Predictive Correlation for Binary Diffusion Coefficients in Dense Carbon Dioxide

Toshitaka Funazukuri, Yoshihisa Ishiwata, and Noriaki Wakao
Dept. of Materials Science and Chemical Engineering, Yokohama National University, Yokohama 240, Japan

Binary diffusion coefficients of some organic compounds in carbon dioxide at 313.2 K and 16.0/25.0 MPa were measured by using the Taylor-Aris tracer response technique. We propose a new correlation of Schmidt numbers as a function of solvent molar volumes for predicting binary diffusion coefficients in dense CO_2 *and self-diffusion coefficients of dense* CO_2*. The correlation was also found to be valid for predicting self-diffusion coefficients of dense* CH_4 *at* $F_v/A^* < 40$ *or* $v_2/(\tilde{v}_2)_0 > 1.62$*.*

Introduction

Over the past two decades, a number of studies have been made on supercritical (SC) fluid extraction as a novel separation process to fractionate valuable substances from natural products. Carbon dioxide has been widely used as a solvent because of the advantages of its mild critical condition, nonflammability, and nontoxicity. Despite the growing number of separation studies, measurements of the physical properties, especially binary molecular diffusion coefficients (D_{12}), in SC CO_2 have been limited (Takahashi, 1972; Swaid and Schneider, 1979; Feist and Schneider, 1982; Takahashi and Hongo, 1982; Lauer et al., 1983; Sassiat et al., 1987; Funazukuri et al., 1989, 1991; Liong et al., 1991). In fact, few studies on binary diffusion coefficients in SC CO_2 for solutes of valuable substances, which are commonly high molecular weight compounds, have been reported (for example, Funazukuri et al., 1989, 1991; Liong et al., 1991). Furthermore, the ability to predict D_{12} in SC solvents has not been well established.

Funazukuri et al. (1991) found that the ratio of Schmidt number ($Sc = \mu_2/\{\rho_2 D_{12}\}$, where μ_2 = solvent viscosity, ρ_2 = solvent density, and D_{12} = binary diffusion coefficient) at a prescribed pressure to that at atmospheric pressure ($Sc^* = \mu_2^*/\{\rho_2^* D_{12}^*\}$) was almost independent of the solute molecular weight for D_{12} data of C_{16}- to C_{24}- unsaturated fatty acid methyl esters (C_{16}- to C_{24}- AME) in SC CO_2. Based on this evidence, Funazukuri et al. proposed the following empirical equation to predict D_{12} in SC CO_2:

$$\ln\left(\frac{Sc}{Sc^*} - 1\right) = -1.40 \ln\left[\frac{v_2 - (v_2)_0}{(v_2)_0}\right] + 1.48 \qquad (1)$$

where v_2 is CO_2 molar volume, and $(v_2)_0$ is the minimum free diffusion volume, which is equal to $1.384 N\sigma_2^3/\sqrt{2}$ (N = Avogadro's number, σ_2 = effective hard sphere diameter of CO_2). Equation 1 not only well correlated the D_{12} data of C_{16}- and C_{24}- AME, but also the CO_2 self-diffusion coefficients (D_{22}) reported in the literature. In this study, D_{12}'s for 12 nonelectrolytic organic compounds in SC CO_2 were measured by the tracer response technique. We propose a new correlation, modifying Eq. 1, for predicting binary- and self-diffusion coefficients in/of CO_2.

Theoretical Background

Determination of binary diffusion coefficients

The theoretical basis for measuring tracer dispersion in a cylindrical tube was developed by Taylor (1953, 1954a,b) and Aris (1956). Later, Alizadeh et al. (1980) rigorously analyzed this tracer response technique for measurement of molecular diffusion coefficients.

When a tracer species is injected into a stream of CO_2 flowing at a laminar flow rate u in a tubing (length L and radius r), the normalized concentration of the tracer species C^+ at the column exit is given by

$$C^+ = \frac{1}{2\sqrt{\left(\pi\theta \dfrac{D_{\text{eff}}}{uL}\right)}} \exp\left[\frac{-(1-\theta)^2}{\dfrac{4\theta D_{\text{eff}}}{uL}}\right] \qquad (2)$$

where θ is the dimensionless time t/τ (τ is the mean residence time L/u). If

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Correspondence concerning this article should be addressed to T. Funazukuri.

$$\frac{L}{2u} \gg \frac{r^2}{(3.8)^2 D_{12}'} \tag{3}$$

is satisfied, then the effective dispersion coefficient, D_{eff}, is expressed as

$$D_{\mathrm{eff}} = \frac{r^2 u^2}{48 D_{12}'} \tag{4}$$

where D_{12}' is the apparent molecular diffusion coefficient. In our experiment, C^+, denoted by C^+_{exptl}, is obtained from a readout curve at the column exit, and C^+_{exptl} is

$$C^+_{\mathrm{exptl}} = \frac{C_{\mathrm{exptl}}}{\dfrac{1}{\tau}\displaystyle\int_0^\infty C_{\mathrm{exptl}}\,dt} \tag{5}$$

The C^+_{exptl} vs. t curve obtained experimentally through Eq. 5 is compared in the time domain with $C^+_{\mathrm{calc}} - t$ curves calculated from Eq. 2 with assumed values of D_{12}'. The value of D_{12}' is then determined so that the error,

$$\mathrm{error} = \left[\frac{\displaystyle\int_0^\infty (C^+_{\mathrm{exptl}} - C^+_{\mathrm{calc}})^2 dt}{\displaystyle\int_0^\infty (C^+_{\mathrm{exptl}})^2 dt}\right]^{1/2} \tag{6}$$

is minimized ($\mathrm{error} < 0.03$). This determined value of D_{12}' is molecular diffusion coefficient D_{12} unless the D_{12}' value is affected by the flow rate u.

Correlation of Schmidt number with solvent molar volume

According to the Chapman and Enskog theory for nonpolar compounds, the Schmidt numbers at low pressures (nearly atmospheric pressure) for self-diffusion (Sc_S^*) and for binary diffusion (Sc_B^*) are, respectively,

$$Sc_S^* = \frac{\overset{*}{\mu}_2}{\overset{*}{\rho}_2 \overset{*}{D}_{22}} = \frac{A^*}{1.20} \tag{7}$$

and

$$Sc_B^* = \frac{\overset{*}{\mu}_2}{\overset{*}{\rho}_2 \overset{*}{D}_{12}} = \frac{A^*}{1.20}\left(\frac{M_{12}}{M_2}\right)^{1/2}\left(\frac{\sigma_{12}}{\sigma_2}\right)^2 \tag{8}$$

where M_{12} is the average molecular weight $2M_1M_2/(M_1+M_2)$, σ_{12} is a characteristic length which is the mean of core diameters σ_1 and σ_2, and $A^* = \Omega_D/\Omega_V$ (Ω_D and Ω_V are collision integrals for diffusion and viscosity, respectively, based on the 12-6 Lennard-Jones potential). The values of Ω_D and Ω_V are obtained from the correlations of Neufeld et al. (1972).

Using computer calculations, Dymond (1974) obtained viscosity and self-diffusion coefficients of dense fluids,

$$1/\mu_2 = \frac{1.452 \times 10^4}{(\tilde{v}_2)_0^{1/3}(M_2T)^{1/2}}\,[v_2 - (v_2)_0] \tag{9}$$

and

$$D_{22} = \frac{2.306 \times 10^{-5}}{(\tilde{v}_2)_0^{2/3}}\left[\left(\frac{T}{M_2}\right)^{1/2}(v_2 - (v_2)_0\right] \tag{10}$$

where $(v_2)_0 = 1.384\ (\tilde{v}_2)_0$, $(\tilde{v}_2)_0 = N\sigma_2^3/\sqrt{2}$ and all physical properties are in c.g.s. units. Binary diffusion coefficients in dense fluids can also be expressed (Matthews and Akgerman, 1987b) as

$$D_{12} = A_{12}\,\frac{3}{8\sigma_{12}^2}\left(\frac{kNT}{\pi M_{12}}\right)^{1/2}\frac{\alpha}{N}\,[v_2 - (v_2)_0] \tag{11}$$

where A_{12} is the translational-rotational coupling parameter, k is the Boltzmann constant and α is a constant. The ratios of Schmidt numbers for self-(Sc_S) and binary diffusion (Sc_B) at high pressure to those at atmospheric pressure are

$$\frac{Sc_S}{Sc_S^*} = \alpha_S \frac{x}{(x-1)^2}/A^* = \alpha_S F_v/A^* \tag{12}$$

and

$$\frac{Sc_B}{Sc_B^*} = \alpha_B \frac{x}{(x-1)^2}/A^* = \alpha_B F_v/A^* \tag{13}$$

where $F_v = x/(x-1)^2$ and $x = v_2/(v_2)_0$. α_S and α_B are constants if the following two assumptions can be made: (1) the ratio of the hard sphere diameters (σ_{12}/σ_2) is equal to that of the Lennard-Jones diameters; (2) the hard sphere diameters (σ_{12} and σ_2) depend upon temperature and not on solvent density. Equations 12 and 13 indicate that the ratios of the Schmidt numbers for self- and binary diffusion coefficients have the same form, and do not include σ_{12} or σ_2. Moreover, both Schmidt number ratios vary with F_v since A^* is almost 0.9 for nonpolar compounds over a wide range of $T^*(=kT/\epsilon)$. Thus, we can develop a correlation based on Eqs. 12 and 13.

Experiments

Binary diffusion coefficients of twelve compounds (Table 1) in CO_2 were measured at a temperature of 313.2 K and pressures of 16.0 and 25.0 MPa by the Taylor-Aris tracer response technique. The experimental apparatus and the procedures have been described elsewhere (Funazukuri et al., 1989, 1991), except for a pump assembly (JEOL, Japan) which consists of a micropump (Intelligent Cascade Pump, Model CAP-L02), a cooler (Model, CAP-G02) for cooling the pump head, and a gas purifier (Model CAP-G03) installed with a microfilter and adsorption columns to remove particles and organic impurities from the CO_2 (purity: 99.99%, Showa Tansan, Japan). The chemicals were used without further purification prior to the measurements.

Results and Discussion

Measurements of binary diffusion coefficients

In Table 1, the measured binary diffusion coefficients of the 12 compounds at 313.2 K and 16.0/25.0 MPa are presented with 95% confidence limits.

Table 1. Binary Diffusion Coefficients Measured in CO_2 at 313 K

No.	Substance	Molecular Formula	Molec. Weight	V_b^* $[m^3 \cdot mol^{-1}]$	Purity [%]	Supplier	λ^{**} [nm]	D_{12} Measured $[10^{-9}\ m^2 \cdot s^{-1}]^{\dagger}$ at 16.0 MPa	at 25.0 MPa
1.	Myristoleic acid methyl ester	$C_{15}H_{28}O_2$	240.4	3.44×10^{-4}	99	Sigma	205	7.18±0.20 (8)	6.03±0.05 (13)
2.	cis-11-Eicosenoic acid methyl ester	$C_{21}H_{40}O_2$	324.6	4.77×10^{-4}	99	Sigma	205	6.19±0.27 (10)	5.25±0.07 (12)
3.	Erucic acid methyl ester	$C_{23}H_{44}O_2$	352.6	5.21×10^{-4}	99	Sigma	205	5.92±0.30 (8)	5.08±0.05 (12)
4.	Vitamin K_3	$C_{11}H_8O_2$	172.2	1.77×10^{-4}	98.5	Wako	250	9.28±0.17 (13)	7.92±0.08 (10)
5.	Vitamin A acetate	$C_{22}H_{32}O_2$	328.5	4.51×10^{-4}	≈90	Sigma	325	5.95±0.11 (13)	5.47±0.17 (12)
6.	Vitamin K_1	$C_{31}H_{46}O_2$	450.7	6.14×10^{-4}	97	Wako	245	5.43±0.13 (13)	4.95±0.16 (6)
7.	Vitamin E	$C_{29}H_{50}O_2$	430.7	6.03×10^{-4}	98	Tokyo Kasei	200	5.54±0.11 (15)	5.03±0.13 (5)
8.	dl-Limonene	$C_{10}H_{16}$	136.2	1.92×10^{-4}	≈96	Wako	205	10.9±0.33 (10)	8.66±0.08 (10)
9.	cis-Jasmone	$C_{11}H_{16}O$	164.3	2.18×10^{-4}	90	Aldrich	230	8.78±0.08 (18)	7.53±0.08 (15)
10.	Indole (2,3-Benzopyrrole)	C_8H_7N	117.2	1.30×10^{-4}	99	Aldrich	265	10.4±0.1 (14)	9.22±0.06 (13)
11.	Benzene	C_6H_6	78.11	0.960×10^{-4}	99.5	Junsei	210	12.4±0.4 (28)	11.5±0.2 (8)
12.	Naphthalene	$C_{10}H_8$	128.2	1.48×10^{-4}	99	Aldrich	215	11.2±0.5 (12)	9.43±0.05 (10)

*Solute molar volume at normal boiling point estimated by the method of Le Bas (Reid et al., 1987).
**Wavelength for measuring D_{12}.
†The figures in the parentheses indicate the number of the measurements.

Lauer et al. (1983) observed that adsorption of tracer species on the column walls can be neglected if an asymmetry factor S_{10}, defined as the ratio of half peak widths measured at 10% of the peak height, approximately equaled 1. The S_{10} values for most of the compounds used in this study were close to 1. Those for Vitamin K_3 and Vitamin A acetate were 1.1, and those for indole and jasmone were 1.2 and 1.3, respectively.

Figure 1 shows a logarithmic plot of D_{12} vs. solute molecular weight M_1 at 313.2 K and 16.0 MPa for the compounds listed in Table 1 and for C_{16}- to C_{24}- unsaturated fatty acid methyl esters, as reported by Funazukuri et al. (1991). While the plots are somewhat scattered for low molecular weight compounds, D_{12} at 16.0 MPa can be correlated with M_1; the average absolute deviation (AAD)

$$\mathrm{AAD} = \frac{100}{n} \sum^{n} \left| \frac{D_{\mathrm{pred}}}{D_{\mathrm{exptl}}} - 1 \right| \tag{14}$$

is 3.1% ($D_{12} \propto M_1^{-0.5}$).

D_{12} can also be correlated with solute molar volume V_{b1} at normal boiling point ($D_{12} \propto V_{b1}^{-0.5}$, AAD = 2.9%), estimated by the method of Le Bas (Reid, et al., 1987). D_{12}'s at 313.2 K and 25.0 MPa are also correlated with $M_1^{-0.5}$ and $V_{b1}^{-0.5}$.

Sassiat et al. (1987) found that the Wilke-Chang equation (Wilke and Chang, 1955) for the prediction of binary diffusion coefficients in SC CO_2 was valid at CO_2 densities higher than 600 $kg \cdot m^{-3}$. According to this equation, $D_{12}\mu_2/T$ is proportional to $V_{b1}^{-0.6}$, however the plot indicates that the power of V_{b1} is closer to −0.5. V_{b1} can also be replaced by M_1. Because the estimated V_{b1} values do not account for structural difference of isomers, they are nearly proportional to M_1 for high molecular weight compounds.

Sources for diffusion coefficient data

Table 2 lists sources for binary diffusion coefficient (D_{12}) data in CO_2 and for self-diffusion coefficient (D_{22}) data of CO_2 reported in the literature.

Some D_{12} data reported in the literature are examined by using

$$D_{12}/\sqrt{T} = \alpha' [v_2 - (v_2)_0] \tag{15}$$

where α' is a specific value for each solute and the $(v_2)_0$ values for CO_2 (expressed as $m^3 \cdot mol^{-1}$) are estimated by the following polynomial equation from Figure 2 in Van Loef's article of 1977:

$$(v_2)_0 = \sum_{i=0}^{4} c_i T^i \tag{16}$$

where $c_0 = 4.452 \times 10^{-5}$, $c_1 = -1.152 \times 10^{-7}$, $c_2 = 2.749 \times 10^{-10}$, $c_3 = -3.073 \times 10^{-13}$ and $c_4 = 1.290 \times 10^{-16}$.

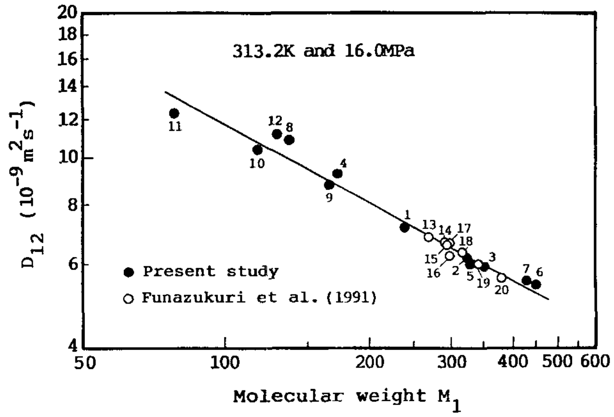

Figure 1. Logarithmic plot of measured binary diffusion coefficient D_{12} in CO_2 at 313.2 K and 16.0 MPa vs. solute molecular weight M_1.

(1 to 12. The compounds listed in Table 1; 13. $C_{16:1}$- AME; 14. $C_{18:3}$- AME; 15. $C_{18:2}$- AME; 16. trans-$C_{18:1}$- AME; 17. $C_{18:1}$- AME; 18. $C_{20:5}$- AME; 19. $C_{22:6}$- AME; 20. $C_{24:1}$- AME).

Table 2. Data Sources for Binary Diffusion Coefficients of Various Solutes in CO_2 and for Self-Diffusion Coefficients of CO_2

Solute	Investigators	Temperature [K]	Density [kg·m^{-3}]	No. of Data
Gaseous Solute				
$^{14}CO_2$	O'Hern and Martin (1955)	273.2-373.2	0.47-730	42
	Takahashi and Iwasaki (1966)	298.2-348.2	10-828	99
	Robinson and Stewart (1968)	273.2-295.7	786-992	7
$^{14}C_2H_4$	Takahashi and Hongo (1982)	298.2-348.2	17-790	48
$^3HCH_3$	Takahashi (1972)	298.2-348.2	23-492	24
^{85}Kr	Durbin and Kobayashi (1962)	308.2	10-153	7
Liquid or Solid Solute				
Acetone	Sassiat et al. (1987)	303.2-333.2	510-880	7
Benzene	Sassiat et al. (1987)	303.2-333.2	510-880	11
	Swaid and Schneider (1979)	308.2-328.2	282-800*	22
	Feist and Schneider (1982)	313.2	280-795*	6
Chrysene	Sassiat et al. (1987)	303.2-333.2	800-880	3
Naphthalene	Feist and Schneider (1982)	313.2	280-795*	7
	Lauer et al. (1983)	288.3-328.1	704-900	14
	Sassiat et al. (1987)	303.2-333.2	510-880	11
	Funazukuri et al. (1989)	313.2-328.2	792-805	5
Phenanthrene	Sassiat et al. (1987)	303.2-333.2	510-880	7
Phenol	Feist and Schneider (1982)	313.2	360-795*	5
n-Propylbenzene	Swaid and Schneider (1979)	308.2-328.2	358-800*	21
Pyrene	Sassiat et al. (1987)	303.2-333.2	650-880	3
Trimethylbenzene	Swaid and Schneider (1979)	308.2-328.2	358-800*	20
	Sassiat et al. (1987)	303.2-333.2	510-880	7
FAME**	Funazukuri et al. (1991)	308.2-328.2	739-929	26
FAEE†	Liong et al. (1991)	308-318	600-850	85

*D_{12} data at CO_2 densities lower than 600 kg·m^{-3} were not used to obtain the correlation.

**C_{16}- to C_{24}- unsaturated fatty acid methyl esters.

†$C_{18:0}$-, $C_{22:6}$- and $C_{22:0}$- ethyl esters, and $C_{20:5}$- and $C_{22:6}$- methyl esters.

In the dense gas region, many workers have confirmed Eq. 15, as a simplification of Eq. 11, to be valid for binary diffusion coefficients (Sun and Chen, 1985a,b, 1986, 1987; Matthew and Akgerman, 1987a,b; Erkey et al., 1990; Funazukuri et al., 1991; Liong et al., 1991). Figure 2 shows plots of $D_{12}/\sqrt{T}$ vs. CO_2 free volume $[v_2-(v_2)_0]$ for naphthalene, measured by Feist and Schneider (1982), Lauer et al. (1983), Sassiat et al. (1987), and Funazukuri et al. (1989), together with those of $D_{22}/\sqrt{T}$ for CO_2 self-diffusion data (O'Hern and Martin, 1955; Takahashi and Iwasaki, 1966; Robinson and Stewart, 1968). CO_2 densities were not available in the article by Takahashi and Iwasaki (1966) so we obtained these values from the IUPAC data (Angus et al., 1976). Plots for CO_2 self-diffusion increase with increasing $v_2-(v_2)_0$ values, and the slope at $v_2-(v_2)_0>5\times10^{-5}$ m^3·mol^{-1} is slightly different from that in Eq. 10. In contrast, the data of Feist and Schneider deviate increasingly from Eq. 15 (represented by a dotted line in Figure 2) as $v_2-(v_2)_0$ increases, while at $v_2-(v_2)_0<5\times10^{-5}$ m^3·mol^{-1} the plots of all investigators are consistent. Similarly, for benzene and trimethylbenzene (Swaid and Schneider, 1979), and benzene (Feist and Schneider, 1982) the D_{12} data deviate increasingly with increasing molar volume of CO_2. Lauer et al. (1983) pointed out that they were not able to reproduce the data of Feist and Schneider at CO_2 densities lower than 600 kg·m^{-3} because of severe tailing of response signals. We also were unable to obtain accurate D_{12} data in this CO_2 density range with our apparatus due to unstable CO_2 flow, although the response curves were quite symmetric. Thus, the data of Schneider and coworkers at CO_2 densities lower than 600 kg·m^{-3} were not used in this study.

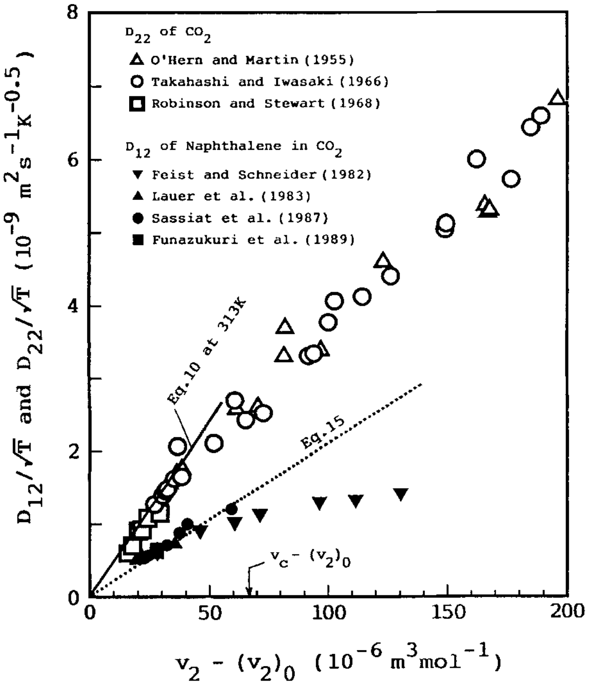

Figure 2. Plots of $D_{12}/\sqrt{T}$ for naphthalene and $D_{22}/\sqrt{T}$ for CO_2 vs. CO_2 free volume $v_2-(v_2)_0$.

Correlation development: self-diffusion coefficients

As mentioned above, Sc/Sc^* is a function of F_v/A^*. Figure

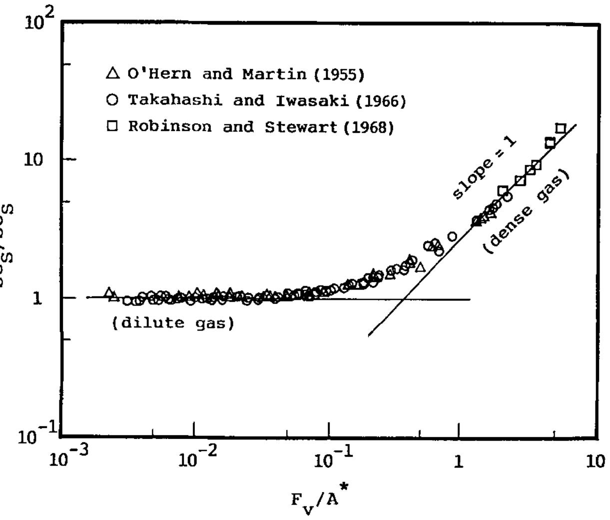

Figure 3. Logarithmic plot of Sc_S/Sc_S^* vs. F_v/A^* [$=x/(x-1)^2$; $x=v_2/(v_2)_0$] for CO_2 self-diffusion.

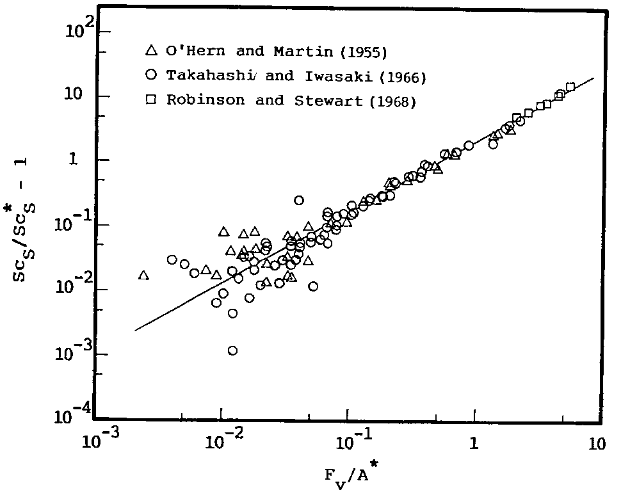

Figure 4. Logarithmic plot of Sc_S/Sc_S^*-1 vs. F_v/A^* for CO_2 self-diffusion.

The same data as in Figure 3.

3 presents this relationship using the data for D_{22} of CO_2 in the literature. The self-diffusion coefficients of CO_2 at atmospheric pressure were estimated from the data of Weissman (1964). As depicted, the plots represent a smooth curve which is asymptotic to $Sc/Sc^*=1$ at low values of F_v/A^*, and also asymptotic to a straight line with a slope of unity at high values of F_v/A^*. Thus, we can assume that the ratio Sc/Sc^* is made up of both dilute gas and dense gas terms, as follows:

$$\frac{Sc}{Sc^*}=\frac{Sc}{Sc^*}\text{ (dilute gas)}+\frac{Sc}{Sc^*}\text{ (dense gas)} \tag{17}$$

where Sc/Sc^* (dilute gas) is unity, and the dense gas term on the righthand side can correspond to Eqs. 12 and 13 for self- and binary diffusion, respectively. Consequently, we obtain:

$$\frac{Sc}{Sc^*}=1+\beta F_v/A^* \tag{18}$$

where β is constant. As depicted in Figure 4, Eq. 18 well represents the D_{22} data of CO_2. The CO_2 viscosities were estimated from the data recommended by Vesovic et al. (1990). At $F_v/A^*<0.1$ the plots are scattered since Sc_S is close to Sc_S^*, and the absolute deviations for D_{22} are very small in this region.

Figure 5 shows the same plot as in Figure 4 for CH_4 self-diffusion coefficient data measured by Harris (1978) and Harris and Trappeniers (1980) using the NMR spin-echo technique. The hard sphere diameters (σ_2) were obtained from the data of Harris and Trappeniers (1980). We determined the correlation for self-diffusion coefficients by using these accurate data. As depicted, the data are well correlated (AAD = 2.6%, AD_{max} = 11%) except at F_v/A^* higher than 40 [or $v_2/(\tilde{v}_2)_0<1.62$], where Eqs. 9 and 10 may no longer be valid. Note that at 110, 140 and 160 K, where the liquid and the vapor phases coexist, Sc_s^* are estimated for the vapor phases at atmospheric pressure for 140 and 160 K data, and at saturated vapor pressure of 0.88 bar for 110 K data. Viscosities of CH_4 were estimated by the correlation of Assael et al. (1990).

By using the data at F_v/A^* lower than 40, the following correlation was obtained:

$$\frac{Sc_S}{Sc_S^*}=1+2.18\left(\frac{F_v}{A^*}\right)^{1.12} \tag{19}$$

The power of F_v/A^* was determined to be 1.12, while it was expected to be 1 from Eq. 12. Eq. 19 is also valid for the D_{22} data of CO_2 (AAD = 3.9%, AD_{max} = 37%), represented by a

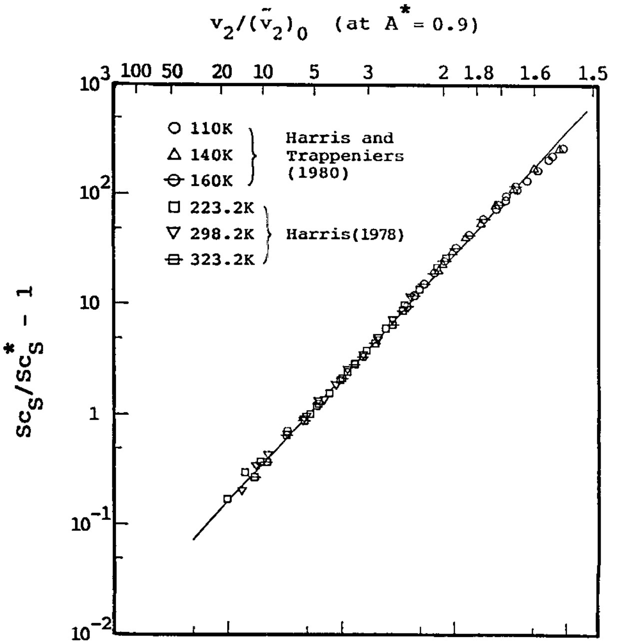

Figure 5. Logarithmic plot of Sc_S/Sc_S^*-1 vs. F_v/A^* for CH_4 self-diffusion.

solid line in Figure 4, while the data are more scattered than those for CH_4 at lower F_v/A^* values.

Correlation development: binary diffusion coefficients

Many investigators confirm that Eq. 11 is valid for binary diffusion coefficients in dense gaseous solvents. However, the problem with Eq. 11 arises from the difficulty in accurately estimating the effective hard sphere diameter of a solute having large molecular weight, as Erkey and Akgerman (1989) pointed out. Thus, it is preferable that a predictive correlation for D_{12} does not involve the σ_{12} term.

If we assume that the value of σ_{12} is independent of solvent density, then Sc_B/Sc_B^* is independent of σ_{12}, as expressed by Eq. 13. If Eq. 13 is valid, the estimation of σ_{12} is not required. This is tested in Figure 6a (at 313.2 K and 790 ~ 800 kg·m^{-3}) and in Figure 6b (at 313.2 K and 880 kg·m^{-3}). Note that the D_{12}^* values were estimated by the method of Fuller et al. (Reid et al., 1987). The values of $Sc_B/Sc_B^* - 1$ slightly depend on the solute molecular weights while Eq. 13 indicates that the plots are parallel to the x-axes. This discrepancy may result from either small density dependence of σ_{12} values or from uncertainty in the estimation of molecular diffusion coefficients at atmospheric pressure. Thus, we introduce the correction term $(M/m)^\beta$, where β is constant and was determined to be -0.089, M is the larger molecular weight, and m is the lower molecular weight between solute and solvent species. The correlation was obtained as follows:

$$\frac{Sc_B}{Sc_B^*} = 1 + 2.18\left(\frac{M}{m}\right)^{-0.089}\left(\frac{F_v}{A^*}\right)^{1.12} \qquad (20)$$

$$\approx 1 + 2.45\left(\frac{M}{m}\right)^{-0.089} F_v^{1.12} \qquad (20a)$$

The validity of Eq. 20 is tested in Figure 7a for D_{12} data of fatty acid methyl and ethyl esters in SC CO_2, obtained by Funazukuri et al. (1991) and Liong et al. (1991), both measured with the Taylor-Aris tracer response technique. Note that the values of ϵ_1/k were estimated from the equation ($\epsilon_1/k = T_{c1}/1.2593$, where T_{c1} = critical temperature of solute), which Chung et al. (1988) used for the viscosity prediction method of dense fluids. While the data of Liong et al. at lower F_v/A^* values deviate slightly, the data of both workers are consistent with Eq. 20 (AD_{max} = 11%), as represented by the solid line. Figure 7b shows the same plot for acetone and various aromatic solutes in SC CO_2 measured by Sassiat et al. (1987) with the same technique. Equation 20 well represents these data (AD_{max} = 18%). Figure 7c shows the same plot for gaseous solutes in CO_2. Again, while the data are scattered (AD_{max} = 22%), Eq. 20 was found to be valid. M and m are molecular weights of the solvent and the solute, respectively, for $^3HCH_3$ and $^{14}C_2H_4$. The average absolute deviation in Eq. 20 was 4.8% (AD_{max} = 22%) for the D_{12} data listed in Table 2.

It can be expected that Eq. 20 is applicable to the other solvent-solute systems. It is preferable to predict D_{12} using only common physical properties which are easily estimated or measured. In the prediction of D_{12} from Eq. 20, D_{12}^* is only required for a solute. This can be measured directly or is easily estimated (for example, by the method of Fuller et al. cited in Reid et al., 1987). Viscosity μ_2 and molar volume $(v_2)_0$ are required for a solvent. From an engineering point of view, common organic or low molecular weight compounds, such as CO_2, C_3H_8, SF_6 and so on, are used as dense solvents in supercritical fluid extraction/chromatography, and the binary diffusion coefficients are more important than the self-diffusion coefficients. The viscosity data of these solvents are available under supercritical conditions, and the values of $(v_2)_0$ can either be estimated as a function of temperature from the viscosity data, or are available in the literature.

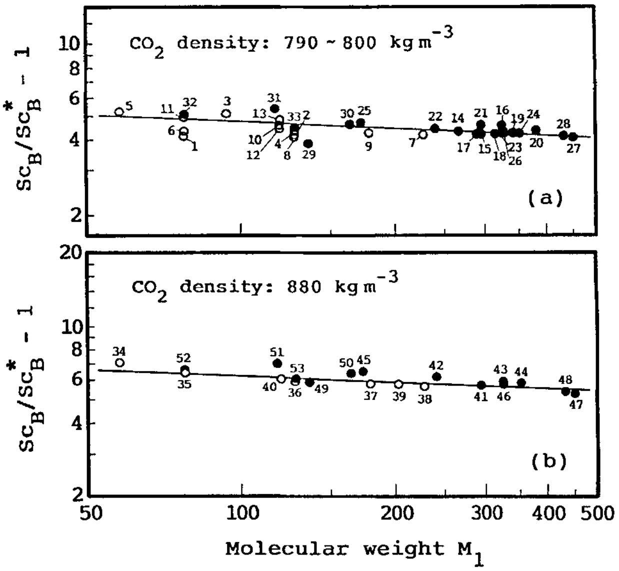

Figure 6. Logarithmic plot of $Sc_B/Sc_B^* - 1$ vs. solute molecular weight, M_1, for compounds measured in the present study (●) and in the reference of Funazukuri et al. (1991) (●), and those reported in the literature (○), at a temperature of 313.2 K.

a. 790-800 kg·m^{-3}; b. 880 kg·m^{-3}.

From Feist and Schneider (1982): 1. Benzene; 2. Naphthalene; 3. Phenol

From Lauer et al. (1983): 4. Naphthalene

From Sassiat et al. (1987): 5. Acetone; 6. Benzene; 7. Chrysene; 8. Naphthalene; 9. Phenanthrene; 10. 1,3,5-Trimethylbenzene

From Swaid and Schneider (1979): 11. Benzene; 12. *n*-Propylbenzene; 13. 1,3,5-Trimethylbenzene

From Funazukuri et al. (1991): 14. $C_{16:1}$- AME; 15. $C_{18:1}$- AME; 16. $C_{18:2}$- AME; 17. $C_{18:3}$- AME; 18. $C_{20:5}$- AME; 19. $C_{22:6}$- AME; 20. $C_{24:1}$- AME; 21. trans-$C_{18:1}$- AME

From present study: 22. $C_{14:1}$- AME; 23. $C_{20:1}$- AME; 24. $C_{22:1}$- AME; 25. Vitamin K_3; 26. Vitamin A acetate; 27. Vitamin K_1; 28. Vitamin E; 29. dl-Limonene; 30. cis-Jasmone; 31. Indole; 32. Benzene; 33. Naphthalene

From Sassiat et al. (1987): 34. Acetone; 35. Benzene; 36. Naphthalene; 37. Phenanthrene; 38. Chrysene; 39. Pyrene; 40. 1,3,5-Trimethylbenzene

From Funazukuri et al. (1991): 41. $C_{18:2}$- AME

From present study: 42. $C_{14:1}$- AME; 43. $C_{20:1}$- AME; 44. $C_{22:1}$- AME; 45. Vitamin K_3; 46. Vitamin A acetate; 47. Vitamin K_1; 48. Vitamin E; 49. dl-Limonene; 50. cis-Jasmone; 51. Indole; 52. Benzene; 53. Naphthalene

Conclusions

Binary diffusion coefficients of twelve compounds in SC CO_2 at a temperature of 313.2 K and pressures of 16.0 and

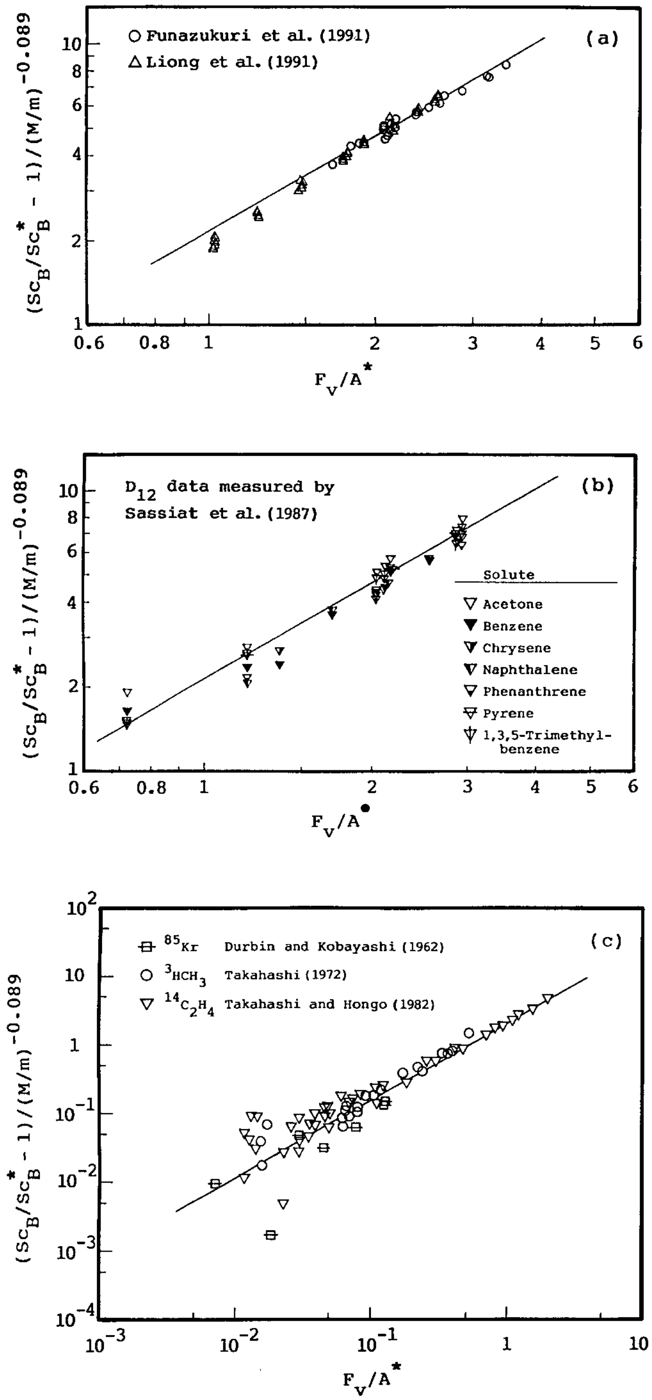

Figure 7. Logarithmic plot of $(Sc_B/Sc_B^* - 1)/(M/m)^{-0.089}$ vs. F_v/A^* for: (a) fatty acid methyl/ethyl esters by Funazukuri et al. (1991) and Liong et al. (1991); (b) acetone and aromatic compounds by Sassiat et al. (1987); (c) gaseous solutes by Durbin and Kobayashi (1962), Takahashi (1972), and Takahashi and Hongo (1982).

25.0 MPa were measured by the tracer response technique. We proposed an empirical equation in Eq. 20, and this equation was valid throughout a range of dilute to dense gases with good accuracy for predicting binary and self-diffusion coefficients in dense CO_2 as well as self-diffusion coefficients of CH_4 at $F_v/A^* < 40$ or $v_2/(\tilde{v}_2)_0 > 1.62$.

Notation

A^* = Ω_D/Ω_V, ratio of collision integrals
A_{12} = translational-rotational coupling parameter
AAD = average absolute deviation, defined as Eq. 14
AD_{max} = maximum absolute deviation defined as $100 \times |D_{pred}/D_{exptl} - 1|_{max}$, %
C = tracer response concentration, $mol \cdot m^{-3}$
C^+ = normalized tracer response concentration
D_{12} = binary diffusion coefficient in CO_2, $m^2 \cdot s^{-1}$
D_{12}' = apparent diffusion coefficient, $m^2 \cdot s^{-1}$
D_{22} = self-diffusion coefficient of CO_2, $m^2 \cdot s^{-1}$
D_{eff} = effective axial dispersion coefficient, $m^2 \cdot s^{-1}$
F_v = $x/(x-1)^2$
k = Boltzmann constant, $J \cdot K^{-1}$
L = column length, m
M, m = molecular weight
M_{12} = $2M_1M_2/(M_1+M_2)$, average molecular weight
N = Avogadro's number
n = number of data points
r = tube radius, m
Sc = Schmidt number ($= \mu_2/\rho_2 D_{12}$ or $\mu_2/\rho_2 D_{22}$)
T = temperature, K
T^* = dimensionless temperature ($= kT/\epsilon$)
t = time, s
u = flow rate of carbon dioxide, $m \cdot s^{-1}$
V_{b1} = solute molar volume at normal boiling point, $m^3 \cdot mol^{-1}$
v_2 = molar volume of solvent, $m^3 \cdot mol^{-1}$
$(v_2)_0$ = minimum free diffusion volume of solvent, $= 1.384(\tilde{v}_2)_0$, $m^3 \cdot mol^{-1}$
$(\tilde{v}_2)_0$ = $N\sigma_2^3/\sqrt{2}$, $m^3 \cdot mol^{-1}$
x = $v_2/(v_2)_0 = v_2/[1.384(\tilde{v}_2)_0]$

Greek letters

α, β = constant
ϵ = intermolecular potential parameter, J
θ = t/τ
μ = viscosity, $Pa \cdot s$
ρ = density, $kg \cdot m^{-3}$
σ = hard sphere diameter, m
σ_{12} = $(\sigma_1 + \sigma_2)/2$
τ = L/u, mean residence time, s
Ω_D = collision integral for diffusion
Ω_V = collision integral for viscosity

Superscript

$*$ = at atmospheric pressure (except for A^* and T^*)

Subscripts

1 = solute
2 = solvent
B = binary diffusion
c = critical
calc = calculated
exptl = experimentally obtained
pred = predicted
S = self-diffusion

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