Diffusion Coefficients for Binary Alkane Mixtures to 573 K and 3.5 MPa

An automated Taylor dispersion apparatus, designed to operate from 298 to 573 K and 101 to 3,450 kPa (14.7 to 500 psia), was used to measure diffusion coefficients at infinite dilution for the solutes *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane in the solvents *n*-heptane and *n*-dodecane. Dodecane viscosity and density also were measured at all conditions. Various predictive theories are tested in light of the new data, and a correlation based on the data at high temperature and pressure is presented. The data are well represented by a free-volume expression of the form $D_{AB}/\sqrt{T} = \beta\,(V - V_D)$. The data given here extend the available data base for alkane/alkane diffusion by 100 to 200 K, and allow evaluation of predictive theory over an extended range of temperatures.

M. A. Matthews, Aydin Akgerman
Chemical Engineering Department
Texas A&M University
College Station, TX 77843

Introduction

Straight-chain hydrocarbons and their derivatives are important constituents of many petrochemical processes such as hydrotreating, reforming, Fischer-Tropsch synthesis, and coal liquefaction. The extent of mass transfer limitations within such processes is not well characterized, in part due to a lack of data on the rate of diffusion of the various constituents. In particular, there are few data at temperatures and pressures above ambient. Most existing predictive equations contain constants and/or adjustable parameters whose values are obtained by fitting data obtained at near-ambient temperatures. Among these are the equations given by Wilke and Chang (1955), Lusis and Ratcliff (1968), and Shieh and Lyons (1969). The first two are based on hydrodynamic theory, while the third relates diffusivity to density in *n*-alkane mixtures. Chen and Chen (1985b) proposed a hydrodynamic-type equation based on examination of diffusion coefficients in *n*-alkanes at temperatures to 373 K.

This work provides mutual diffusion coefficients of several *n*-alkane solutes at low concentration in two alkane solvents. It is found that available predictive equations exhibit large errors in certain temperature regions, and a new correlation based on a rough-hard-sphere/free-volume approach is given.

Experimental Procedure

Diffusivities were measured using the Taylor dispersion method. The application of the method to high temperature and pressure has been demonstrated in a number of recent papers (Chen and Chen, 1985a, b, c). The theoretical basis for the experiment was given by Taylor (1953) and Aris (1956). A rigorous evaluation of design criteria was given by Alizadeh et al. (1980), and the present device was designed in accordance with their criteria.

In the Taylor dispersion method, a narrow pulse of solute dissolved in a solvent is injected into a tube in which the solvent is moving in slow laminar flow. The injected pulse disperses after moving to a position far downstream of the injection point, and assumes a normal distribution due to the combined effects of diffusion and the laminar velocity profile. The center of gravity of the peak moves with the mean velocity of the laminar flow $\bar{u}$. The dispersion of a narrow pulse of solute flowing in laminar flow in a circular tube is described by the effective dispersion coefficient K:

$$K = D_{AB} + \frac{R_t^2 \bar{u}^2}{48 D_{AB}} \tag{1}$$

Using a concentration monitor at a fixed location L downstream of the injection point, concentration vs. time data are recorded. The work of Pratt and Wakeham (1975) and Levenspiel and Smith (1957) allows one to use the normalized first and second temporal moments $\bar{t}$ and σ^2 to obtain D_{AB}. Let:

$$\zeta = \frac{K}{\bar{u}L} \tag{2}$$

then

$$\bar{t}_{id} = \frac{L}{\bar{u}}(1 + 2\zeta_0) \tag{3}$$

$$\sigma_{id}^2 = \left(\frac{L}{\bar{u}}\right)^2 (8\zeta_0^2 + 2\zeta_0) = \frac{8\zeta_0^2 + 2\zeta_0}{(1 + 2\zeta_0)^2}\,\bar{t}_{id}^2 \tag{4}$$

The normalized first temporal moment $\bar{t}_{id}$ and the normalized, centralized second temporal moment σ_{id}^2 are ideal in that they are what would be calculated if there were no imperfections in the apparatus. In reality, there are minor corrections to be made to the experimentally observed moments (Alizadeh et al., 1980). In this work observed moments are calculated by finite summation of concentration vs. time data:

$$S = \sum C(t)\Delta t$$

$$\bar{t}_{obs} = \frac{1}{S}\sum tC(t)\Delta t$$

$$\sigma_{obs}^2 = \frac{1}{S}\sum (t - \bar{t}_{obs})^2 C(t)\Delta t \tag{5}$$

The observed moments are converted to ideal moments by applying the correction terms given by Alizadeh et al. These account for mixing in the detector, for connecting tubing between the diffusion tube and detector, and for finite width of the injection pulse. The final working equation is

$$D_{AB} = \frac{1}{2}\left\{\frac{L^2}{\bar{t}_{id}}(1 + 2\zeta_0)\zeta_0 - \left[\frac{L^4}{\bar{t}_{id}^2}\zeta_0(1 + 2\zeta_0) - \frac{4L^2R_t^2}{48\bar{t}_{id}^2(1 + 2\zeta_0)^2}\right]^{1/2}\right\} \tag{6}$$

where

$$\zeta_0 = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + (\bar{t}_{id}^4 + 4\bar{t}_{id}^2\sigma_{id}^2)^{1/2}}{(8\bar{t}_{id}^2 - 4\sigma_{id}^2)} \tag{7}$$

Equation 6 accounts for diffusion in both the axial and radial directions, and reduces the potential systematic errors to about ±0.5%.

The experimental apparatus is shown in Figure 1. The solvent is sparged with helium to remove air and is pumped through a pulse damper consisting of capillary tubing and a back-pressure regulator in series. System pressure downstream of the pulse damper is maintained by a second regulator located at the outlet.

Two calibrated strain gauge pressure transducers and a valve manifold are used to measure the pressure drop across a narrow bore tube. The Hagen-Poiseuille equation is then used to calculate solvent viscosity at the conditions of the diffusion experiment.

After passing the transducers, solvent flows out of the heated enclosure to the reference cell of an LDC/Milton Roy Refractomonitor III differential refractive index detector. We have modified the detector cell to withstand high pressure so that the response peak is recorded at the same pressure as the experi-

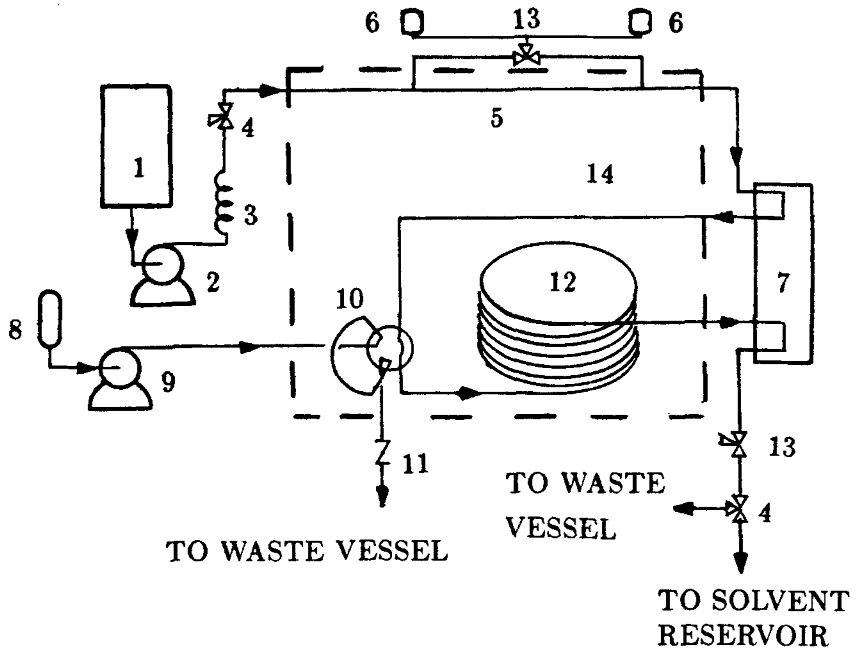

Figure 1. Taylor dispersion apparatus.

1. Solvent reservoir
2. Solvent pump
3. Capillary tube pulse damper
4. Back-pressure regulators
5. Narrow bore tube viscometer
6. Pressure transducers
7. Refractive index detector
8. Sample solution
9. Sample injection pump
10. Six-port sample injection valve
11. Adjustable check valve
12. Coiled dispersion tube
13. Three-way valves
14. Heated enclosure

ment. Solvent then flows back to the heated enclosure, in which a six-port chromatographic sample injection valve is located. The sample solution (usually 4 to 8 mol % of solute dissolved in solvent) is prepared externally to the heated enclosure and pumped into the sample loop. Pressure on the sample loop is maintained with an adjustable check valve, thus the sample is injected at the same temperature and pressure as the diffusion coil. A pneumatic drive allows switching of the valve in about 10 ms, effectively eliminating any interruption of solvent flow during sample injection (Harvey and Stearns, 1984).

The solute pulse next flows to the diffusion coil (43.55 m length, R_t = 0.000523 m). The tube radius was determined gravimetrically at 298 K by weighing the mass of water contained in a given length. This radius value was confirmed by measuring the retention time of a sample at a known volumetric flow rate. The radius and length are corrected for thermal expansion at temperatures above 298 K. Thermal expansion will lead to systematic underprediction of the diffusivity if unaccounted for. The dispersed solute peak leaves the heated enclosure and flows through the sample cell of the detector, then through the second back-pressure regulator.

The heated enclosure is constructed from aluminum pipe. The diffusion tube is coiled on an aluminum ring (0.157 m radius) that fits snugly inside the pipe. The ends are covered with aluminum plate, and the void space inside the enclosure is filled with aluminum shot so that the system is thermally massive and stable, with good internal heat conduction.

Two personal computers are used for data acquisition and temperature control. One computer is dedicated to on-line monitoring of the detector signal. The second computer is used for monitoring pressure and temperature, and also for controlling the temperature in the enclosure. The heated enclosure is stable to better than ±0.5 K over the course of 12 h.

The solvent density at the experimental conditions is calculated from the peak retention time, using the method recently demonstrated by Matthews and Akgerman (1987). The retention time of a solute pulse is a function of the dispersion tube volume, mass flow rate, and density. The tube volume $V_t^{(1)}$ may be calibrated using a solvent of known density ρ_1 by performing the Taylor dispersion experiment and measuring the retention time $t_{id}^{(1)}$ and mass flow rate $\dot{m}_1$. The density of any other solvent at condition 2 may be calculated as follows:

$$\rho_2 = \rho_1 \frac{\dot{m}_2}{\dot{m}_1} \frac{\bar{t}_{id}^{(2)}}{\bar{t}_{id}^{(1)}} \frac{V_t^{(1)}}{V_t^{(2)}} \tag{8}$$

The tube volume $V_t^{(2)}$ is corrected for thermal expansion. Densities measured using this technique are shown to be accurate to better than ±0.2% (Matthews and Akgerman, 1987).

Results and Discussion

Before extensive data gathering, calibration experiments were performed to show that the detector response was linear with concentration and that there were no contributions from secondary flow in the coiled tube. A comparison of diffusivities in *n*-heptane with literature shows good agreement, as reported in Table 1. The differences are less than 5% except for tetradecane. There are few data on these systems, but there are two measurements of decane diffusivity in heptane. There is quite a discrepancy in those values, which emphasizes the uncertainty associated with diaphragm cell techniques.

Table 1. Comparison of Diffusion Coefficients at Infinite Dilution in Heptane at 298 K, 101 kPa

	$D \times 10^9$ m²/s	
Solute	This Work	Literature
Octane	2.91	2.80*
Decane	2.61	2.54,** 3.08†
Dodecane	2.24	2.15**
Tetradecane	2.05	1.89**
Hexadecane	1.84	1.78‡

*Interpolated from Alizadeh and Wakeham (1982); technique: Taylor dispersion

**Lo (1974); technique: diaphragm cell

†Moore and Welleck (1974); technique: unsteady-state diaphragm

‡Bidlack et al. (1969); technique: optical diffusiometer

Most of the experimental data are at a fixed pressure of 1,380 or 3,450 kPa. For diffusion in heptane, temperatures were limited to 473 K (safely below the critical temperature). Table 2 shows all results for diffusion of *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane in *n*-heptane and *n*-dodecane. The diffusion coefficients shown are the average of three values with a standard deviation typically 0.5% to 3% of the mean. Dodecane viscosity (uncertainty ±3%) and density (uncertainty less than ±0.2%) were measured in this laboratory. Available literature data were used for heptane viscosity (Stephan and Lucas, 1979) and density (Orwoll and Flory, 1967) and are included in Table 2 for completeness.

In Figure 2, the measured diffusivities of octane in dodecane are compared with the predictions from the Wilke-Chang (1955) equation, the Shieh and Lyons (1969) correlation, the Lusis-Ratcliff (1968) correlation, and the correlation for *n*-

Table 2. Tracer Diffusion Coefficients and Solvent Density and Viscosity*

Temp. K	Press. kPa	$D \times 10^9$ m²/s					ρ kg/m³	$\eta \times 10^3$ Pa · s
		C_8	C_{10}	C_{12}	C_{14}	C_{16}		
			Solvent: *n*-Heptane					
299	101	2.91	2.61	2.36	2.05	1.85	679.4	0.390
	3,550	—	—	2.18	1.99	1.80	682.8	0.406
374	379	—	5.67	—	—	4.20	612.7	0.196
	3,475	6.24	5.51	4.97	4.46	4.09	618.1	0.205
427	710	—	—	—	—	6.82	557.8	0.127
	3,475	10.1	8.70	7.80	6.89	6.44	567.5	0.134
477	1,406	—	—	—	—	10.8	501.9	0.085
	3,475	15.08	12.9	11.9	10.8	10.1	518.5	0.092
			Solvent: *n*-Dodecane					
304	1,413	1.31	1.15	—	0.92	0.75	742.2	1.259
373	1,413	3.43	3.05	—	2.18	2.10	691.6	0.527
	3,433	3.43	—	—	—	—	692.9	0.532
443	1,446	6.76	5.76	—	4.43	4.09	636.6	0.287
	3,434	6.62	—	—	—	—	639.6	0.294
514	1,448	11.3	9.83	—	7.70	7.08	578.0	0.186
	3,433	11.2	—	—	—	—	581.8	0.191
566	1,417	17.0	14.9	—	12.0	11.3	523.1	0.141
	3,440	15.9	—	—	—	—	531.8	0.155

*Heptane viscosity from Stephan and Lucas (1979), density from Orwoll and Flory (1967); dodecane viscosity and density measured in this work.

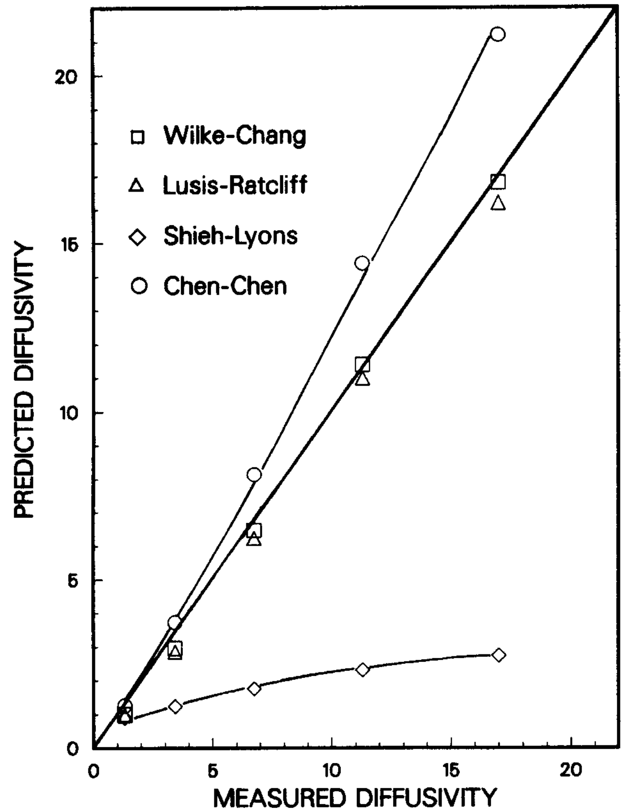

Figure 2. Evaluation of some available correlations for diffusion of octane in dodecane over a wide temperature range.

alkanes recommended by Chen and Chen (1985b). The octane/dodecane system is typical of all systems studied. The two oldest hydrodynamic equations (Wilke-Chang and Lusis-Ratcliff) actually perform best. The equation of Chen and Chen tends to overpredict at the highest temperatures (corresponding to highest diffusivities), while the empirical relation of Shieh and Lyons badly underpredicts at temperatures above ambient.

Dymond (1974) has shown that computer calculations for self-diffusivity of rough hard sphere molecules may be represented by a free-volume type equation. Following the example of Chen et al. (1982) for mutual diffusion, this is expressed in the form:

$$\frac{D_{AB}}{\sqrt{T}} = \beta\,(V_B - V_D) \tag{9}$$

For diffusion at infinite dilution, the coefficient β is a function of the solute and solvent interaction, while V_D is a function only of the solvent and represents the molar volume at which diffusivity approaches zero. This relationship is demonstrated in Figure 3 for diffusion in *n*-dodecane.

Although the relationship demonstrated in Figure 3 has been demonstrated previously (Chen and Chen, 1985b; Chen et al. 1982; Dymond, 1974) the drawback to use of Eq. 9 has been how to determine β and V_D. For mutual diffusion in *n*-alkanes the following simple relationships for V_D and β are found:

$$V_D = 0.308\,V_C$$

$$\beta = 32.88\,M_A^{-0.61}\,V_D^{-1.04} \tag{10}$$

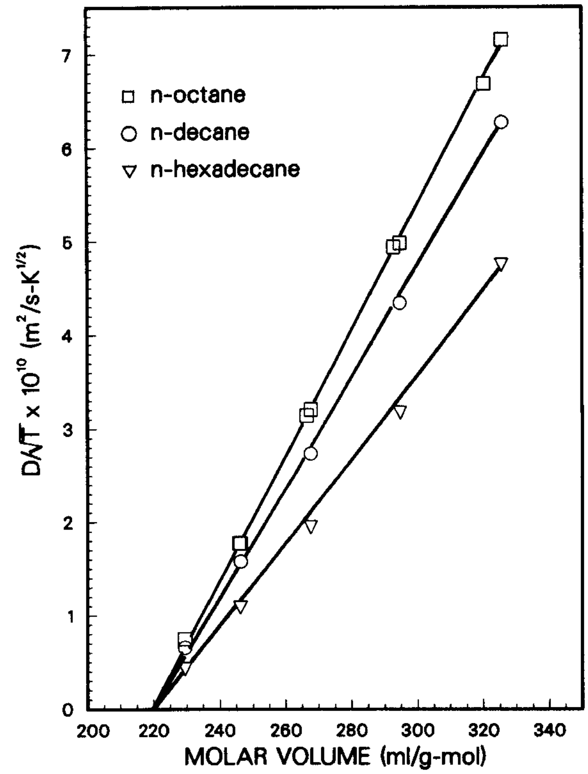

Figure 3. Free-volume relation for diffusion coefficients in the solvent *n*-dodecane.

— Eqs. 9, 10

Thus, knowing only the solvent critical volume V_C and the solute molecular weight M_A, one can calculate the diffusion coefficient of solute B in dilute concentration using Eqs. 9 and 10. The average absolute percent deviation of Eq. 9 is 2.9% for these data, with all errors less than 10% except for one error of 13.4%. These findings are in accord with those of Batchinski (1913) and Hildebrand (1971).

Equations 9 and 10 were tested using the data of Alizadeh and Wakeham (1982) at infinite dilution and the self-diffusion data of Ertl and Dullien (1973). Comparison of the correlation to these data is given in Figure 4. The data of Alizadeh and Wakeham for the solvents heptane and octane can be fitted with an average absolute percent deviation of 3.4%, and the self-diffusion data of Ertl and Dullien for heptane, decane, dodecane, and tetradecane can be fitted to 5%. As is evident from Figure 4, Eqs. 9 and 10 show promise as a general relationship for predicting mutual and self-diffusion coefficients in linear hydrocarbon.

Conclusions

The data presented here for diffusion of normal alkane solutes in heptane and dodecane extend to higher temperatures than any previous work on these systems. Existing correlations may fail to predict the behavior of the diffusion coefficient over a wide temperature range.

A generalized free-volume expression based on rough hard sphere theory has been shown to work well in predicting both interdiffusion and self-diffusion in several *n*-alkane solvents. The only data needed to use the correlation are solvent critical

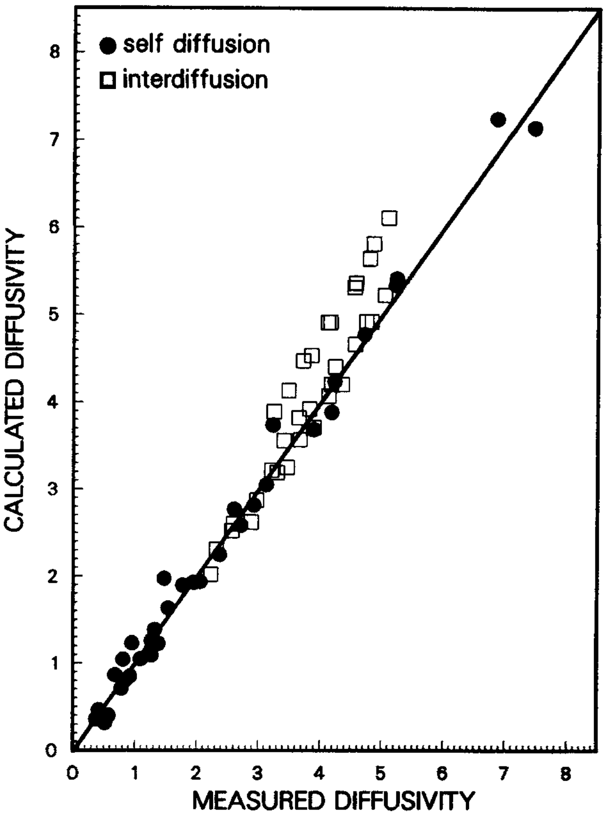

Figure 4. Comparison of predictive equation to literature data.

$D_{AB} \times 10^9\ m^2/s$
□ Alizadeh and Wakeham (1982)
● Ertl and Dullien (1973)

volume, solute molecular weight, and solvent molar volume at the temperature and pressure of interest.

Acknowledgment

This work was supported by the U. S. Department of Energy, Contract No. DE-AC22-84PC 70032. Mr. Matthews gratefully acknowledges Tenneco and the College of Engineering for fellowship support.

Notation

$C(t)$ = concentration at time $t(i)$
D_{AB} = molecular diffusivity of solute A in solvent B
K = effective dispersion coefficient
L = length of diffusion tube
$\dot{m}$ = mass flow rate
M = molecular weight
R_t = radius of diffusion tube
S = zeroth temporal moment
t = time from instant of sample injection
$\bar{t}$ = normalized first temporal moment (retention time)
Δt = time interval between concentration measurements
T = absolute temperature
$\bar{u}$ = mean velocity of laminar flow
V = molar volume
V_c = solvent critical volume
V_D = minimum free volume for diffusion
V_t = volume of diffusion tube

Greek letters

η = viscosity, cp
ρ = fluid density
σ^2 = normalized, centralized second temporal moment
ζ_0 = variable relating temporal to spatial moments, Eqs. 2, 7

Subscripts

id = ideal
obs = observed
A, B = solute, A, or solvent, B

Literature Cited

Alizadeh, A. A., C. A. Nieto de Castro, and W. A. Wakeham, "The Theory of the Taylor Dispersion Technique for Liquid Diffusivity Measurements," *Int. J. Thermophys.*, **1**, 243 (1980).

Alizadeh, A. A., and W. A. Wakeham, "Mutual Diffusion Coefficients for Binary Mixtures of Normal Alkanes," *Int. J. Thermophys.*, **8**, 307 (1982).

Aris, R., "On the Dispersion of a Solute in a Fluid Flowing Through a Tube," *Proc. Roy. Soc.*, **A285**, 67 (1956).

Batchinski, A. J., "Investigations on the Internal Friction of Liquids," *Z Physik. Chem.*, **84**, 643 (1913).

Bidlack, D. L., T. K. Kett, C. M. Kelly, and D. K. Anderson, "Diffusion in the Solvents Heptane and Carbon Tetrachloride," *J. Chem. Eng. Data*, **14**, 342 (1969).

Chen, H. C., and S. H. Chen, "Corresponding States Correlation of Tracer Diffusion in Liquids," *Ind. Eng. Chem. Fundam.* **24**, 183 (1985a)

———, "Tracer Diffusion of Crown Ethers in *n*-Decane and *n*-Tetradecane: An Improved Correlation for Binary Systems Involving Normal Alkanes," *Ind. Eng. Chem. Fundam.* **24**, 187 (1985b).

———, "Taylor Dispersion Measurements of the Diffusivities of Polymethylenes in Dilute Solutions," *Chem. Eng. Sci.*, **40**(8), 521 (1985c).

Chen, S. H., H. T. Davis, and D. F. Evans, "Tracer Diffusion in Polyatomic Liquids. III," *J. Chem. Phys.*, **77**(5), 2540 (1982).

Dymond, J. H., "Corrected Enskog Theory and the Transport Coefficients of Liquids," *J. Chem. Phys.*, **60**, 969 (1974).

Ertl, H., and F. A. L. Dullien, "Self-Diffusion and Viscosity of Some Liquids as a Function of Temperature," *AIChE J.*, **19**(6), 1215 (1973).

Harvey, M. C., and S. D. Stearns, "High-Speed Switching of Liquid Chromatographic Injection Valves," *Analyt. Chem.*, **56**, 837 (1984).

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

Levenspiel, O., and W. K. Smith, "Notes on the Diffusion-type Model for the Longitudinal Mixing of Fluids in Flow," *Chem. Eng. Sci.*, **6**, 227 (1957).

Lo, H. Y., "Diffusion Coefficients in Binary Liquid *n*-Alkane Systems," *J. Chem. Eng. Data*, **19**, 236 (1974).

Lusis, M. A., and G. A. Ratcliff, "Diffusion in Binary Liquid Mixtures at Infinite Dilution," *Can. J. Chem. Eng.*, **46**, 385 (1968).

Matthews, M. A., and A. Akgerman, "A New Method for Measuring Fluid Densities Using the Taylor Dispersion Experiments," *Int. J. Thermophys.*, **8**, 363 (1987).

Moore, J. W., and R. M. Welleck, "Diffusion Coefficients of *n*-Heptane and *n*-Decane in *n*-Alkanes and *n*-Alcohols at Several Temperatures," *J. Chem. Eng. Data*, **19**, 136 (1974).

Orwoll, R. A., and P. J. Flory, "Equation of State Parameters for Normal Alkanes. Correlation with Chain Length," *J. Am. Chem. Soc.*, **89**, 6814 (1967).

Pratt, K. C., and W. A. Wakeham, "The Mutual Diffusion Coefficient for Binary Mixtures and Water and the Isomers of Propanol," *Proc. Roy. Soc.*, **A842**, 401 (1975).

Shieh, J. C., and P. A. Lyons, "Transport Properties of Liquid *n*-Alkanes," *J. Phys. Chem.* **78**(10), 3258 (1969).

Stephan, K., and K. Lucas, "Viscosity of Dense Fluids," Plenum, New York (1979).

Taylor, G. I., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube," *Proc. Roy. Soc.*, **A219**, 186 (1953).

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

Manuscript received July 29, 1986, and revision received Dec. 23, 1986.