is based on 357 data measurements: 205 measurements for straight chain, aliphatic alkanes; 75 measurements for straight chain, aliphatic alcohols; 77 measurements for straight chain, aliphatic esters and acids. A total of 68 of these data points were taken from Fuller et al. (1966) which comprised all data for the FSG correlation that involved straight chain, saturated hydrocarbons, alcohols and esters. The various gases associated with these data in the FSG study include air, H_2, D_2, O_2, He, N_2, Ar, and CO_2. All of these gases are included in this study, and their atomic diffusion volumes were used as in FSG.

References for the other 289 data points for the present work are listed in Table 1. All available data were used for compounds with straight chain methylene groups regardless of temperature or other gaseous component. For these compounds, we could find no published diffusion data later than 1986. There is no (clear) evidence that later data were accurate than the earlier, and we accepted all published results at face value (Marrero and Mason, 1972).

In some cases, the cited data were results for the diffusion coefficient temperature dependence. In those cases, the reported temperature correction was used to extrapolate the

Table 1. Sources of Mutual Gaseous Diffusion Coefficient Measurement Data*

Gas Class

n-Alkane

- Mack (1925)
- Boynton and Brattain** (1929)
- Coward and Georgeson (1937)
- Bradley and Shellard (1949)
- Altshuer and Cohen (1960)
- Nafikov and Usmanov (1966)
- Arnold and Toor (1967)
- Galloway and Sage (1967)
- Huang et al. (1968)
- Lugg (1968)
- Grob and El-Wakil (1969)
- Jacobs et al. (1970)
- Barr and Watts (1972)
- Elliott and Watts (1972)
- Wilhelm and Battino (1972)
- Wilhelm and Battino (1973)
- Wakeham and Slater (1974)
- Pritchard and Currie (1982)
- Katsanos and Karaiskakis (1982)
- Pommersheim et al. (1982)
- Katsanos and Karaiskakis (1983)
- Ilaysov and Negretov (1985)

n-Alcohol

- Boynton and Brattain** (1929)
- Gilliland (1934)
- Lee and Wilke (1954)
- Seager et al. (1963)
- Huang et al. (1968)
- Lugg (1968)
- Mrazek et al. (1968)
- Katan (1969)
- Pommersheim et al. (1982)
- Ashraf et al. (1986)

n-Ester and Acids

- Boynton and Brattain** (1929)
- Gilliland (1934)
- Bradley et al. (1946)
- Lugg (1968)
- Grob and El-Wakil (1969)
- Katan (1969)

*Source citations arranged in chronological order in each gas class. The second component in the mixture(s) with the *n*-alkane, *n*-alcohol, ester or acid can be either air, H_2, He, etc.; the source document needs to be consulted for the information about the specific gas pair, see Literature Cited. Here, sources cited by Fuller et al. (1966) are not reported.

**Boynton and Brattain (1929) summarized D_{12} values published in scientific journals prior to the early 1900s.

Table 2. Diffusion Volume Parameters

	$-CH_2-$	$-OH$	$-COO-$
Multipliers	1.084 ± 0.014	1.30 ± 0.170	1.53 ± 0.077
Diffusion Vol.	22.18 ± 0.31	9.70 ± 1.27	42.01 ± 2.11

measurements to 25°C. The extrapolated values were then used in the regression. For all other data, temperature effects were corrected using the FSG temperature exponent of 1.75.

Results

The new database of diffusivity measurements was compared to diffusivities calculated using Eq. 1 and diffusion volume parameters reported by FSG. The original correlation of FSG, was, in fact, remarkably effective in accommodating the new data collected for this note. The FSG parameters gave a sum of squares of relative error of 3.78 for this data (357 points). The average of the absolute value of the relative error was 0.0712. Although this average error is larger for this data than was reported in the original work, the correlation of FSG is better than might be expected since much of the additional data goes considerably beyond the limits of the range of data used by FSG. Thus, one result of this study is to verify that the FSG correlation is useful for extrapolation of this data which is outside the range of the original study.

The fit is significantly improved, however, by modifying the calculation for the diffusion volume terms in the FSG equation for calculation of the diffusivities of straight chain aliphatic compounds. The diffusion volume contribution of the methylene group, $-CH_2-$, is 20.46 m^3/mole as calculated from FSG. A multiplying factor for all the methylene groups in the new database was determined by nonlinear regression minimizing the sum of squares of the relative error for prediction of diffusivities. With the modified diffusion volume for $-CH_2-$, the sum of squares of prediction error is reduced to 2.86. The F-test shows that the reduction in the sum-of-squares reduction with the addition of this parameter is significant at greater than the 99% confidence level ($F = 115 \gg F$ (0.99, 1,356) single $\cong 6.7$).

We further modified the FSG equation with the addition of multiplying factors for the diffusion volumes of the $-OH$ and $-COO-$ groups. The FSG values of 7.46 and 27.46 m^3/mole were modified by multipliers in a three parameter nonlinear regression which minimized the sum of squares for the relative prediction errors for diffusivities. The resulting values for the multiplying factors and standard deviations for the three functional groups are listed in Table 2. Adding modification of the $-OH$ and $-COO-$ groups to the correlation reduced the sum of squares of residual error to 2.52 and the average prediction error to 6.52%. The confidence level for the sum of squares reduction with these parameters is greater than 99% ($F = 59.0 \gg F$ (0.99, 3,354) $\cong 3.8$.

The lead factor in the numerator of Eq. 2 was determined by FSG to be 1.00×10^{-3}. We investigated changing this multiplicative coefficient, but changing this parameter did not significantly improve the predictive power of the equation. A plot of measured and predicted diffusivities with the modified FSG equation using the three parameters from Table 2 is shown in Figure 1.

Discussion

For a maximum likelihood estimate, the residuals should be weighted by the inverse of the standard deviation of the measurement. However, much of these data did not include that information and the regression parameters reported here minimized the relative error. Thus, these results are *not* necessarily maximum likelihood estimates. Since the sum of squares criteria is relative error, the vertical distances between the data points and correlation line on the log-log plot in Figure 1 is effectively a histogram of the weighted residuals. If the weighting factors are true measures of the standard deviation of the measurement errors, then the variance of the weighted residuals resulting should not differ (statistically) from a uniform probability distribution.

The standard deviations of the diffusion volume parameters listed in Table 2 were calculated in the manner as usually reported for the results of multiple regression. Such limits do not, however, represent the true variability of the parameters. In this database, there are no measurements with both an $-OH$ group and a $-COO-$ linkage in the same molecule. Thus, the codependence between parameters collapses to the two-dimensional plots in Figure 2 showing the linear approximation for the 95% confidence region for the $-OH$ group and the $-COO-$ linkage as compounded with the $-CH_2-$ group.

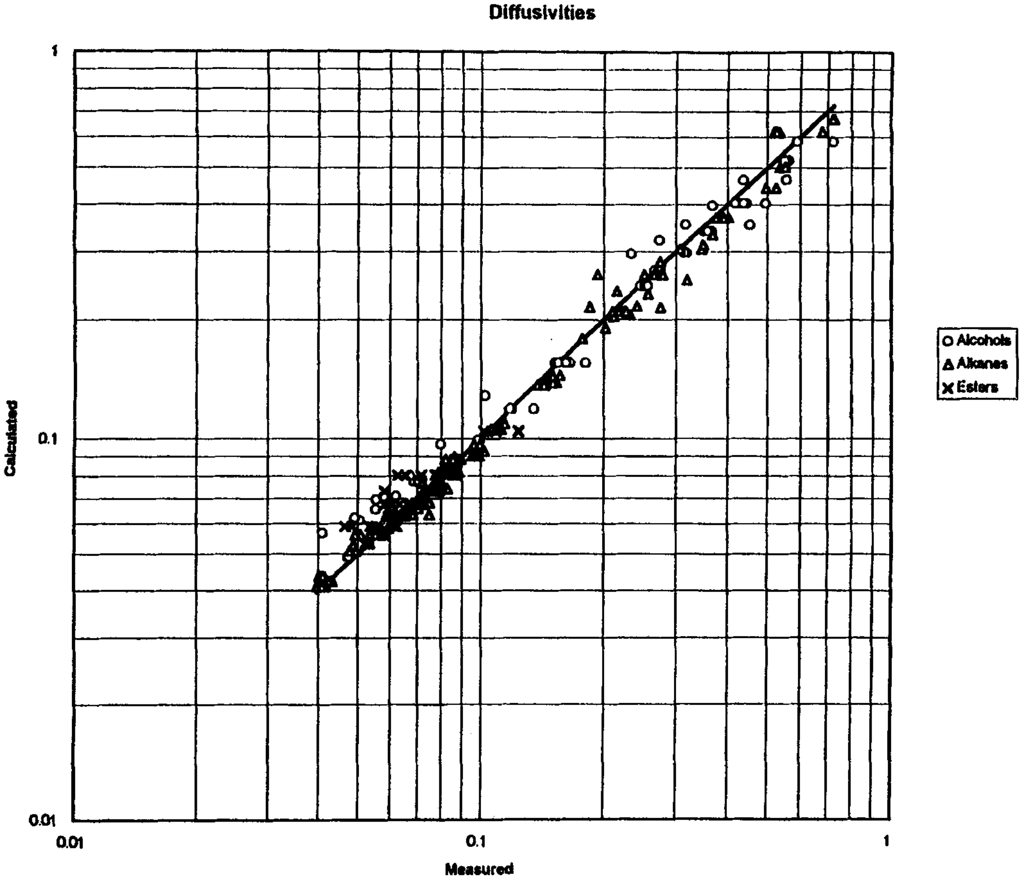

Figure 1. Measured and calculated values for diffusivity.

The diffusitivies are calculated using the semi-empirical equation of Fuller, Schettler and Giddings (1966). The same constants including diffusion volumes are used except that diffusion volumes of the methylene, hydroxyl and carboxy groups are multiplied by the factors in Table 2.

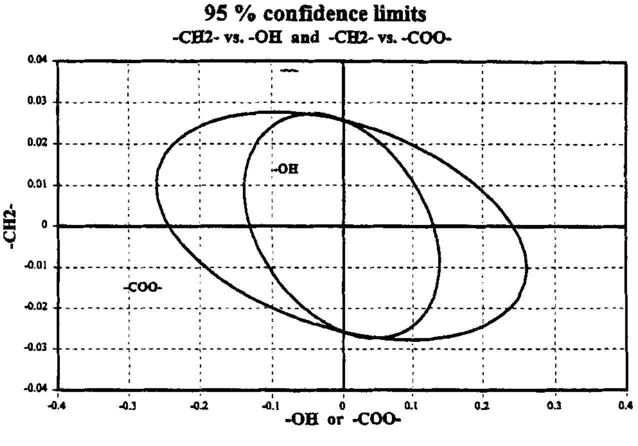

Figure 2. Confidence limits for diffusion volume multiplying factors.

The standard deviations as calculated for the correlation matrix are given in Table 2. The area inside this curve represents the 95% confidence limits for the parameters. Because of parameter dependency, the variation of these parameters extends beyond ± 1.96 times the standard deviation.

This study demonstrates the utility of introducing factors for adjusting the FSG correlation diffusion volumes of specific molecular structures to improve the fit of experimental data.

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