

INFINITE-DILUTION BINARY DIFFUSION COEFFICIENTS FOR UNSATURATED FATTY ACIDS AND THEIR DERIVATIVES IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

Following the previous studies [*Fluid Phase Equil.*, **in press** and *J. Chem. Eng. Data*, **accepted**], the binary diffusion coefficients D_{12} and the partition ratios k of solute in polymer layer to fluid phase were measured at infinite-dilution in supercritical carbon dioxide for unsaturated fatty acids and their derivatives (methyl-/ethyl-esters and mono-/di-/tri-glycerides; molecular weight = 282 to 951) at 313.21 K and 8 to 30 MPa by shot response technique using a poly(ethylene glycol) coated capillary column. The validities of the Wilke-Chang equation and the Schmidt number correlation were examined for D_{12} data in the present and previous studies. An empirical correlation was proposed which was expressed in terms of molecular weight of solute, temperature and CO₂ viscosity.

INTRODUCTION

Binary diffusion coefficients D_{12} play an important role in engineering calculations. In fact the accurate knowledge of the diffusion mechanism is fundamental for equipment design, process development and efficient operation of supercritical carbon dioxide (SC CO₂) extraction and so on. However, measurements of D_{12} of lipids [1-7] in SC CO₂ are limited, comparing with the other physicochemical properties.

As the most popular experimental method for determination of D_{12} , the Taylor dispersion technique has been employed by many researchers. Up to now, the moment method was mainly used to analyze the experimental data. However, the D_{12} of lipids are generally difficult to measure with an uncoated column using the Taylor dispersion technique because of the adsorption of the solute on the column wall surface like stainless steel [8] or Teflon [9]. Moreover, the moment method does not give reliable information when the response curve is distorted or noisy [10].

Recently, the authors [11-15] have developed the shot response technique with a polymer coated capillary column to measure D_{12} and k for various highly viscous or solid solutes in supercritical fluid. This method is suitable for measuring binary diffusion coefficients of polar

solute in SC CO₂ with two assumptions: the adsorption isotherm is linear and the tracers instantly reach equilibrium on the inner wall of the column.

The objectives of this work are: (1) to measure the binary diffusion coefficients of unsaturated fatty acids and their derivatives at infinite-dilution in SC CO₂ using shot response technique; (2) to examine the validity of the Wilke-Chang equation [16] and the Schmidt number correlation [10]; (3) to obtain an empirical correlation for the binary diffusion coefficients of unsaturated fatty acids and their derivatives.

THEORY

When a tracer species is injected as a shot to a fully developed laminar flow in a cylindrical tube, the average cross-sectional tracer concentration C_a can be described as follows [11]:

$$C_a(t) \approx \left(\frac{m}{\rho R^2} \right) \frac{1}{(1+k)\sqrt{4\rho at}} \exp\left(-\left(L - \frac{u_a}{1+k}t \right)^2 / 4at \right) \quad (1)$$

$$a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{(1+k)^3} \frac{u_a^2 R^2}{48D_{12}} \quad (2)$$

where m is the injected amount of the tracer species, R the inner radius of tube, L the length of tube, u_a the average velocity of the fluid, and t is time. When u_a is measured, D_{12} and k can be simultaneously determined by the curve fitting method [11].

EXPERIMENTAL SECTION

The experimental apparatus and procedure for measuring D_{12} in SC CO₂ have been reported in detail elsewhere [10-15]. Same as the previous studies [14,15], the poly(ethylene glycol) coated capillary column (UACW-15W-1.0F, 0.515 mm I.D., 15.30 m long, film thickness 1 μ m, coil diameter of 270 mm, Frontier Laboratories Ltd. Japan) was employed. A high pressure multi-UV detector monitored the absorption at wavelengths from 195 to 250 nm at increments of 1 nm, corresponding to time interval of 1.6 s for every measurement. The temperature and pressure were controlled within the fluctuation of ± 0.01 K and ± 0.001 MPa, respectively. CO₂ with purity higher than 99.995% (which contains water < 40 ppm) was purchased from Showa Tansan Co., Japan. Hexane (purity 95%) was from Aldrich, and lipids from Sigma. The lipids are sorted in order of molecular weight, including those studied in the previous works [14,15], and shown in **Table 1**. The purities of linolenic acid ethyl ester, oleic acid methyl ester, DHA methyl ester and trilinolenin were 98%, and the remainings were 99%. Each lipid in 0.2 μ L of hexane solution was injected into the column. The concentration of hexane solution was 0.005-0.01 g/ml. The measurement was started more two or three hours after the system temperature and pressure had reached the desired values and the flow system became stabilized. Only single pulse was loaded for each run. For the determination of D_{12} and k values, the wavelength of 211 nm was employed for DHA methyl ester and ethyl ester, and 200 nm for the other lipids. For the whole measurements, following conditions were observed: (1) for Reynolds number, $15 < Re < 72$; (2) for Schmidt number, $5 < Sc < 30$, and (3) for Dean number, $3 < DeSc^{1/2} < 8$. In this study, the density values were calculated with the equation of Pitzer & Schreiber [17] and Span & Wagner [18], and the viscosities were estimated by the method of Fenghour et al. [19].

Table 1. Parameter values for each solute used in the Wilke-Chang equation and the Schmidt number correlation

Solute	No. of data	Molecular weight	Wilke-Chang equation	Schmidt number correlation		Ref.
			V_b , cm ³ /mol	S_{vw} , nm	S , nm	
<i>a</i> -Linolenic acid	56	278.4	401.4	0.838	0.848	[14]
Linoleic acid	71	280.4	408.8	0.843	0.854	[15]
Oleic acid	42(22)	282.5	416.2	0.848	0.871	p
Elaidic acid	15(3)	282.5	416.2	0.848	0.871	p
Linoleic acid ME	2	294.5	425.2	0.858	0.903	p
Oleic acid ME	19	296.5	432.6	0.863	0.922	p
Elaidic acid ME	2	296.5	432.6	0.863	0.909	p
EPA	55	302.5	431.0	0.858	0.891	[14]
Arachidonic acid	75	304.5	438.4	0.863	0.891	[15]
Linolenic acid EE	5	306.5	441.6	0.868	0.937	p
Linoleic acid EE	5	308.5	449.0	0.873	0.925	p
Oleic acid EE	5	310.5	456.4	0.878	0.919	p
Elaidic acid EE	5	310.5	456.4	0.878	0.919	p
DHA	63	328.5	468.0	0.881	0.927	[14]
DHA ME	18	342.5	484.4	0.895	0.871	p
DHA EE	28	356.5	508.2	0.909	0.887	p
Monoolein	11	356.5	491.8	0.901	0.930	p
Dilinolein	8	617.0	872.6	1.088	1.055	p
Diolenin	9	621.0	887.4	1.094	1.039	p
Trilinolenin	6	873.4	1238.6	1.221	1.173	p
Trilinolein	6	879.4	1260.8	1.228	1.158	p
Triolein	10	885.4	1283.0	1.236	1.148	p
Trielaidin	4	885.4	1283.0	1.236	1.148	p
Triarachidonin	26	951.5	1349.6	1.256	1.143	p
total	546(25)	AAD%	11.2%	5.49%	2.70%	

ME: methyl ester, EE: ethyl ester, p: present study.

Almost data in this study were measured at 313.21 K. No of the present data measured at 343.15 K are indicated by the figures in parenthesis ().

RESULTS AND DISCUSSION

Figure 1 shows the density dependence of D_{12} and k at 313.21 K for oleic acid, oleic acid methyl-/ethyl-esters and mono-/di-/tri-oleins in SC CO₂, together with the root mean square fitting errors. Error values were smaller than 0.03. D_{12} and k decrease gradually when density increases, as shown in **Figures 1a** and **1b**, respectively. At the same densities, the D_{12} values are ordered as methyl-, ethyl-esters, acid, mono-, di-, and tri-glycerides of oleic acid, but not in order of molecular weight.

Figure 2 shows the Wilke-Chang equation plotted for all present and previous data [14, 15]. Note that the molar volumes of lipids at boiling point denoted by V_b were calculated from the method of Le Bas [20] and listed in **Table 1**. As shown in this figure, the slope of the measured data is slightly smaller from the Wilke-Chang equation under supercritical conditions. Similar results were obtained by Feist & Schneider [8]. The average absolute deviation (AAD%) is 11.2% for 546 data and shown in **Table 1**.

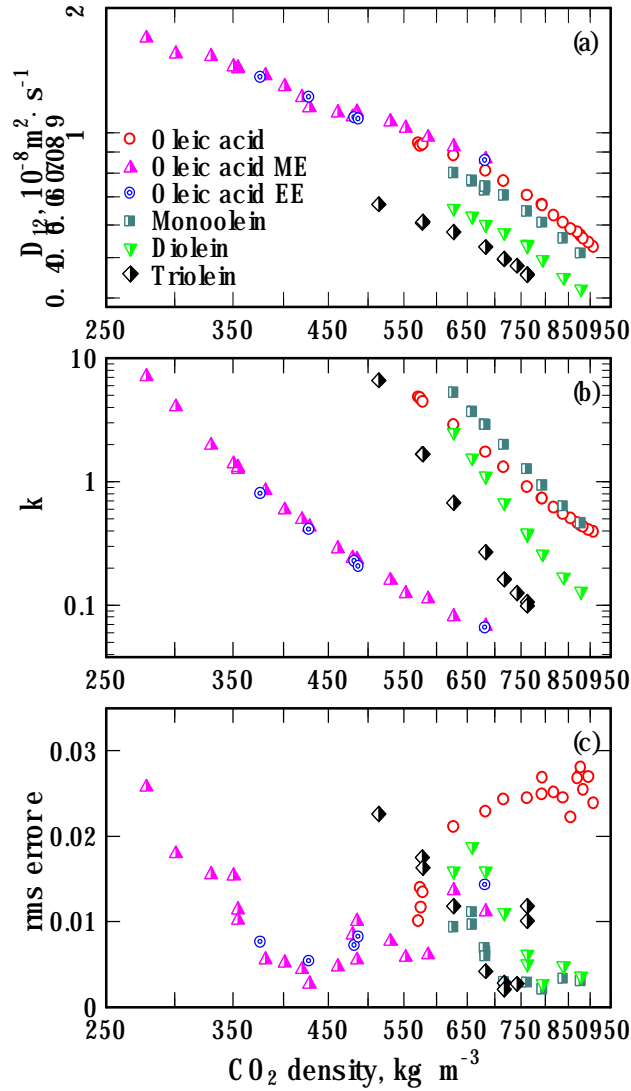


Figure 1. Effects of CO_2 density on (a) D_{12} , (b) k , (c)

The Schmidt number correlation proposed by Funazukuri et al. [10] has been applied for various solutes [10-15]. The van der Waals diameters s_{vW} were used instead of the hard-sphere diameters to predict D_{12} of lipids. s_{vW} values obtained by Bondi [21] are listed in **Table 1** (s_{vW} for CO_2 is 0.397 nm). The Bondi's van der Waals diameters seem to be inaccurate for larger molecules such as monoolein, dilinolein, diolein, trilinolenin, trilinolein, triolein, trielaidin and triarachidonin. Therefore, the van der Waals diameters are adjusted for the fitting and shown as s in **Table 1**. The Schmidt number correlation is compared in **Figure 3** with the experimental data with the adjusted values. AAD% is 5.49% for the Bondi's van der Waals diameters, and 2.70% for the adjusted values.

In this study the following empirical correlation was proposed:

$$D_{12} = 4.77 \times 10^{-9} \frac{T}{h^{0.778} M_1^{0.375}} \quad (3)$$

where h is the viscosity of CO_2 ($\text{Pa} \cdot \text{s}$) and M_1 the molecular weight of solute.

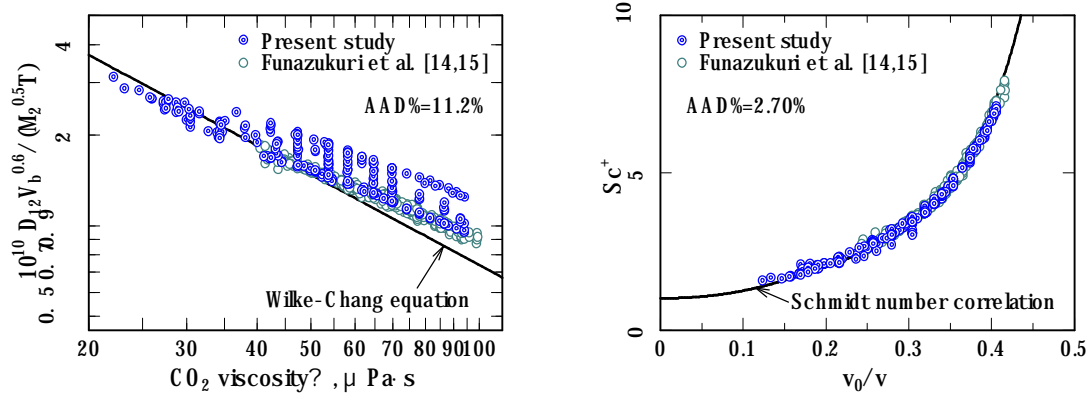


Figure 2. Comparison of measured data with the Wilke-Chang equation (M_2 is the molecular weight of CO_2) and the Schmidt number correlation for the measured data in the present and previous studies.

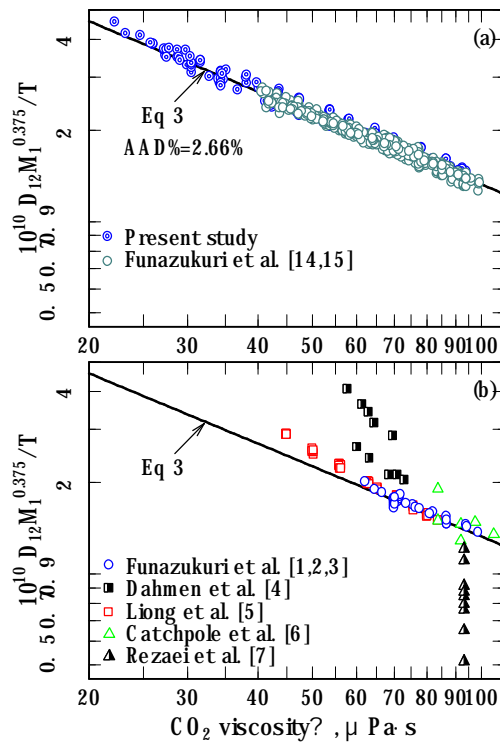


Figure 4. D_{12} correlation by the eq 3 for present and literature data. In Figure 4a, the measured D_{12} values of lipids were compared with the predicted from eq 3. As seen in Figure 4a, the present data were well represented by eq 3 with AAD% of 2.87% for 226 data, and AAD% of 2.66% for 546 data including the previous studies [14,15]. In Figure 4b, the D_{12} data measured by Funazukuri et al. [1-3] and Catchpole et al. [6] roughly agreed with

Figure 4. D_{12} correlation by the eq 3 for present and literature data.

those predicted by eq 3. On the other hand, the D_{12} data measured by Dahmen et al.[4] and some data of Liong et al. [5] indicate larger than those predicted by eq 3, while the D_{12} data measured by Rezaei et al. [7] show lower values. For the studies, Dahmen et al. [4] employed the input-output response technique and the others by the Taylor dispersion technique, and all used the moment method for the analysis.

CONCLUSIONS

Binary diffusion coefficients and partition ratios for nineteen lipids in SC CO₂ at infinite-dilution were measured at 313.21 and 343.15 K and 8 to 30 MPa with a polymer coated column by shot response technique. It was observed that the diffusivities were ordered as $D_{12}(\text{methyl-ester}) > D_{12}(\text{ethyl-ester}) > D_{12}(\text{acid}) > D_{12}(\text{mono-glyceride}) > D_{12}(\text{di-glyceride}) > D_{12}(\text{tri-glyceride})$ at the same conditions. The reliability of correlation for diffusion coefficients was evaluated for the Wilke-Chang equation and the Schmidt number correlation. The Schmidt number correlation was better if the van der Waals diameters were adjusted. An empirical equation denoted by eq 3 was proposed for infinite-dilution binary diffusion coefficients of unsaturated fatty acid and their derivatives in supercritical carbon dioxide.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Education, Culture, Sports, Science and Technology through Grant-in-Aids for Scientific Research (No. 13650817 and No. 14655284).

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