

Figure 3. Density of *n*-hexadecane at 205 psia: \square , measured; —, calculated from Orwoll and Flory (1967); ---, best fit of data.

pressures well above ambient.

Glossary

D_{AB} diffusivity of solute A in solvent B, m^2/s
 L dispersion tube length

\dot{m} mass flow rate
 R dispersion tube radius
 T absolute temperature, K
 \bar{t} first temporal moment (retention time)
 V molar volume of solvent, $cm^3/g\text{-mol}$
 V_t dispersion tube volume
 β coefficient in correlation of eq 5
 ρ solvent density, g/cm^3
 σ^2 second temporal moment (variance)
 ζ_0 defined by eq 3
 η viscosity, cP

Registry No. *n*-Octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3.

Literature Cited

- (1) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. *Int. J. Thermophys.* **1980**, *1*(3), 243.
- (2) Matthews, M. A.; Akgerman, A. "Diffusivities of Synthesis Gas and Fischer-Tropsch Products in Slurry Media"; Quarterly Report, Jan-Mar 1986, U.S. Department of Energy DE-AC2284PC 70032.
- (3) Matthews, M. A.; Akgerman, A. *Int. J. Thermophys.* **1987**, *8*, 363.
- (4) Matthews, M. A.; Akgerman, A. *AIChE J.*, in press.
- (5) Matthews, M. A. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1986.
- (6) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6814.
- (7) *TRC Thermodynamic Tables—Hydrocarbons*; Thermodynamics Research Center, Texas A&M University System: College Station, TX, 1986.

Received for review August 25, 1986. Accepted March 30, 1987. This work was supported by Contract DE-AC22-84PC 70032 from the U.S. Department of Energy.

High-Temperature Diffusion of Hydrogen, Carbon Monoxide, and Carbon Dioxide in Liquid *n*-Heptane, *n*-Dodecane, and *n*-Hexadecane

Michael A. Matthews, John B. Rodden, and Aydin Akgerman*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

Mutual diffusion coefficients at infinite dilution have been measured for hydrogen, carbon monoxide, and carbon dioxide in the solvents *n*-heptane, *n*-dodecane, and *n*-hexadecane. The data cover the temperature range from 25 to 293 °C and pressures of 1415 and 3450 kPa. The Taylor dispersion method was used for diffusion measurements. It was found that the Sovova correlation for diffusion of dissolved gases in liquids failed to predict diffusivities at temperatures above ambient. A free-volume approach to correlation is indicated instead.

Introduction

Diffusion coefficients of hydrogen, carbon monoxide, and carbon dioxide are needed in evaluation of mass transport in high-temperature applications such as hydrogenation, hydro-treating, Fischer-Tropsch synthesis, coal liquefaction, etc. The

data in the literature are at temperatures and pressures near ambient, and predictive theories based on these data cannot reliably be extrapolated to the high-temperature range. The objective of this work was to measure diffusion coefficients for these gases at temperatures to 293 °C and pressures to 3450 kPa (500 psia).

Experimental Technique

Mutual diffusion coefficients of the three gases were measured by using the Taylor dispersion method. The present device and working equations have been described previously (1). In this method, a narrow pulse of solute (A) diluted in the solvent (B) is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance σ^2 is dependent on the average flow velocity \bar{u} and molecular diffusivity D_{AB} . At the end of the diffusion tube the concentration vs. time data $C(t)$

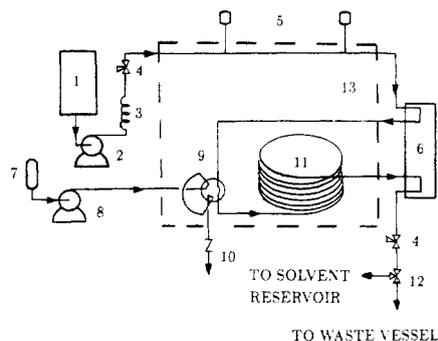


Figure 1. Schematic diagram of high-pressure high-temperature Taylor dispersion apparatus: 1, solvent reservoir; 2, solvent pump; 3, capillary tubing pulse damper; 4, back pressure regulators; 5, pressure transducers; 6, refractive index detector; 7, sample solution; 8, sample injection pump; 9, 6-port sample injection valve; 10, adjustable check valve; 11, coiled dispersion tube; 12, 3-way valve; 13, heated enclosure.

are recorded as the peak elutes. The normalized first and second temporal moments \bar{t} and σ^2 are calculated by finite summation (eq 1–3), and then the diffusion coefficient is calculated from eq 4.

$$M = \sum C(t)\Delta t \quad (1)$$

$$\bar{t} = \frac{1}{M} \sum tC(t)\Delta t \quad (2)$$

$$\sigma^2 = \frac{1}{M} \sum (t - \bar{t})^2 C(t)\Delta t \quad (3)$$

$$D_{AB} = \frac{1}{2} \left[\bar{u}L\zeta_0 - \left[(\bar{u}L\zeta_0)^2 - \left(\frac{\bar{u}^2 R^2}{12} \right) \right]^{1/2} \right] \quad (4)$$

where

$$\bar{u} = \frac{L}{t} (1 + 2\zeta_0) \quad (5)$$

$$\zeta_0 = \frac{2\sigma^2 - \bar{t}^2 + [\bar{t}^4 + 4\bar{t}^2\sigma^2]^{1/2}}{(8\bar{t}^2 - 4\sigma^2)} \quad (6)$$

Equation 4 accounts for molecular diffusion in both axial and radial directions within the dispersion tube. The tube length L and radius R are corrected for thermal expansion effects which are significant at temperatures above 100 °C. Alizadeh et al. (2) have recently discussed the Taylor dispersion method in extensive detail. By designing the present apparatus in accord with the discussion of Alizadeh et al. (2), the systematic errors are reduced to the order of 0.5%.

The apparatus is shown in Figure 1. The solvent is sparged with helium and pumped through a capillary restrictor and backpressure regulator, which act to dampen pulses from the metering pump. The solvent flows through the reference side of the concentration detector (LDC/Milton Roy Refractometer) and back into the heated enclosure where the solute sample is injected. The sample was prepared by saturating the solvent with gas at room temperature. The saturation pressure was 50 psig for CO₂ and 150 psig for CO and hydrogen. The peak disperses in the tube, where the retention time is approximately 3 h, and then passes through the sample side of the detector and out of the system.

Concentration vs. time data were collected with the aid of a digital voltmeter and a microcomputer. Typically, at least 100 time vs. concentration points were collected and stored on disk for each response peak. The first and second moments were subsequently calculated by finite summation (eq 1–3).

Temperature measurements were made with six thermistors placed at various locations within the heated enclosure. The

Table I. Diffusion Coefficients of Gases in Alkane Solvents ($D_{AB} \times 10^9 \text{ m}^2/\text{s}$)

$T, ^\circ\text{C}$	P, kPa	H ₂	CO	CO ₂
Solvent: <i>n</i> -Heptane				
25	1014	24.0 ± 1.2	8.12 ± 0.2	
154	3448	70.7 ± 0.3	25.3 ± 0.02	
Solvent: <i>n</i> -Dodecane				
31	1393	10.9 ± 0.2	4.73 ± 0.21	3.90 ± 0.04
99	1412	27.1 ± 1.2	10.7 ± 0.4	8.68 ± 0.1
99	3444	24.9 ± 0.8	9.54 ± 0.25	8.68 ± 0.06
172	1445	46.3 ± 0.03	16.4 ± 0.4	15.6 ± 0.2
170	3454	41.0 ± 1.0	17.6 ± 0.2	15.6 ± 0.1
240	1451	78.0 ± 4.8	27.0 ± 0.7	25.1 ± 0.1
242	3435	70.3 ± 1.3	26.0 ± 1.5	24.7 ± 0.2
294	1463	118 ± 2	43.4 ± 0.8	37.0 ± 0.4
293	3439	112 ± 1	43.1 ± 1.3	34.9 ± 0.3
Solvent: <i>n</i> -Hexadecane				
50	1421	10.5 ± 0.3	4.01 ± 0.14	3.48 ± 0.03
50	3460	10.3 ± 0.6	3.86 ± 0.07	3.47 ± 0.09
98	1404	20.8 ± 0.1	6.72 ± 0.15	6.57 ± 0.01
98	3439	18.9 ± 0.4	7.19 ± 0.18	6.53 ± 0.12
170	1397	35.1 ± 1.6	13.6 ± 0.2	12.5 ± 0.1
170	3426	35.2 ± 2.5	13.1 ± 0.5	12.4 ± 0.1
240	1412	51.2 ± 2.5	22.5 ± 0.6	20.2 ± 0.2
240	3428	49.7 ± 1.7	21.5 ± 0.1	19.9 ± 0.1
291	1404	69.0 ± 6.0	32.3 ± 0.5	27.4 ± 0.1
291	3409	64.0 ± 4.3	28.7 ± 0.7	27.2 ± 0.4

thermistors were calibrated against a Rosemount platinum RTD which had been certified by the U.S. National Bureau of Standards. The temperatures were averaged to give the reported values, which have an estimated uncertainty of less than ±1 °C. Pressures were measured with a strain gauge pressure transducer calibrated against a Ruska air dead-weight gauge. The pressure is estimated to be accurate to ±3.4 kPa.

Hexadecane was obtained from Alfa Chemicals, dodecane from Phillips Chemicals, and *n*-heptane from MCB Reagents. Bottled gases were used as received. The minimum stated purity for the solvents was 99 mol %, which was confirmed by gas chromatography.

Results and Discussion

Measured diffusion coefficients are given in Table I as the mean of three repeat measurements. Also given are the standard deviations about the mean. Standard deviations are typically less than ±5% of the mean for the CO and CO₂ data. For hydrogen, the standard deviations are usually somewhat larger because hydrogen, being the least soluble at saturation conditions, gives the least intense response peak. Random noise in the signal thus gives larger relative error.

These data extend the available temperature range for diffusion measurements by about 200 °C. Previous predictive equations are almost exclusively based on data taken at ambient temperatures. The most prevalent approach to data correlation is based on hydrodynamic theory, wherein the diffusion coefficient is taken to be inversely proportional to the solvent viscosity η , or some arbitrary power of the viscosity. The most recent general correlation for the diffusivity of gases in liquids was developed by Sovova (3) in which the diffusion coefficient is determined by the viscosity of the solvent and the molar volume V_A of the solute. For *n*-alkane solvents, Sovova presents the following correlation

$$D_{AB} = 33.74\eta^{-0.5}V_A^{-0.6} \quad (7)$$

where η is in centipoise and V_A is in cm³/g-mol.

The predictions of this equation are compared to our measured values in Figures 2 and 3, where diffusion coefficients are

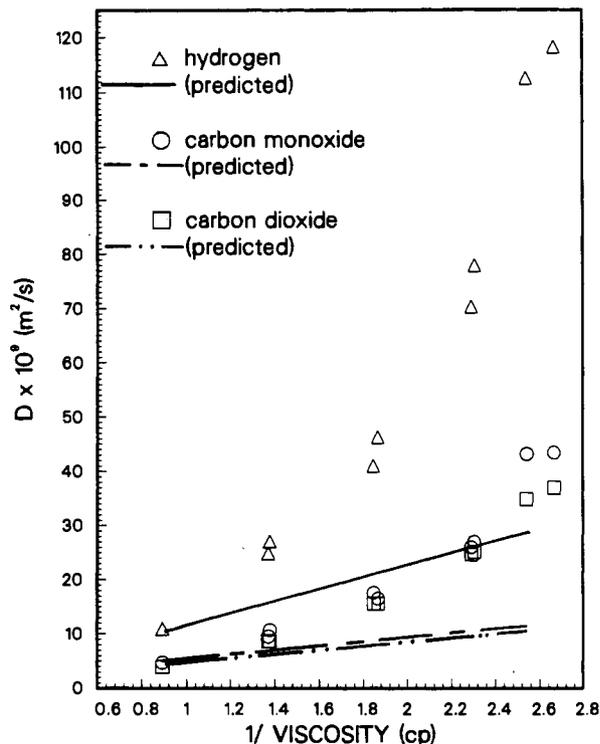


Figure 2. Comparison of measured diffusivities in dodecane to predictions from the Sovova correlation.

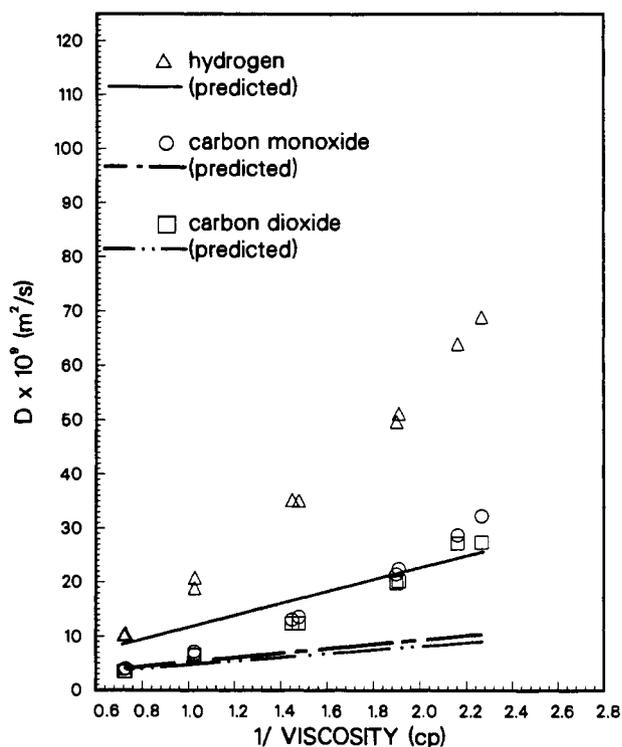


Figure 3. Comparison of measured diffusivities in hexadecane to predictions from the Sovova correlation.

plotted against the reciprocal of the square root of the solvent viscosity. The values of V_A used are those recommended by Sovova (6). It is evident that at temperatures above ambient temperatures the correlation fails badly.

Dymond (4), Chen and Chen (5), and Sun and Chen (7) have suggested a superior method for correlation of diffusion coefficients which is based on the free volume in the solvent. Figures 4, 5, and 6 show the linear relationship between $D_{AB}/T^{1/2}$ and solvent molar volume V for the three gas

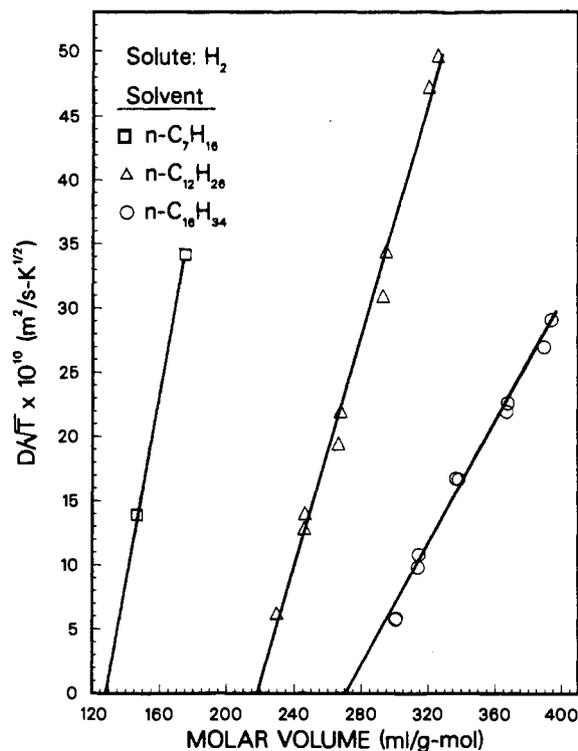


Figure 4. Free-volume relation for the solute hydrogen over the temperature range 25–293 °C. Straight lines represent eq 8 with the parameters from Table II.

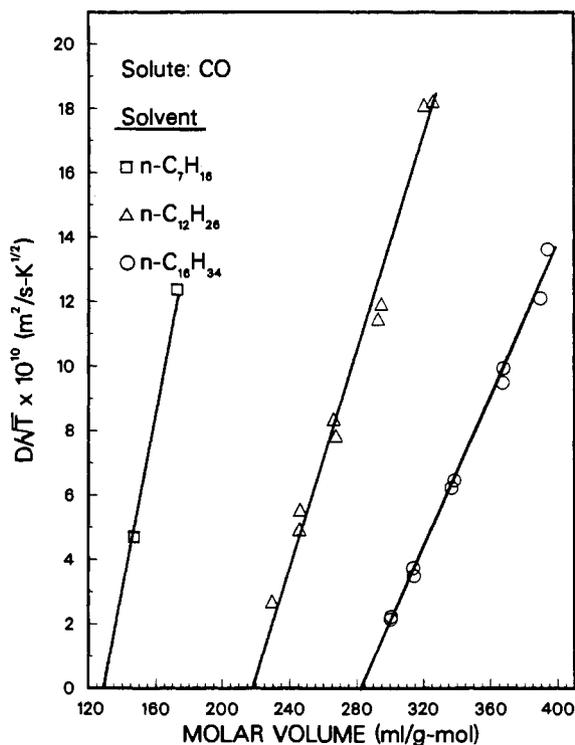


Figure 5. Free-volume relation for the solute carbon monoxide over the temperature range 25–293 °C. Straight lines represent eq 8 with the parameters from Table II.

solutes. This confirms the form of the expression suggested by the above authors

$$\frac{D_{AB}}{T^{1/2}} = \beta(V - V_D) \quad (8)$$

where the parameters β and V_D are given in Table II. The average absolute deviation for eq 8 is 4%, with the largest

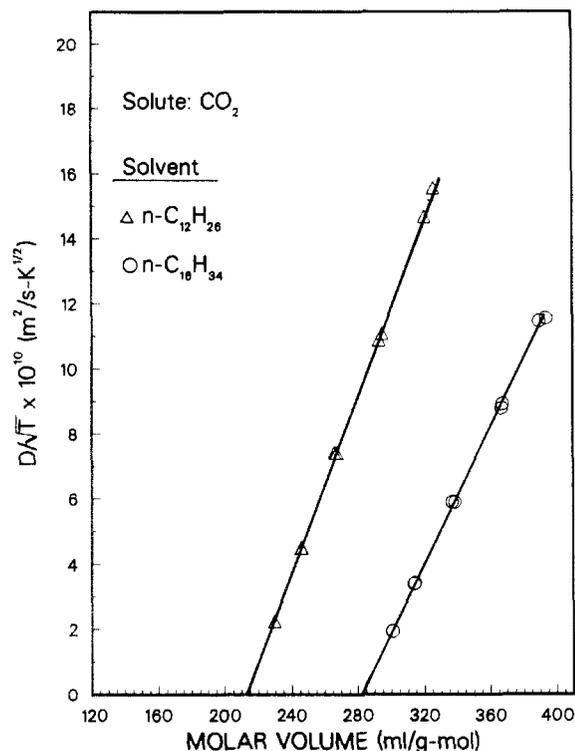


Figure 6. Free-volume relation for the solute carbon dioxide over the temperature range 30–293 °C. Straight lines represent eq 8 with the parameters from Table II.

Table II. Best Fit Parameters for Eq 8^a

solute	solvent					
	heptane		dodecane		hexadecane	
	V_D	β	V_D	β	V_D	β
H ₂	128	0.0698	218	0.0449	272	0.0237
CO	129	0.0259	215	0.0162	283	0.0117
CO ₂			213	0.0137	282	0.0104

^a D_{AB} in 10^9 m²/s, V_D in cm³/mol, β in m²·(mol/s)·cm³·K^{1/2}.

deviations occurring at the lowest temperatures.

Conclusions

This work extends the data base for diffusion coefficients of hydrogen, carbon monoxide, and carbon dioxide in alkane solvents to the high-temperature region, where few dissolved

gas measurements of any kind are available. The data will aid in design calculations of mass-transfer resistances at high temperature, and in the development of predictive theories for diffusion. Previously, data were available only at temperatures near ambient, and it is likely that correlations based on such data will not extrapolate reliably to higher temperatures. This point is demonstrated for the recently proposed Sovova correlation. The validity of a free-volume relationship over a wide temperature range is demonstrated, which suggests a superior method of correlation compared to the hydrodynamic approach.

Glossary

D_{AB}	diffusivity of solute A in solvent B
L	dispersion tube length
M	zeroth temporal moment
R	dispersion tube radius
T	absolute temperature, K
t	time
\bar{t}	first temporal moment
\bar{u}	average velocity of laminar flow
V	molar volume of solvent, cm ³ /mol
V_A	molar volume of solute at normal boiling point, cm ³ /mol
V_D	molar volume of solvent at which diffusion goes to zero, cm ³ /mol
β	coefficient in eq 8
σ^2	second temporal moment (variance)
ζ_0	defined by eq 6
η	solvent viscosity

Registry No. H₂, 1333-74-0; CO₂, 124-38-9; CO, 630-08-0; *n*-heptane, 142-82-5; *n*-dodecane, 112-40-3; *n*-hexadecane, 544-76-3.

Literature Cited

- (1) Matthews, M. A.; Akgerman, A. *AIChE J.*, in press.
- (2) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. *Int. J. Thermophys.* **1980**, *1*, 243.
- (3) Sovova, H. *Collect. Czech. Chem. Commun.* **1976**, *41*, 3715.
- (4) Dymond, J. H. *J. Chem. Phys.* **1974**, *3*, 969.
- (5) Chen, H. C.; Chen, S. H. *Ind. Eng. Chem. Fund.* **1985**, *24*, 187.
- (6) Chen, S. H.; Davis, H. T.; Evans, D. F. *J. Chem. Phys.* **1982**, *77*, 2540.
- (7) Sun, C. K. J.; Chen, S. H. *AIChE J.* **1985**, *31*, 1510.

Received for review August 25, 1986. Accepted March 30, 1987. This work was supported by Contract DE-AC22-84PC 70032 from the U.S. Department of Energy.