J. Chem. Eng. Data **2007,** *52,* 555−559

Binary Diffusion Coefficients of Arachidonic Acid Ethyl Esthers, *cis*-5,8,11,14,17-Eicosapentaenoic Acid Ethyl Esthers, and cis-4,7,10,13,16,19-Docosahexanenoic Acid Ethyl Esthers in Supercritical Carbon Dioxide

Yisong Han, Yiwen Yang, and Pingdong Wu*

National Laboratory of Secondary Resources Chemical Engineering, Zhejiang University, Hangzhou 310027, China

The binary diffusion coefficients of arachidonic acid ethyl esthers (AA-EE), *cis*-5,8,11,14,17-eicosapentaenoic acid ethyl esters (EPA-EE), and *cis*-4,7,10,13,16,19-docosahexaenoic acid ethyl esthers (DHA-EE) in supercritical carbon dioxide were measured at temperatures from 308.15 K to 338.15 K and pressures from 8.42 MPa to 29.95 MPa by the Taylor−Aris capillary peak broadening method. The obtained diffusion coefficients are in the range of (5.54×10^{-5}) $cm^2 \cdot s^{-1}$ to (13.8×10^{-5}) $cm^2 \cdot s^{-1}$ with small differences between AA-EE, EPA-EE, and DHA-EE. The measured D_{12} values were fitted with absolute average deviations of less than 2 % by three predictive models: Scheibel, Catchpole−King, and He−Yu−Su.

Introduction

Supercritical fluids (SCFs) have been received wide attention because their density is as high as liquids and their viscosity is as low as gases. Moreover, it is easy to change the properties such as solubility and diffusion coefficients of solutes in them by adjusting the temperature and the pressure. Especially for supercritical carbon dioxide, it is nontoxic, nonflammable, moderate, and inexpensive. It has become the most widely used and safest SCF.

AA (arachidonic acid), EPA (*cis*-5,8,11,14,17-eicosapentaenoic acid), and DHA (*cis*-4,7,10,13,16,19-docosahexaenoic acid) are polyunsaturated fatty acids and are vital for health. AA is mainly purified from fermentation broth. EPA and DHA are mainly purified from marine species like tuna, sardine, and capelin. The conventional processes usually include vacuum distillation and HPLC. Because these three fatty acids are heat-labile and easily oxidized, processing under high temperature, coming into contact with tetrahydrofuran (which tends to produce peroxide), or being exposed to air will debase the quality of them. Applying supercritical carbon dioxide extraction or supercritical carbon dioxide chromatography[1,2] to purify AA, EPA, and DHA can avoid these disadvantages.

The binary diffusion coefficient is one of the important physical properties for the engineering design of extraction and chromatography processes. Since the ethyl esters (EE) of AA, EPA, and DHA are of more benefit to the human body than their acid type, it will be more significant to measure the binary diffusion coefficients of AA-EE, EPA-EE, and DHA-EE in supercritical CO_2. Up to now, there have been some studies on the binary diffusion coefficients in supercritical CO_2. Funazukuri and co-workers[3−6] have measured the binary diffusion coefficients of some solids or viscous liquids such as phenol, β-carotene, α-tocopherol, vitamin K_3, and ubiquinone CoQ10 in supercritical CO_2 by the CIR method.[9] Higashi et al.[8−10] studied the diffusion of naphthalene and dimethylnaphthalene isomers in supercritical CO_2 using a pseudo-steady-state solid dissolution method. The Taylor−Aris capillary peak broadening (CPB) method[11−13] has been claimed to be relatively accurate and less time-consuming.[14] Some researchers have used this method to measure the binary diffusion coefficients of some liquids in supercritical CO_2 such as nC_5−nC_{14} alkanes,[15] benzene and its derivatives,[16−19] terpenes,[20,21] and ketones.[22−24]

Funazukuri et al.,[26−29] Kong et al.,[30,31] and Rezaei and Temelli[34] have measured the diffusivity of a series of long-chain fatty acids and their esters in supercritical CO_2. However, as to the ethyl esters of AA-EE, EPA-EE, and DHA-EE, only the binary diffusion coefficients of DHA-EE under temperature from 308 K to 318 K and pressure from 96.7 MPa to 188.0 MPa were measured by Liong et al.[32] This work intended to study the characteristics of the diffusion of the ethyl esters of AA-EE, EPA-EE ,and DHA-EE in supercritical CO_2 under a wide condition of temperatures (from 308.15 K to 338.15 K) and pressures (from 8.42 MPa to 29.95 MPa).

Fundamentals. In this work, the CPB method was used to determine the binary diffusion coefficients D_{12}. The D_{12} can be expressed as the function of residence time and peak width at half-height as follows:

$$D_{12} = \frac{L}{4t_r}\left[H - \left(H^2 - \frac{r_0^{\,2}}{3}\right)^{1/2}\right] \tag{1}$$

$$H = \frac{LW_{1/2}^{\,2}}{5.54t_r^{\,2}} \tag{2}$$

where H is the theoretical plate height (cm); L is the dispersion column length (cm); r_0 is the inner radius of the dispersion column (cm); t_r is the residence time (s); $W_{1/2}$ is the half-height peak width (s).

To eliminate the error caused by the secondary-flow effect when the solvent flows too fast through the dispersion coiled column and to make the course resemble flowing in a straight tube, the criteria given in eq 3 should be satisfied:[35]

$$De(Sc)^{1/2} < 10 \tag{3}$$

---

* Corresponding author. Tel: +86-571-87984733. Fax: +86-571-87952773. E-mail: wupd@zju.edu.cn.

10.1021/je060456h CCC: \$37.00

where

$$De = \frac{\rho U_0 d_{\text{tube}}}{\eta}\left(\frac{d_{\text{tube}}}{d_{\text{coil}}}\right)^{1/2} \quad \text{(Dean number)} \qquad (4)$$

$$Sc = \frac{\eta}{\rho D_{12}} \quad \text{(Schmidt number)} \qquad (5)$$

ρ is the density of CO_2 (g·cm^{-3}); U_0 is the velocity of the mobile phase (cm·s^{-1}); η is the viscosity of CO_2 (P); d_{tube} is the inner diameter of the dispersion column (cm); d_{coil} is the diameter of the coil (cm). ρ and η were calculated by the Span and Wagner equation of state[36] and the Sovová−Procházka method,[37] respectively.

Experimental Section

The apparatus used was similar to Figure 1 of Funazukuri and Nishimoto.[38] The chromatographic pump (2J-X) with a cooling head was from Zhejiang Scientific Apparatus Ltd., Hangzhou, China. The dispersion column was a stainless steel coiled column (0.0762 cm i.d. × 1300 cm), and the diameter of the coil was 24 cm. The column was connected to a UV−vis detector (model 0200-000, AllTech) directly to eliminate the dead volume. The injector (model 7025, Rheodyne) was equipped with a 5-μL sample loop. A restrictor tube (stainless steel tube of 50 cm × 0.01 cm i.d.) was mounted between the outlet of the UV−vis detector and the back pressure valve (model 26-3220, Tescom) to stabilize the flow rate. The response curves were measured at a wavelength of 210 nm; 20 % (wt) solution of fatty acid ethyl esters in *n*-hexane was prepared for injection. Fatty acid EEs were from Sigma Chemical Co. (purity > 99 %), and *n*-hexane was from Hangzhou Solvent Ltd., Hangzhou, China (spectroscopic grade).

Laminar flow of supercritical CO_2 was maintained at a velocity of 0.02 cm·s^{-1} to 0.05 cm·s^{-1} where the effect of the velocity was negligible. At a definite temperature, pressure, and flow rate condition, the sample was injected through the injection loop. The binary diffusion coefficients of AA-EE, EPA-EE, and DHA-EE were measured one by one, with three parallel runs for each solute.

Results and Discussion

The D_{12} values of DHA-EE measured at (308.15 and 318.15) K were compared with those measured by Liong et al.[32] (see Figure 1). The average deviation of seven D_{12} values obtained under the same experimental conditions in the two works was within 1 %. The $D_{12,\text{AA-EE}}$, $D_{12,\text{EPA-EE}}$, and $D_{12,\text{DHA-EE}}$ values listed in Table 1 were the average of three parallel runs, the average deviations of which were less than 1 %.

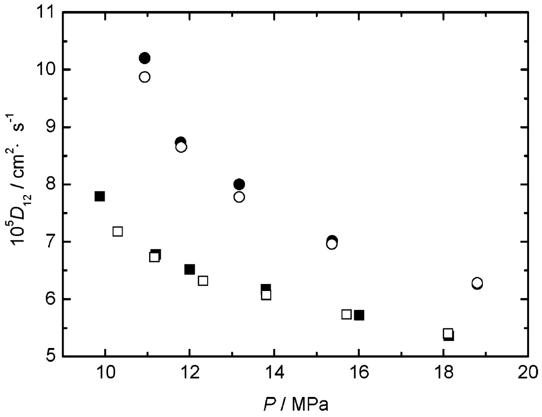

Figure 1. Diffusion coefficients of DHA-EE in supercritical CO_2: ■, ref 32, 308.15 K; ○, ref 32, 318.15 K; □, this work, 308.15 K; ○, this work, 318.15 K.

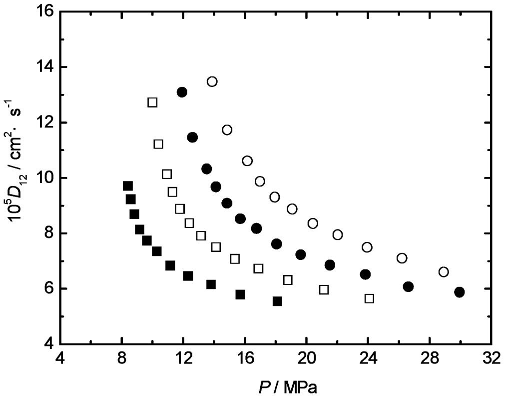

Figure 2. Relationship between diffusion coefficients of AA-EE and pressure: ■, 308.15 K; □, 318.15 K; ●, 328.15 K; ○, 338.15 K.

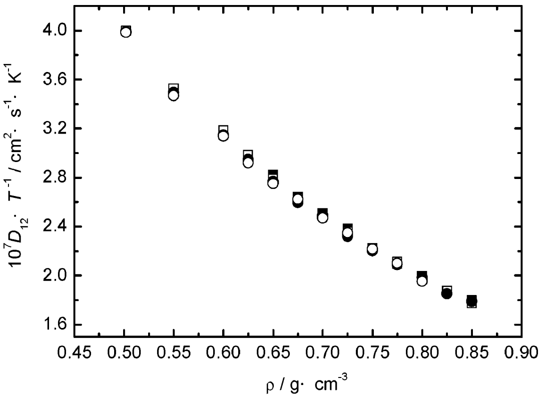

Figure 3. Relationship between $D_{12,\text{AA-EE}}/T$ and ρ: ■, 308.15 K; □, 318.15 K; ●, 328.15 K; ○, 338.15 K.

It can be seen from Table 1 that the D_{12} values of the three esters in supercritical carbon dioxide are as follows: at 308.15 K and 18.11 MPa D_{12} values of AA-EE, EPA-EE, and DHA-EE are 5.54 × 10^{-5} cm^2·s^{-1}, 5.54 × 10^{-5} cm^2·s^{-1}, and 5.40 × 10^{-5} cm^2·s^{-1}, respectively. At 338.15 K and 13.88 MPa the corresponding values are 13.47 × 10^{-5} cm^2·s^{-1}, 13.80 × 10^{-5} cm^2·s^{-1}, and 12.80 × 10^{-5} cm^2·s^{-1}, respectively. Under the same condition, the D_{12} values of AA-EE, EPA-EE, and DHA-EE are close to each other. The ratios $D_{12,\text{AA-EE}}/D_{12,\text{EPA-EE}}$ are between 0.97 and 1, and the ratios of $D_{12,\text{AA-EE}}/D_{12,\text{DHA-EE}}$ are between 1.003 and 1.05.

Figure 2 represents $D_{12,\text{AA-EE}}$ versus pressure at temperatures from 308.15 K to 338.15 K. It can be seen that $D_{12,\text{AA-EE}}$ decreases with pressure rapidly at lower pressures and then gradually levels off. This phenomenon is mainly due to the fact that the density and viscosity of carbon dioxide, two very important factors for diffusion, change sharply at lower pressures. In addition, it can be seen from Figure 2 also that D_{12} increases with temperature at a definite pressure. If D_{12}/T is plotted versus ρ (see Figure 3), it was found that curves at all temperatures almost coincide with each other. This indicates that the density of CO_2 is the essential factor that affects the diffusion. The same characters were obtained for EPA-EE and DHA-EE in this work. Treatment of the D_{12} values of fatty acids and their esters of Funazukuri et al,[28,29] Kong et al.,[30] and Liong et al.[32,33] were as in Figure 3; the same results were obtained as well. On the basis of this method of treatment, when the D_{12}

Table 1. D_{12} of AA-EE (1), EPA-EE (2), and DHA-EE (3) in Supercritical CO_2

T/K = 308.15		T/K = 318.15		T/K = 328.15		T/K = 338.15	
P/MPa	$10^5 D_{12}{}^a$/cm^2·s^{-1}	P/MPa	$10^5 D_{12}{}^a$/cm^2·s^{-1}	P/MPa	$10^5 D_{12}{}^a$/cm^2·s^{-1}	P/MPa	$10^5 D_{12}{}^a$/cm^2·s^{-1}
AA-EE							
8.42	9.71 (±0.06)	10.01	12.72 (±0.10)	11.93	13.09 (±0.14)	13.88	13.47 (±0.07)
8.59	9.12 (±0.05)	10.39	11.21 (±0.06)	12.61	11.46 (±0.04)	14.86	11.73 (±0.07)
8.84	8.69 (±0.05)	10.94	10.13 (±0.09)	13.53	10.32 (±0.03)	16.17	10.61 (±0.06)
9.18	8.14 (±0.04)	11.32	9.49 (±0.05)	14.13	9.67 (±0.04)	16.99	9.87 (±0.02)
9.65	7.73 (±0.03)	11.80	8.88 (±0.04)	14.84	9.08 (±0.03)	17.95	9.30 (±0.04)
10.30	7.34 (±0.04)	12.40	8.36 (±0.02)	15.71	8.52 (±0.02)	19.08	8.87 (±0.01)
11.17	6.83 (±0.02)	13.17	7.91 (±0.02)	16.77	8.17 (±0.03)	20.43	8.35 (±0.03)
12.32	6.45 (±0.01)	14.14	7.50 (±0.03)	18.06	7.61 (±0.04)	22.03	7.94 (±0.03)
13.81	6.15 (±0.01)	15.36	7.07 (±0.02)	19.63	7.23 (±0.02)	23.94	7.49 (±0.01)
15.71	5.78 (±0.04)	16.89	6.72 (±0.02)	21.53	6.85 (±0.02)	26.22	7.11 (±0.02)
18.11	5.54 (±0.01)	18.80	6.31 (±0.03)	23.84	6.51 (±0.02)	28.92	6.60 (±0.01)
		21.14	5.96 (±0.03)	26.62	6.07 (±0.02)		
		24.10	5.64 (±0.02)	29.95	5.87 (±0.02)		
EPA-EE							
8.42	9.77 (±0.03)	10.01	13.00 (±0.12)	11.93	13.33 (±0.07)	13.88	13.80 (±0.04)
8.59	9.32 (±0.06)	10.39	11.57 (±0.07)	12.61	11.64 (±0.05)	14.86	11.90 (±0.07)
8.84	8.81 (±0.04)	10.94	10.30 (±0.03)	13.53	10.45 (±0.06)	16.17	10.69 (±0.04)
9.18	8.32 (±0.07)	11.32	9.62 (±0.03)	14.13	9.76 (±0.04)	16.99	9.92 (±0.03)
9.65	7.76 (±0.04)	11.80	8.96 (±0.04)	14.84	9.19 (±0.02)	17.95	9.34 (±0.01)
10.30	7.39 (± 0.02)	12.40	8.42 (± 0.02)	15.71	8.55 (± 0.03)	19.08	8.97 (± 0.03)
11.17	6.90 (±0.04)	13.17	7.96 (±0.06)	16.77	8.26 (±0.02)	20.43	8.44 (±0.04)
12.32	6.51 (±0.05)	14.14	7.54 (±0.02)	18.06	7.69 (±0.03)	22.03	8.00 (±0.03)
13.81	6.19 (±0.02)	15.36	7.13 (±0.02)	19.63	7.25 (±0.03)	23.94	7.51 (±0.01)
15.71	5.82 (±0.03)	16.89	6.76 (±0.04)	21.53	6.91 (±0.02)	26.22	7.11 (±0.01)
18.11	5.54 (±0.01)	18.80	6.34 (±0.02)	23.84	6.51 (±0.02)	28.92	6.64 (±0.02)
		21.14	6.00 (±0.02)	26.62	6.11 (±0.02)		
		24.10	5.66 (±0.01)	29.95	5.89 (±0.02)		
DHA-EE							
8.42	9.56 (±0.05)	10.01	12.13 (±0.01)	11.93	12.38 (±0.07)	13.88	12.80 (±0.08)
8.59	9.02 (±0.05)	10.39	10.87 (±0.03)	12.61	11.07 (±0.05)	14.86	11.34 (±0.06)
8.84	8.51 (±0.06)	10.94	9.87 (±0.04)	13.53	10.10 (±0.05)	16.17	10.32 (±0.06)
9.18	8.11 (±0.02)	11.32	9.24 (±0.04)	14.13	9.39 (±0.05)	16.99	9.75 (±0.03)
9.65	7.61 (±0.02).	11.80	8.65 (±0.02)	14.84	8.96 (±0.04)	17.95	9.13 (±0.04)
10.30	7.18 (±0.04)	12.40	8.19 (±0.04)	15.71	8.45 (±0.05)	19.08	8.64 (±0.05)
11.17	6.73 (±0.03)	13.17	7.78 (±0.02)	16.77	8.04 (±0.02)	20.43	8.23 (±0.02)
12.32	6.32 (±0.04)	14.14	7.34 (±0.02)	18.06	7.56 (±0.02)	22.03	7.78 (±0.03)
13.81	6.07 (±0.03)	15.36	6.96 (±0.01)	19.63	7.11 (±0.02)	23.94	7.34 (±0.04)
15.71	5.73 (±0.01)	16.89	6.60 (±0.06)	21.53	6.73 (±0.02)	26.22	6.92 (±0.01)
18.11	5.40 (±0.02)	18.80	6.28 (±0.04)	23.84	6.41 (±0.02)	28.92	6.54 (±0.01)
		21.14	5.87 (±0.02)	26.62	6.01 (±0.06)		
		24.10	5.55 (±0.02)	29.95	5.69 (±0.07)		

[a] The values in parentheses are the maximum deviation to the average value of the measured data, in percent of the average value.

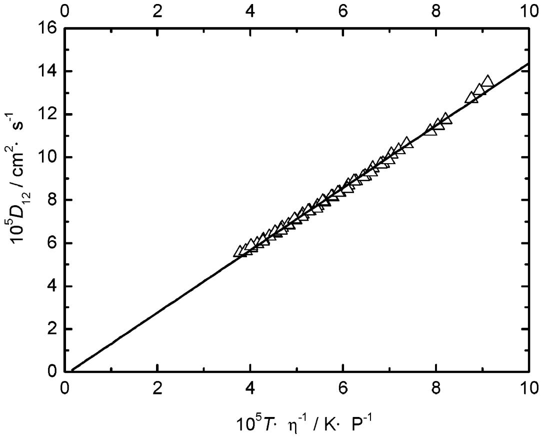

Figure 4. Relationship between diffusion coefficient of AA-EE and T/η: solid line, $y = -0.14348 + 1.45206x$.

value of a fatty acid ester at a given temperature and density of carbon dioxide is known, the D_{12} value at other temperatures can be easily estimated.

Figure 4 shows the curve of $D_{12,\mathrm{AA-EE}}$ plotted versus T/η. It points out that the relationship is linear and the intercept is −0.14348, a value almost equal to zero. This relationship is similar to that of stearic acid EE by Liong et al.[32] The curves of $D_{12,\mathrm{EPA-EE}}$ and $D_{12,\mathrm{DHA-EE}}$ versus T/η have the similar character.

$D_{12,\mathrm{EPA}}$, $D_{12,\mathrm{EPA-EE}}$, and $D_{12,\mathrm{EPA-ME}}$ are compared in Figure 5. $D_{12,\mathrm{EPA}}$ and $D_{12,\mathrm{EPA-ME}}$ are from Funazukuri et al.[29] and Liong et al.,[32] respectively. Though the D_{12} resources of EPA and its ethyl or methyl esters (ME) are different, they are comparable by the following analysis: (i) the system errors between the apparatus of this work and Liong et al.[32] are very small, which indicates that the differences between $D_{12,\mathrm{EPA-EE}}$ and $D_{12,\mathrm{EPA-ME}}$ are affected insignificantly by the system errors; (2) Funazukuri, Kong, and co-workers[3,39] compared the CIR method with the CPB method and found that for weak-polar and non-viscous liquids the D_{12} values under the same conditions obtained by the above two methods agree with each other very well, whereas for polar or viscous ones the values by CIR method are relatively greater because symmetry of the peaks obtained by the CIR method is much closer to unit. Since EPA is a kind of viscous liquid, less D_{12} values would be obtained on the apparatus in this work. It can be seen from Figure 5 that the difference between D_{12} values of EPA and its esters are not significant in the range of T/η from 3.0 × 10^{-5} K·P^{-1} to 5.5 × 10^{-5} K·P^{-1}. However, when T/η is greater than 5.5 × 10^{-5} K·P^{-1}, the D_{12}

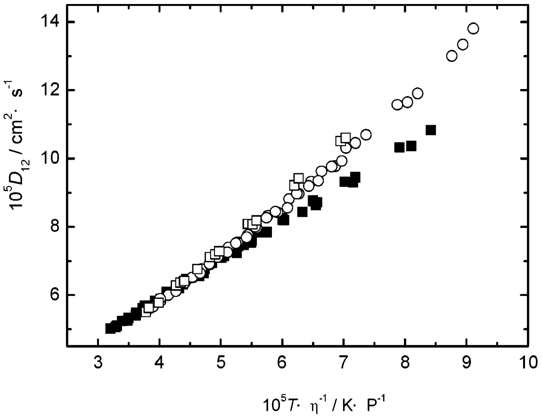

Figure 5. Relationship between D_{12} and T/η: ■, EPA in ref 29 by CIR method; □, EPA-ME in ref 32 by CPB method; ○, EPA-EE in this work by CPB method.

Table 2. Related Parameters for Modeling

parameters[a]	CO_2	AA-EE	EPA-EE	DHA-EE
M/g·mol^{-1}	44.01	332.50	330.50	356.50
V_b/cm^3·mol^{-1}	33.32	478.60[b]	471.20[b]	508.20[b]
V_c/cm^3·mol^{-1}	94	1195[c]	1175[c]	1265[c]
P_c/MPa	7.383	11.638[c]	11.834[c]	11.038[c]
T_c/K	304.2	840.3[c]	833.8[c]	867.1[c]
$^2\chi$		8.339[d]	8.339[d]	9.047[d]
D_c/10^{-4} cm^{-2}·s^{-1}	4.94[e]			

[a] M = molecular weight; P_c = critical pressure; T_c = critical temperature; V_c = molar critical volumn; V_b = molar volume at normal boiling point; $^2\chi$ = second order of the molecular connectivity index; D_c = self-diffusion coefficient of CO_2 at the critical point. [b] Estimated by the Le Bas method.[48] [c] Estimated by Lydersen's method.[48] [d] Estimated according to Figure 20 of Liong et al.[33] [e] Estimated by eq 4 of Fuller et al.[49]

values of EPA are apparently less than those of its esters, although the molecular weight and V_b of EPA are smaller than those of its esters. Similar phenomena are observed for the other two groups of fatty acids and their esters (AA, AA-EE) and (DHA, DHA-EE, and DHA-ME). Kong et al.[30] studied the binary diffusion coefficients of γ-linolenic acid and its EEs and MEs and found that the D_{12} values under the same condition were smaller than those of its EE or ME. Thus, it can be concluded that the functional group of a solute plays an important role in its binary diffusion coefficient.

Modeling of the Diffusion Data. The experimental data were correlated by 10 models: nine of them are purely predictive models including hydrodynamic equations (Wilke−Chang,[40] Lusis−Ratcliff,[41] Scheibel,[42] and Hayduck−Minhas[43]), molecular connectivity equation (Wells[44]), hard sphere equation (Catchpole−King[45]), free volume equations (Funazukuri−Hachisu−Wakao,[26] Dymond−Liong,[32] and He−Yu−Su[46]); the other one is a free volume based equation with two adjustable parameters (Dymond[47]). The parameters needed in the 10 models are listed in Table 2. The correlated results are listed in Table 3.

Average absolute deviations (AAD %) of the 10 models for all the fatty acid EEs in Table 3 indicate that three among the nine purely predictive models, Scheibel, Catchpole−King, and He−Yu−Su provide excellent prediction with the AAD less than 2 %. Wilke−Chang and Lusis−Ratchcliff equations are not satisfactory. In Dymond's model, ($V_2 - V_D$) is defined as free volume, and V_D is taken as $0.308V_c$ for all solutes. It was found that the deviation of the predicted diffusion coefficients of the three esters is about 10 %. Better results were obtained if V_D is regarded as an adjustable parameter for each solute· As shown in Figure 6, each of the obtained V_D are less than $0.308V_c$, and the AADs by the Dymond equation with the fitted V_D values are small enough.

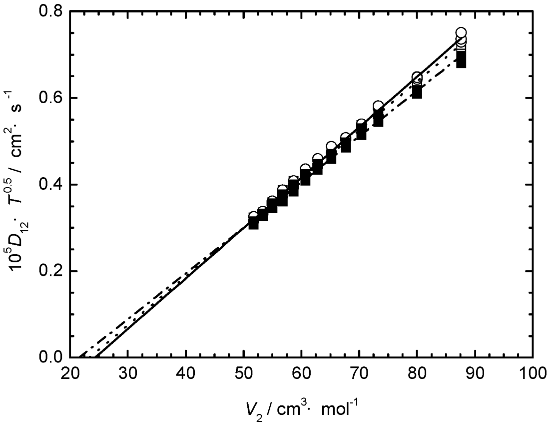

Figure 6. $D_{12}/T^{0.5}$ as a function of V_2: V_2, CO_2 molecular volume; dotted line, $D_{12}/T^{0.5} = 1.102 \times 10^{-3}(V_2 - 23.36)$ for AA-EE; solid line, $D_{12}/T^{0.5} = 1.165 \times 10^{-3}(V_2 - 24.33)$ for EPA-EE; dashed line, $D_{12}/T^{0.5} = 1.056 \times 10^{-3}(V_2 - 21.58)$ for DHA-EE; □, AA-EE; ○, EPA-EE; ■, DHA-EE.

Table 3. Average Absolute Deviation (AAD %) of Models

	AAD %		
model	AA-EE	EPA-EE	DHA-EE
Wilke−Chang[40]	15.18	15.16	16.44
Lusis−Ratcliff[41]	19.78	19.41	19.36
Scheibel[42]	0.92	1.09	1.62
Hayduck−Minhas[43]	8.94	8.84	10.60
Wells[44]	2.49	2.68	3.85
Funazukuri−Hachisu−Wakao[26]	7.06	7.50	8.51
Catchpole−King[45]	1.06	1.03	1.33
Dymond[47]	1.14	1.02	1.29
Dymond−Liong[32]	3.76	3.21	3.98
He−Yu−Su[46]	0.79	0.78	1.54

Conclusion

The binary diffusion coefficients of AA-EE, EPA-EE, and DHA-EE measured at temperatures from 308.15 K to 338.15 K and pressures from 8.42 MPa to 29.95 MPa are (5.54 to 13.47) × 10^{-5} cm^2·s^{-1}, (5.54 to 13.80) × 10^{-5} cm^2·s^{-1}, and (5.40 to 12.80) × 10^{-5} cm^2·s^{-1}, respectively. The Scheibel, Catchpole−King, and He−Yu−Su equations can predict the experimental data quite well.

Literature Cited

(1) Pettinello, G.; Bertucco, A.; Pallado, P.; Stassi, A. Production of EPA enriched mixtures by supercritical fluid chromatography: from the laboratory scale to the pilot plant. *J. Supercrit. Fluids* **2000**, *19*, 51−60.

(2) Alkio, M.; Gonzalez, C.; Jäntti, M.; Aaltonen, O. Purification of polyunsaturated fatty acid esters from tuna oil with supercritical fluid chromatography. *JAOCS, J. Am. Oil Chem. Soc.* **2000**, *77*, 315−321.

(3) Funazukuri, T.; Kong, C. Y.; Murooka, N.; Kagei, S. Measurements of binary diffusion coefficients and partition ratios for acetone, phenol, α-tocopherol, and β-carotene in supercritical carbon dioxide with a poly(ethylene glycol)-coated capillary column. *Ind. Eng. Chem. Res.* **2000**, *39*, 4462−4469.

(4) Funazukuri, T.; Kong, C. Y.; Kagei, S. Binary diffusion coefficients, partition ratios and partial molar volumes at infinite dilution for β-carotene and α-tocopherol in supercritical carbon dioxide. *J. Supercrit. Fluids* **2003**, *27*, 85−96.

(5) Funazukuri, T.; Ishiwata, Y. Diffusion coefficients of linoleic acid methyl ester, vitamin K_3 and indole in mixtures of carbon dioxide and *n*-hexane at 313.2 K, and 16.0 MPa and 25.0 MPa. *Fluid Phase Equilib.* **1999**, *164*, 117−129.

(6) Funazukuri, T.; Kong, C. Y.; Kagei, S. Infinite-dilution binary diffusion coefficients, partition ratio, and partial molar volume for ubiquinone CoQ10 in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2002**, *41*, 2812−2818.

(7) Lai, C. C.; Tan, C. S. Measurement of molecular diffusion coefficients in supercritical carbon dioxide using a coated capillary column. *Ind. Eng. Chem. Res.* **1995**, *34*, 674−680.
(8) Higashi, H.; Iwai, Y.; Oda, T.; Nakamura, Y.; Arai, Y. Concentration dependence of diffusion coefficients for supercritical carbon dioxide + naphthalene system. *Fluid Phase Equilib.* **2002**, *197*, 1161−1167.
(9) Higashi, H.; Iwai, Y.; Uchida, H.; Arai, Y. Diffusion coefficients of aromatic compounds in supercritical carbon dioxide using molecular dynamics simulation. *J. Supercrit. Fluids* **1998**, *13*, 93−97.
(10) Higashi, H. H.; Iwai, Y.; Nakamura, Y.; Yamamoto, S.; Arai, Y. Correlation of diffusion coefficients for naphthalene and dimethylnaphthalene isomers in supercritical carbon dioxide. *Fluid Phase Equilib.* **1999**, *166*, 101−110.
(11) Taylor, G. Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. London* **1953**, *219*, 186−203.
(12) Taylor, G. Condition under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. R. Soc. London* **1954**, *225*, 473−477.
(13) Aris, R. On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. London* **1956**, *235*, 67−73.
(14) Wakeham, W. A.; Nagashima, A.; Sengers, V. J. *Measurement of the Transport Properties of Fluid*; Blackwell Scientific Publication: Oxford, 1991, p 233.
(15) Umezawa, S.; Nagashima, A. Measurement of the diffusion coefficients of acetone, benzene, and alkane in supercritical CO_2 by the Taylor dispersion method. *J. Supercrit. Fluids* **1992**, *5*, 242−250.
(16) Bueno, J. L.; Suárez, J. J.; Medina, I. Experimental binary diffusion coefficients of benzene and derivatives in supercritical carbon dioxide and their comparison with the values from the classic correlations. *Chem. Eng. Sci.* **2001**, *56*, 4309−4319.
(17) González, L. M.; Bueno, J. L.; Medina, I. Determination of binary diffusion coefficients of anisole, 2,4-dimethylphenol, and nitrobenzene in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **2001**, *40*, 3711−3716.
(18) González, L. M.; Bueno, J. L.; Medina, I. Measurement of diffusion coefficients for 2-nitroanisole, 1,2-dichlorobenzene and *tert*-butylbenzene in carbon dioxide containing modifiers. *J. Supercrit. Fluids* **2002**, *24*, 219−229.
(19) Swaid, I; Schneider, G. M. Determination of binary diffusion coefficients of benzene and alkylbenzene in supercritical CO_2 between 308 and 328 K in the pressure range 80 to 160 bar with supercritical fluid chromatography (SFC). *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 869−974.
(20) Silva, C. M.; Filho, C. A; Quadri, M. B.; Macedo, E. A. Binary diffusion coefficients of α-pinene and β-pinene in supercritical carbon dioxide. *J. Supercrit. Fluids* **2004**, *32*, 167−175.
(21) Filho, C. A.; Silva, C. M.; Quadri, M. B.; Macedo, E. A. Infinite dilution diffusion coefficients of linalool and benzene in supercritical carbon dioxide. *J. Chem. Eng. Data* **2002**, *47*, 1351−1354.
(22) Filho, C. A; Silva, C. M.; Quadri, M. B.; Macedo, E. A. Tracer diffusion coefficients of citral and D-limonene in supercritical carbon dioxide. *Fluid Phase Equilib.* **2003**, *204*, 65−73.
(23) Dahmen, N.; Kordikowski, A.; Schneider, G. M. Determination of binary diffusion coefficients of organic compounds in supercritical carbon dioxide by supercritical fluid chromatography. *J. Chromatogr.* **1990**, *505*, 169−178.
(24) Funazukuri, T.; Kong, C. Y.; Kagei, S. Infinite-dilution binary diffusion coefficients of 2-propanone, 2-butanone, 2-pentanone, and 3-pentanone in CO_2 by the Taylor dispersion technique from 308.15 to 328.15 K in the pressure range from 8 to 35 MPa. *Int. J. Thermophys.* **2000**, *21*, 1279−1290.
(25) Funazukuri, T.; Kong, C. Y.; Kagei, S. Binary diffusion coefficients of acetone in carbon dioxide at 308.2 and 313.2 K in the pressure range from 7.9 to 40 MPa. *Int. J. Thermophys.* **2000**, *21*, 651−669.
(26) Funazukuri, T.; Hachisu, S.; Wakao, N. Measurements of binary diffusion coefficients of $C_{16}-C_{24}$ unsaturated fatty acid methyl esters in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **1991**, *30*, 1323−1329.
(27) Funazukuri, T.; Kong, C. Y.; Kagei, S. Effects of molecular weight and degree of unsaturation on binary diffusion coefficients for lipids in supercritical carbon dioxide. *Fluid Phase Equilib.* **2004**, *219*, 67−73.
(28) Funazukuri, T.; Kong, C. Y.; Kikuchi, T.; Kagei, S. Measurements of binary diffusion coefficient and partition ratio at infinite dilution for linoleic acid and arachidonic acid in supercritical carbon dioxide. *J. Chem. Eng. Data* **2003**, *48*, 684−688.
(29) Funazukuri, T.; Kong, C. Y.; Kagei, S. Binary diffusion coefficient, partition ratio, and partial molar volume for docosahexaenoic acid, eicosapentaenoic acid and α-linolenic acid at infinite dilution in supercritical carbon dioxide. *Fluid Phase Equilib.* **2003**, *206*, 163−178.
(30) Kong, C. Y.; Withanage, N. R. W.; Funazukuri, T.; Kagei, S. Binary diffusion coefficients and retention factors for γ-linolenic acid and its methyl and ethyl esters in supercritical carbon dioxide. *J. Supercrit. Fluids* **2006**, *37*, 63−71.
(31) Kong, C. Y.; Withanage, N. R. W.; Funazukuri, T.; Kagei, S. Binary diffusion coefficients and retention factors for long-chain triglycerides in supercritical carbon dioxide by the chromatographic impulse response method. *J. Chem. Eng. Data* **2005**, *50*, 1635−1640.
(32) Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion coefficients of long-chain esters in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **1991**, *30*, 1329−1335.
(33) Liong, K. K.; Wells, P. A.; Foster, N. R. Diffusion of fatty acid esters in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 390−399.
(34) Rezaei, K. A.; Temelli, F. Using supercritical fluid chromatography to determine diffusion coefficients of lipids in supercritical CO_2. *J. Supercrit. Fluids* **2000**, *17*, 35−44.
(35) Moulijn, J. A.; Spijker, R.; Kolk, J. F. M. Axial dispersion of gases flowing through coiled columns. *J. Chromatogr.* **1977**, *142*, 155−166.
(36) R. Span, W. Wagner, A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.
(37) Sovová, H.; Procházka, J. Calculations of compressed carbon dioxide viscosities. *Ind. Eng. Chem. Res.* **1993**, *32*, 3162−3169.
(38) Funazukuri, T.; Nishimoto, N. Tracer diffusion coefficients of benzene in dense CO_2 at 313.2 K and 8.5−30 MPa. *Fluid Phase Equilib.* **1996**, *125*, 235−243.
(39) Kong, C. Y.; Funazukuri, T.; Kagei, S. Binary diffusion coefficients and retention factors for polar compounds in supercritical carbon dioxide by chromatography impulse response method. *J. Supercrit. Fluids* **2006**, *37*, 359−366.
(40) Wilke, C. R.; Chang, P. Correlation of diffusion coefficients in dilute solution. *AIChE J.* **1955**, *1*, 264−270.
(41) Lusis, M. A.; Ratcliff, G. A. Diffusion, in binary liquid mixtures at infinite dilute. *Can. J. Chem. Eng.* **1968**, *46*, 385−387.
(42) Scheibel, E. G. Liquid diffusivities. *Ind. Eng. Chem.* **1954**, *46*, 2007−2008.
(43) Hayduk, W.; Minhas, B. S. Correlation of prediction of molecular diffusivities in liquids. *Can. J. Chem. Eng.* **1982**, *60*, 295−299.
(44) Wells, P. A. Diffusion in supercritical fluids. Ph.D. Dissertation. The University of New South Waless, Kensington, Australia, 1991.
(45) Catchpole, O. J.; King, M. B. Measurement and correlation of binary diffusion coefficients in near critical fluids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1828−1837.
(46) He, C. H.; Yu, Y. S.; Su, W. K. Tracer diffusion coefficients of solutes in supercritical solvents. *Fluid Phase Equilib.* **1998**, *142*, 281−286.
(47) Chen, S. H.; Davis, H. T.; Evans, D. F. Tracer diffusion in polyatomic liquids. III. *J. Chem. Phys.* **1982**, *77*, 2540−2544.
(48) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: Singapore, 1977.
(49) Fuller, E. N.; Schettler, P. D.; Giddings, J. C. A new method for prediction of binary gas-phase diffusion coefficients. *Ind. Eng. Chem.* **1966**, *58*, 18−27.

Received for review October 13, 2006. Accepted December 4, 2006.

JE060456H