# Correlation Between Tracer Diffusivity, Solvent Viscosity, and Solute Sizes

**H. T. DAVIS**

**Departments of Chemical Engineering**
**and Materials Science and of Chemistry**
**University of Minnesota**
**Minneapolis, Minnesota 55455**

**and**

**T. TOMINAGA and D. F. EVANS**

**Department of Chemical Engineering**
**Carnegie-Mellon University**
**Pittsburgh, Pennsylvania 15213**

Recently, Evans, Tominaga, and Chan (1979) found that the tracer diffusivity $D$ of the compounds shown in Table 1 can be reduced by the formula,

$$D\eta^p = \frac{AT}{298.2\mathrm{K}}, \tag{1}$$

where $\eta$ is the viscosity of the solvent, $T$ the temperature, and $A$ and $p$ constants for each solute. The formula was tested for 18 different organic solvents (including several alcohols as well as nonpolar solvents) at temperatures of 283.2, 298.2, and 313.2K. The viscosities of the solvents for which Equation (1) was demonstrated to be valid ranged over a factor of forty ($\eta = 0.0004$ to 0.013 kg/ms). One study, however, (Hiss and Cussler 1973) suggests that the formula is also applicable in very viscous solutions ($\eta = 0.520$ kg/ms).

The parameter $p$ is a linear function of the inverse of the radius of the solute size. For the largest solute studied, tetradodecyltin, a value of $p = 0.95$ was obtained. This is close to the Stokes Law prediction of $p = 1$. For the smallest solute, argon, a value of $p = 0.449$ was obtained, implying that with decreasing radius the diffusion coefficient becomes increasingly less dependent on viscosity.

In this note, we demonstrate that the formula holds for conditions quite different from those under which $A$ and $p$ were fitted, and we report a relationship between $A$ and $p$. With the relationship, Equation (1) becomes a one-parameter correlation equation between diffusivity and viscosity. *Furthermore, with the correlation between p and molecular size, Eq. (1) becomes a zero-parameter correlation.* Although the correlation between $D$ and $\eta$ given in Eq. (1) was observed by others, (Steel, Stokes, and Stokes 1958, Haydick and Cheng 1972, Haydick and Buckley 1972) the relationship between $p$ or $A$ and other properties of the system was not found previously.

In Table 2, the self-diffusion coefficients are predicted for Ar, Kr, Xe, and $CH_4$ at a variety of temperatures and pressures, using Eq. (1) with the solute parameters given in Table 1. Agreement between prediction of the formula and experiment is as good as or better than extant molecular theory, even for these simple systems.

We found that $\ln A$ and $p$ depend linearly on one another. Linear regression analysis of the values of $\ln A$ and $p$ of Table 1 yields the straight line fit

$$\ln(10^{10}A) = -11.670p + 6.013 \tag{2}$$

with a coefficient of determination of 0.9963. The last column of Table 1 gives values of $A$ predicted by Eq. (2) from the empirical values of $p$. Clearly, Eq. (2) is a good fit for the relationship between $A$ and $p$.

Estimating the radii $r$ of a solute molecules from the low pressure saturated liquid densities of the pure solutes, Evans et al. (1979) found a linear relationship between $p$ and $r^{-1}$. In Table 3, the solutes, the densities used to determine $r$ and the values of $r$ are listed. The empirical values of $p$ fit the relationship

$$p = -\frac{0.1296\ nm}{r} + 1.166 \tag{3}$$

TABLE 1. PARAMETERS $A$ AND $p$ FOR VARIOUS SOLUTES.[a] $D$ IN M²/SEC, $\eta$ IN KG/MS (FROM REF. 1).

| | From Reference 1 | | From Eq. (2) |
|---|---|---|---|
| | $p$ | $A \times 10^{10}$ | $A \times 10^{10}$ |
| Ar | $0.44_9$ | 2.17 | 2.17 |
| $CH_4$ | $0.47_2$ | 1.59 | 1.66 |
| Kr | $0.49_9$ | 1.12 | 1.21 |
| Xe | $0.56_3$ | 0.550 | 0.572 |
| $CCl_4$ | $0.71_7$ | 0.112 | 0.0950 |
| $(CH_3)_4Sn$ | $0.73_2$ | 0.0895 | 0.0797 |
| $(C_2H_5)_4Sn$ | $0.77_7$ | 0.0498 | 0.0471 |
| $(C_3H_7)_4Sn$ | $0.81_7$ | 0.0297 | 0.0296 |
| $(C_4H_9)_4Sn$ | $0.84_9$ | 0.0207 | 0.0204 |
| $(C_{12}H_{25})_4Sn$ | $0.94_2$ | 0.00571 | 0.00686 |

[a] The solvents with which the parameters were determined include hexane, decane, tetradecane, benzene, cyclohexane, carbontetrachloride, acetone, acetonitrile, methanol, ethanol, 2-propanol, 1-heptanol and 1-octanol. Most measurements were at 298.2K, although some systems were also studied at 283.2K and 313.2K.

TABLE 2. COMPARISON OF CALCULATED AND OBSERVED SELF-DIFFUSION COEFFICIENTS.[a,b,c]

| Fluid | $T$ (K) | $\rho_m \times 10^3$ (kg/m³) | $\eta \times 10^4$ (kg/ms) | $D_{calc} \times 10^9$ m²/sec | $D_{obs} \times 10^9$ m²/sec |
|---|---|---|---|---|---|
| Ar | 90 | 1.374 | 2.32 | 2.81 | 2.43 |
| " | 110 | 1.238 | 1.40 | 4.31 | 4.80 |
| " | 130 | 1.065 | 0.90 | 6.20 | 7.45 |
| " | 150 | 0.773 | 0.48 | 9.50 | 9.98 |
| Xe | 184.3 | 2.795 | 3.7 | 2.90 | 2.48 |
| $CH_4$ | 100 | 0.448 | 1.46 | 3.44 | 3.0 |
| " | 125 | 0.405 | 0.80 | 5.71 | 7.0 |
| " | 125 | 0.428 | 0.94 | 5.30 | 6.2 |
| " | 131.2 | 0.395 | 0.71 | 6.39 | 8.0 |
| " | 139 | 0.393 | 0.73 | 6.63 | 8.4 |

[a] Observed diffusivities and argon viscosity taken from J. Naghizadeh and S. A. Rice, *J. Chem. Phys.*, **36**, 2710 (1962).

[b] Methane viscosities taken from N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, John Wiley, N.Y. (1975).

[c] Xe viscosity estimated from argon values using the law of corresponding states.

---

0001—1541—80—3243—0313—$00.75. © The American Institute of Chemical Engineers, 1980.

TABLE 3. RADII $r$ OF SEVERAL MOLECULES ESTIMATED FROM $r = n^{-1/3}$. $n$ IS THE NUMBER DENSITY OF THE MOLECULES IN A PURE SATURATED LIQUID STATE AT A LOW VAPOR PRESSURE.

| | | From Ref. 1 | From Eq. (3) | From Ref. 1 | From Eq. (4) |
|---|---|---|---|---|---|
| | $r(nm)$ | $p$ | $p$ | $A\times10^{10}$ | $A\times10^{10}$ |
| Ar | 0.181 | $0.44_9$ | 0.450 | 2.17 | 2.14 |
| $CH_4$ | 0.189 | $0.47_2$ | 0.480 | 1.59 | 1.50 |
| Kr | 0.200 | $0.49_9$ | 0.517 | 1.12 | 0.969 |
| Xe | 0.207 | $0.56_3$ | 0.539 | 0.550 | 0.750 |
| $CCl_4$ | 0.272 | $0.71_7$ | 0.688 | 0.112 | 0.1309 |
| $(CH_3)_4Sn$ | 0.307 | $0.73_2$ | 0.743 | 0.0895 | 0.0694 |
| $(C_2H_3)_4Sn$ | 0.345 | $0.77_7$ | 0.790 | 0.0498 | 0.0404 |
| $(C_3H_7)_4Sn$ | 0.380 | $0.81_7$ | 0.825 | 0.0297 | 0.0269 |
| $(C_4H_9)_4S$ | 0.410 | $0.84_9$ | 0.849 | 0.0207 | 0.0201 |
| $(C_{12}H_{25})_4Sn$ | 0.565 | $0.94_2$ | 0.936 | 0.00571 | 0.00732 |

with a coefficient of determination 0.9921. Values of $p$ predicted from Eq. (3) are given in the fourth column of Table 3. The agreement of fitted and observed $p$ is quite good, the fitted values generally being within a percent or two of observed values—in the worst case, $CCl_4$, fitted and observed $p$ are within 5%. We also analyzed the data by dividing the solvent into two groups, one, the compact molecules benzene, cyclohexane, carbon tetrachloride and tetrabutyltin, and the second, the other solvents given in Table 1. In general, the least squares fit using two solvent groups was only a little or no better than using only one group.

As mentioned, with Eqs. (2) and (3), Eq. (1) provides a correlation between solvent viscosity and solute diffusivity with no undetermined parameters. Combining Eq. (3) with Eq. (2), we obtain

$$10^{10}A = 0.0005036 \exp\,(1.5124\ nm/r) \tag{4}$$

Predictions of Eq. (4) are compared with observed values of $A$ in Table 3. The average absolute percent difference between Eq. (4) and observed values is about 13%. The worst case is tetradodecyltin for which the predicted $A$ is 28% too high.

With Eqs. (3) and (4), Eq. (1) becomes a powerful predictive tool. For a given solute whose diffusivity is desired in a given solvent, we need only the solvent viscosity and the density $n$ of the liquid solute at a low vapor pressure. Then estimating $r = n^{-1/3}$, computing $p$ from Eq. (3) and $A$ from Eq. (4), we estimate $D$ from Eq. (1). On the basis of the comparisons made in Table 3, the estimated $D$ is expected to be within (often well within) about 25% of the actual value.

The accuracy of Eq. (1) over such a wide range of conditions begs for a simple theoretical basis, as does the dependence of $p$ and $A$ on molecular size. We presently have no such theory, but we believe Eq. (1), with Eqs. (3) and (4), constitutes an important empiricism for engineering estimates of diffusivity.

## ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for financial support of this work.

## NOTATION

$A$ = solute dependent constant in Eqs. (1), (2), and (4)
$D$ = tracer diffusivity
$n$ = solvent number density
$p$ = solute dependent constant in Eqs. (1), (2), and (3)
$r$ = solute radius
$T$ = absolute temperature

### Greek Letters

$\eta$ = solvent viscosity
$\rho_m$ = solvent mass density

## LITERATURE CITED

Evans, D. F., T. Tominaga, and T. Chan, *J. Solution Chem.*, **8**, 461 (1979).
Haydick, W. and W. D. Buckley, *Chem. Eng. Sci.*, **27**, 1997 (1972).
Haydick, W. and S. Cheng, *Chem. Eng. Sci.*, **26**, 635 (1971).
Hiss, T. G. and E. L. Cussler, *AIChE J.*, **19**, 698 (1973).
Steel, B. J., J. M. Stokes, and R. H. Stokes, *J. Phys. Chem.*, **62**, 1514 (1958).

*Manuscript received May 2, 1979; revision received August 8, and accepted August 20, 1979.*

---

# Two-Phase Pressure Drop in Cocurrent Downflow in Packed Beds: Air-Silicone Oil Systems

**L. D. CLEMENTS**

**Department of Chemical Engineering**
**Texas Tech University**
**Lubbock, Texas 79409**

**and**

**P. C. SCHMIDT**

**Chevron Research Company**
**Richmond, California 94802**

Since the advent of hydrogen processing technology to crack and desulfurize-denitrify petroleum fractions in trickle bed reactors, these units have become ubiquitous in the refinery complexes of the world. The design and successful operation of trickle bed reactors depends on both an adequate knowledge of the heterogeneous catalytic reactions taking place and the fluid mechanical behavior of the gas-liquid-solid system. Accurate prediction of two-phase pressure drop in packed bed reactors is necessary, not only for specification and sizing and major equipment, but also as a subjective means of insuring an adequate liquid distribution within the bed, by designing for operation at, or in excess of, some predetermined value. In addition, a reasonable estimate of pressure drop as a catalyst run progresses is necessary to insure adequate compressor and pump capacity.

---

0001—1541—80—3060—0314—$00.75. © The American Institute of Chemical Engineers, 1980.