Binary Diffusion Coefficients and Retention Factors for Long-Chain Triglycerides in Supercritical Carbon Dioxide by the Chromatographic Impulse Response Method

Chang Yi Kong,† Nirosha R. W. Withanage,† Toshitaka Funazukuri,*,‡ and Seiichiro Kagei†

Faculty of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, and Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Infinite dilution binary diffusion coefficients D_{12} and retention factors k have been measured in supercritical carbon dioxide for the long-chain triglyceride triarachidonin at 313.2 K at (10 to 30) MPa, and trierucin and trinervonin both at 308.2 K to 323.2 K over the pressure range from (9 to 30) MPa by the chromatographic impulse response method. It was found that the D_{12} predictive correlations proposed previously, D_{12}/T as a function of viscosity and the Schmidt number correlations, were valid for such long-chain triglycerides having molecular weights near or over 1000. Furthermore, partial molar volumes of the solutes were determined from the relationships between k and CO_2 density.

Introduction

Supercritical fluid extraction and fractionation of valuable compounds from natural products have widely been employed in various industries. Accurate prediction of physical properties of the compounds is required for reactor design. The transport properties as well as those related to phase equilibria or solubilities are important for estimating the mass transfer rates in supercritical fluids. Among the transport data in supercritical fluids, those for diffusion coefficients are still limited. In particular, the accurate measurements for large molecular weight compounds such as long-chain triglycerides are very scarce due to the difficulty in measuring experimentally.

Binary diffusion coefficients in supercritical fluids have been made mainly by the Taylor dispersion method for various compounds having a wide range of molecular weights,[1,2] and the capillary tube method has also been employed for solid compounds.[1,2] The Taylor dispersion method has been claimed to be relatively accurate and less time-consuming.[3] However, in measurements for solid or highly viscous solutes, which are high molecular weight and/or polar compounds, it is not easy to inject the solute to a diffusion column in which supercritical fluid is flowing. Moreover, in most Taylor dispersion measurements when a solute dissolved in supercritical fluid, mainly carbon dioxide, has been injected, it is difficult to estimate the accurate amount injected. Although the capillary tube method is also suitable for measuring binary diffusion coefficients of solid solutes,[4−7] the value determined is not that at infinite dilution but a mean value between the saturation and the certain concentration (e.g., zero).

Recently, we have developed the chromatographic impulse response (CIR) method[8−13] to measure binary diffusion coefficients for solid or highly viscous liquid in supercritical fluids using a polymer-coated capillary column instead of an uncoated tube as in the Taylor dispersion method. In this method, the amount of a solute injected can be accurately adjusted by injecting a solute dissolved in a common organic solvent such as hexane. Since the solute and the dissolving solvent as well as some impurities are chromatographically separated, the presence of the organic solvent does not influence the diffusion of the solute in the supercritical fluid. Moreover, the tailing of the response curve in the CIR method can significantly be reduced for polar compounds as compared with that in the Taylor dispersion. Thus, the CIR method is more suitable for measuring high molecular weight compounds. In the present study, binary diffusion coefficients and retention factors for long-chain triglycerides in supercritical carbon dioxide were measured by the CIR method, and partial molar volumes of solutes were estimated from the retention factors determined. Moreover, the validities of the predictive correlations we have proposed for binary diffusion coefficients of such large molecular weight compounds are discussed.

Theory

The theory was described in our previous studies in the CIR method.[2,8,12] A set of the most suitable values for two parameters of infinite dilution binary diffusion coefficient (D_{12}) and retention factor (k) can be determined as to minimize the root-mean-square error (ϵ), defined as eq 1, by the curve-fitting method, comparing between calculated and measured response curves from t_1 to t_2, which are the frontal and the latter time at 10 % peak height of the measured response curve, respectively:

$$\epsilon = (\{\int_{t_1}^{t_2} (C_{a,exp} - C_{a,cal})^2\, dt\}/\{\int_{t_1}^{t_2} (C_{a,exp})^2\, dt\})^{1/2} \quad (1)$$

where $C_{a,exp}$ and $C_{a,cal}$ are cross-sectional average concentrations of tracer species for measured and calculated response curves, respectively.

Experimental Section

The experimental apparatus and procedures were almost the same as described in the previous studies.[8,9] Triarachi-

* Corresponding author e-mail: funazo@chem.chuo-u.ac.jp.
† Yokohama National University.
‡ Chuo University.

10.1021/je050101i CCC: $30.25
Published on Web 08/06/2005

Table 1. D_{12} and k Values, Together with Fitting Errors (ϵ) for Triarachidonin, Trierucin, and Trinervonin

T	P	D_{12}			T	P	D_{12}			T	P	D_{12}		
K	MPa	(10^{-9} m^2·s^{-1})	k	$10^2\epsilon$	K	MPa	(10^{-9} m^2·s^{-1})	k	$10^2\epsilon$	K	MPa	(10^{-9} m^2·s^{-1})	k	$10^2\epsilon$
							Triarachidonin							
313.21	9.95	5.464	3.895	1.03	313.21	13.01	4.612	0.405	0.48	313.21	23.03	3.788	0.103	0.66
	9.98	5.426	3.615	1.08		15.98	4.246	0.213	0.96		23.98	3.817	0.112	0.46
	10.00	5.418	3.313	1.21		16.00	4.247	0.212	0.82		26.00	3.749	0.104	0.49
	10.45	5.231	2.003	0.70		16.00	4.253	0.204	0.90		26.02	3.728	0.079	0.73
	10.84	5.071	1.408	0.78		16.00	4.251	0.208	1.06		26.05	3.694	0.092	0.45
	10.91	5.061	1.361	1.09		17.99	4.077	0.159	0.95		26.99	3.608	0.089	0.59
	11.00	5.082	1.204	0.64		20.03	3.960	0.134	0.85		28.01	3.596	0.084	0.63
	12.00	4.747	0.664	0.81		21.00	3.901	0.118	0.14		29.09	3.602	0.096	0.40
	12.00	4.771	0.657	0.51		22.00	3.864	0.115	0.59		30.24	3.568	0.075	0.84
							Trierucin							
308.15	8.26	5.155	5.309	3.30	313.21	9.50	4.904	4.169	1.30	323.15	11.98	5.287	3.153	3.36
	8.30	4.986	4.403	2.23		9.51	4.922	4.044	1.65		12.03	5.309	2.702	3.42
	8.46	4.726	2.505	1.24		9.55	5.096	3.566	2.11		12.50	5.120	1.486	2.94
	8.48	4.700	2.363	1.62		9.57	4.844	3.584	2.17		12.99	5.011	0.902	1.10
	8.50	4.744	2.254	3.14		9.70	4.823	2.568	2.96		13.00	5.040	0.895	2.18
	8.66	4.553	1.471	1.46		9.84	4.777	1.893	2.66		13.05	5.050	0.857	1.84
	8.80	4.483	1.199	2.83		9.98	4.694	1.554	2.28		13.31	4.975	0.674	1.16
	8.85	4.447	1.057	2.32		10.00	4.651	1.497	1.87		13.49	4.943	0.612	0.86
	8.98	4.470	0.934	1.46		10.00	4.736	1.494	1.24		14.00	4.804	0.432	0.57
	9.05	4.355	0.836	2.16		10.05	4.868	1.340	0.92		14.00	4.829	0.417	1.18
	9.10	4.360	0.778	1.21		10.51	4.599	0.789	1.51		14.53	4.722	0.305	1.60
	9.11	4.507	0.755	1.08		11.00	4.572	0.509	1.17		15.00	4.637	0.241	1.27
	9.11	4.383	0.771	1.62		11.03	4.492	0.494	0.32		15.03	4.603	0.262	1.08
	9.20	4.365	0.698	1.94		11.09	4.445	0.468	1.15		15.03	4.622	0.257	1.60
	9.31	4.350	0.610	1.36		11.50	4.375	0.369	1.08		15.52	4.560	0.219	1.80
	9.40	4.290	0.561	1.17		12.00	4.307	0.273	1.86		16.00	4.495	0.186	1.48
	9.40	4.305	0.563	1.54		13.02	4.131	0.183	1.88		16.51	4.470	0.157	1.03
	9.50	4.275	0.515	1.07		13.50	4.088	0.153	1.63		16.54	4.422	0.162	1.43
	9.51	4.377	0.488	1.16		14.00	4.022	0.135	0.83		17.00	4.409	0.149	1.65
	9.60	4.277	0.471	1.12		14.50	3.996	0.121	0.95		18.00	4.267	0.118	1.30
	10.00	4.205	0.350	0.36		15.00	3.943	0.114	1.01		18.50	4.239	0.107	0.77
	10.01	4.241	0.341	1.11		15.52	3.904	0.100	1.52		20.00	4.110	0.091	0.74
	10.51	4.141	0.257	1.13		15.53	3.920	0.107	0.90		22.01	3.978	0.075	0.70
	11.00	4.001	0.202	0.55		15.97	3.884	0.091	0.68		22.04	3.995	0.075	0.18
	11.00	4.037	0.200	0.91		15.99	3.887	0.098	0.52		24.99	3.819	0.065	0.34
	11.00	4.047	0.202	0.91		16.00	3.883	0.099	0.94		27.02	3.709	0.059	0.37
	11.51	3.962	0.171	1.68		16.02	3.891	0.097	0.50		30.03	3.603	0.054	0.72
	12.01	3.915	0.140	1.65		16.96	3.791	0.089	0.73					
	12.50	3.852	0.143	1.20		21.00	3.564	0.064	0.94					
	13.01	3.821	0.121	0.50		24.95	3.368	0.058	0.40					
	14.01	3.729	0.096	1.11		25.05	3.343	0.055	0.56					
	14.99	3.653	0.085	0.68		27.00	3.287	0.056	0.91					
	16.00	3.588	0.078	0.87		30.06	3.153	0.052	0.81					
	16.02	3.580	0.081	0.59										
	17.52	3.501	0.069	0.63										
	19.98	3.350	0.060	0.24										
	23.01	3.225	0.057	0.23										
	25.01	3.148	0.054	0.62										
	26.45	3.082	0.055	0.65										
	27.03	3.065	0.053	0.41										
	30.02	2.991	0.053	0.46										
							Trinervonin							
308.15	9.00	4.294	1.174	1.87	313.15	9.61	4.762	4.462	2.34	323.15	12.50	4.913	2.056	2.46
	10.00	3.961	0.403	0.81		9.70	4.689	3.712	2.44		13.00	4.848	1.173	1.94
	10.00	4.063	0.425	0.86		10.02	4.546	2.008	2.38		14.00	4.570	0.533	1.28
	10.02	4.032	0.425	0.95		10.48	4.429	1.089	1.86		15.01	4.456	0.310	0.48
	11.00	3.919	0.247	0.94		10.50	4.410	1.063	1.30		16.03	4.298	0.218	0.72
	11.01	3.866	0.253	0.38		11.00	4.331	0.662	1.40		16.98	4.260	0.160	0.63
	12.00	3.774	0.175	1.00		11.03	4.309	0.630	1.44		16.98	4.285	0.159	0.46
	12.49	3.706	0.150	0.73		11.50	4.199	0.440	1.16		17.04	4.299	0.162	0.73
	16.01	3.447	0.086	0.71		11.51	4.208	0.438	1.26		20.00	3.997	0.097	1.49
	20.00	3.258	0.064	0.22		14.00	3.892	0.170	0.81		20.00	3.978	0.094	1.13
	30.02	2.777	0.051	0.34		16.01	3.748	0.109	0.91		25.04	3.695	0.068	0.47
	30.03	2.806	0.052	0.32		20.00	3.459	0.068	0.75		30.02	3.461	0.062	0.68
						25.00	3.252	0.058	0.34					
						30.05	3.113	0.054	0.55					

donin (1,2,3-tri-[(*cis*,*cis*,*cis*,*cis*)-5,8,11,14-eicosatetraenoyl]-glycerol, CAS Registry No. 23314-57-0, $C_{63}H_{98}O_6$, molecular weight $M = 951.5$, purity = 98 %, Sigma), trierucin (1,2,3-tri-[(*cis*)-13-docosenoyl]-glycerol, CAS Registry No. 2752-99-0, $C_{69}H_{128}O_6$, $M = 1053.8$, purity = 99 %, Sigma), and trinervonin (1,2,3-tri-[(*cis*)-15-tetracosenoyl]-glycerol, CAS Registry No. 81913-24-8, $C_{75}H_{140}O_6$, $M = 1137.9$, purity = 98 %, Sigma) were employed without further purification. Each triglyceride was dissolved in liquid hexane at an ambient condition, and the solution was loaded to the poly(ethylene glycol)-coated diffusion column (UACW-15W-1.0F, supplied by Frontier Laboratory Ltd., Fukushima, Japan) with the inner diameter of 0.515 mm, tube length of 15.30 m, bonded polymer film thickness of 1 μm, and coil diameter of 0.27 m through an injector equipped with a 0.2 μL rotor (Rheodyne, 7520) at concentrations of (0.005, 0.01, and 0.006) g/mL for triarachidonin, trierucin, and trinervonin, respectively. Response curves used for determining the parameter values were chosen to be those monitored at 200 nm for all lipids by examining the wavelength dependences on the determined values from 195 to 300 nm. To neglect the secondary flow effect on the

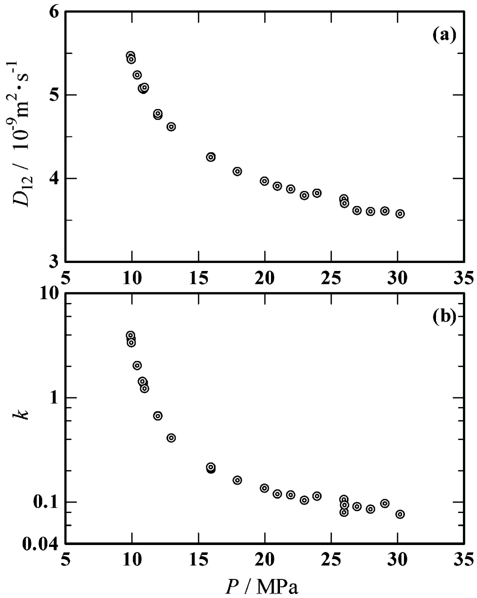

Figure 1. Pressure dependences on (a) D_{12} and (b) k for triarachidonin at 313.21 K.

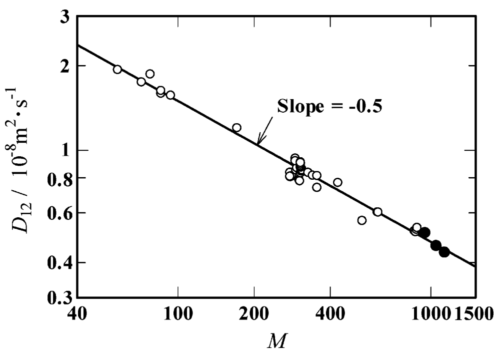

Figure 2. D_{12} as a function of molecular weight M for three triglycerides (●) measured in this study and various solutes (○) reported previously[8–11,13,16–19] at 313 K and 11 MPa.

diffusion, the criterion $De \cdot Sc^{1/2} < 8$ was selected,[2] where the Dean number $De = (\rho u_a d_{tube}/\eta)(d_{tube}/d_{coil})^{1/2}$; u_a is the average solvent velocity; d_{tube} and d_{coil} are the inner diameter of diffusion column and the coil diameter, respectively; and the Schmidt number $Sc = \eta/\rho D_{12}$; ρ and η are the CO_2 density and viscosity, obtained with the equations of Pitzer and Schreiber[14] and by the method of Fenghour et al.,[15] respectively. The uncertainties of T and P were ±0.1 K and ±0.1 MPa, respectively. That of D_{12} decreased with increasing pressure and ranged from ±4 % to ±2 %. Note that the relative standard deviation of CO_2 velocity in each run also decreased with increasing pressure and varied from ±1.5 % to ±0.5 % over the pressure range studied.

Results and Discussion

Table 1 lists the D_{12} and k values for all three triglycerides measured in this study, together with fitting error (ϵ). Figure 1 plots D_{12} value as a function of pressure for triarachidonin at 313.21 K. As has been seen for many solutes, the D_{12} and k values decrease with increase in pressure, and critical slowing down (which is a phenomenon showing anomalous decrease in the vicinity of critical point) of D_{12} value in near critical region was not clearly observed as seen for benzene.[16]

Figure 2 shows D_{12} as a function of molecular weight (M) at 313.21 K and 11 MPa for three triglycerides in the present study and various compounds in our previous studies.[8–11,13,16–19] Over the wide range of molecular weight (i.e., from 58 of acetone to 1138 of trinervonin), the D_{12} values were represented by a straight line in logarithmic plots, and the slope was −0.5: $D_{12}/\text{m}^2\cdot\text{s}^{-1} = 1.498 \times 10^{-8}\, M^{-0.5}$ at 313 K and 11 MPa.

The correlation in eq 2 has been claimed to be valid for many solutes:[2]

$$(D_{12}/\text{m}^2\cdot\text{s}^{-1})/(T/\text{K}) = \alpha(\eta/\text{Pa}\cdot\text{s})^{\beta} \quad (2)$$

where constants α and β are specific to the system and are determined when units of D_{12} and η are m^2·s^{-1} and Pa·s, respectively. Figure 3 indicates D_{12}/T as a function of CO_2 viscosity for (a) triarachidonin and trinervonin and (b) trierucin. The data can be represented with straight lines given by eq 2. The values of average absolute deviation AAD % are presented in Table 2, together with the determined values of α and β. Both solutes having D_{12} data available at various temperatures, trinervonin and trierucin, show the slight temperature dependences. In plots of

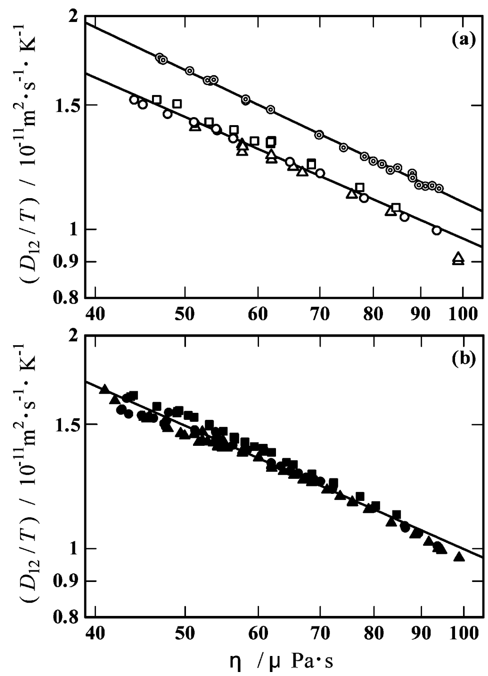

Figure 3. D_{12}/T as a function of CO_2 viscosity for (a) triarachidonin: ◎, 313.21 K and trinervonin: △, 308.15 K; ○, 313.15 K; □, 323.15 K, and (b) trierucin: ▲, 308.15 K; ●, 313.21 K; ■, 323.15 K.

Table 2. Determined α and β Values in Eq 2[a]

solute	α	β	AAD %	N
triarachidonin	3.618×10^{-14}	−0.620	0.55	27
trierucin	4.824×10^{-14}	−0.579	1.91	101
trinervonin	5.046×10^{-14}	−0.571	1.91	38

[a] Constants α and β were determined when units of D_{12} and CO_2 viscosity were in m^2·s^{-1} and Pa·s, respectively, N, number of data points.

Table 3. AAD % Values for Schmidt Number Correlation at Various σ Values[a]

solute	σ_{vw}/nm	AAD %	σ/nm	AAD %	N
triarachidonin	1.256	14.01	1.143	5.37	27
trierucin	1.316	7.79	1.260	5.76	101
trinervonin	1.352	9.15	1.285	5.50	38

[a] σ_{vw}, van der Waals diameter; σ, hard-sphere diameter obtained as to minimize AAD %.

Table 4. Determined Values of Constants b_0 to b_6 in Eq 3

	triarachidonin	trierucin			trinervonin		
	313.21 K	308.15 K	313.21 K	323.15 K	308.15 K	313.15 K	323.15 K
b_0	3.98915757×10^{3}	2.08565140×10^{3}	4.88833998×10^{3}	5.97784168×10^{3}	6.03133418×10^{3}	4.68775942×10^{3}	8.02419058×10^{3}
b_1	$-2.72810039 \times 10^{1}$	$-1.43506506 \times 10^{1}$	$-3.59368261 \times 10^{1}$	$-4.49180116 \times 10^{1}$	$-4.28817818 \times 10^{1}$	$-3.28583821 \times 10^{1}$	$-5.99238860 \times 10^{1}$
b_2	$7.80709565 \times 10^{-2}$	$4.12681196 \times 10^{-2}$	$1.10209720 \times 10^{-1}$	$1.40726773 \times 10^{-1}$	$1.27108760 \times 10^{-1}$	$9.59366076 \times 10^{-2}$	$1.86512121 \times 10^{-1}$
b_3	$-1.19620159 \times 10^{-4}$	$-6.34445335 \times 10^{-5}$	$-1.80358328 \times 10^{-4}$	$-2.35202969 \times 10^{-4}$	$-2.00970895 \times 10^{-4}$	$-1.49276152 \times 10^{-4}$	$-3.09576850 \times 10^{-4}$
b_4	$1.03465146 \times 10^{-7}$	$5.49660631 \times 10^{-8}$	$1.66031992 \times 10^{-7}$	$2.21105777 \times 10^{-7}$	$1.78694963 \times 10^{-7}$	$1.30506613 \times 10^{-7}$	$2.88920062 \times 10^{-7}$
b_5	$-4.78874387 \times 10^{-11}$	$-2.54322833 \times 10^{-11}$	$-8.14861586 \times 10^{-11}$	$-1.10817620 \times 10^{-10}$	$-8.46958204 \times 10^{-11}$	$-6.07664150 \times 10^{-11}$	$-1.43716158 \times 10^{-10}$
b_6	$9.26353938 \times 10^{-15}$	$4.90769925 \times 10^{-15}$	$1.66516617 \times 10^{-14}$	$2.31293641 \times 10^{-14}$	$1.67135842 \times 10^{-14}$	$1.17700253 \times 10^{-14}$	$2.97616667 \times 10^{-14}$
AAD %	3.90	1.84	2.56	1.93	1.52	1.36	1.23
N	27	41	33	27	12	14	12

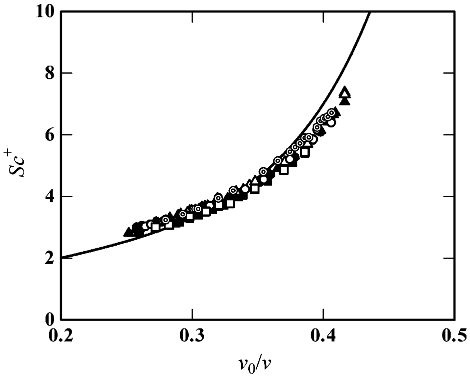

Figure 4. Schmidt number correlation for triarachidonin (σ = 1.143 nm), trierucin (σ = 1.260 nm), and trinervonin (σ = 1.285 nm). The data plotted are the same as in Figure 3a,b.

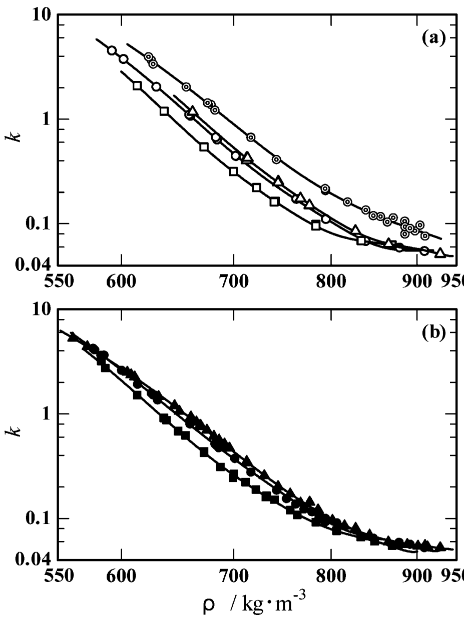

Figure 5. k as a function of CO_2 density for (a) triarachidonin at 313.21 K and trinervonin at (308.15, 313.15, and 323.15) K, and (b) trierucin at (308.15, 313.21, and 323.15) K. The key is the same as in Figure 3a,b.

D_{12}/T as a function of CO_2 viscosity, the solutes we have studied are classified into two groups: the values of the intercept α in eq 2 are independent of temperature and dependent, while the reason is not known. Most compounds studied did not show the temperature dependency, although phenol[8] and ubiquinone CoQ10 (2,3-dimethoxy-5-methyl-6-decaprenyl benzoquinone, CAS Registry No. 303-98-0)[9] did.

Figure 4 shows the Schmidt number correlation (Sc^+) as a function of v_0/v for the three solutes when the hard-sphere diameters were determined as to minimize the deviations from the correlation, where Sc^+ is the ratio of Schmidt number at high pressure to that at atmospheric pressure under isothermal condition, and v_0 and v are CO_2 hard-sphere closest-packed molar volume and CO_2 molar volume, respectively. The values of AAD % are listed in Table 3, together with AAD % when the van der Waals diameters[20] were employed. It is found that the Schmidt number correlation is also valid for large molecular weight triglycerides, while the predicted values are deviated from those measured at higher v_0/v values or higher pressures.

Figure 5 plots the dependences of CO_2 density on retention factor k values for (a) triarachidonin and triner-

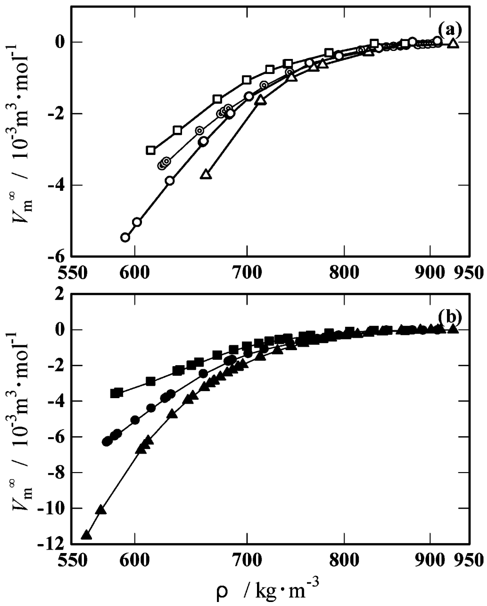

Figure 6. V_m^∞ as a function of CO_2 density for (a) triarachidonin and trinervonin and (b) trierucin. Each V_m^∞ datum plotted was determined at the condition where each D_{12} and k data were measured. The key is the same as in Figure 3a,b.

vonin and (b) trierucin. The k values for the three triglycerides were well-represented in eq 3, and constants involved at each temperature and the AAD % are listed in Table 4:

$$\ln k = \sum_{i=0}^{6} b_i[\ln(\rho/\text{kg·m}^{-3})]^i \quad (3)$$

where b_i values are coefficients of the polynomial correlations, and ρ is the CO_2 density. At CO_2 densities lower than 800 kg·m^{-3}, the data can be represented by the straight lines while the data seem to be leveled off at higher CO_2 densities. Although the reason is not clarified, it can be speculated that the affinity of the polymer to solute molecule does not increase because the polymer considerably absorb CO_2 molecules at high CO_2 densities. Note that the k values except at high CO_2 densities were represented with a simpler correlation with CO_2 density, as seen in the previous studies.[9−13]

Figure 6 plots infinite dilution partial molar volume (V_m^∞) for (a) triarachidonin and trinervonin and (b) trierucin obtained from eq 4 versus CO_2 density:

$$V_m^\infty = R_g T \beta_T \left\{ \left(\frac{\partial \ln k}{\partial \ln \rho} \right)_T + 1 \right\} \quad (4)$$

where V_m^∞ is the infinite dilution partial molar volume of solute in the mobile phase, and R_g and β_T are the gas constant and the isothermal compressibility, respectively. Equation 4 is valid when the partial molar volume of solute (V_s^∞) in the polymer phase coated on the inner surface of the column is negligible as compared with V_m^∞. This assumption is valid near the critical region of CO_2 where V_m^∞ values in supercritical phase have negative large values.[21] The values decrease with decreasing CO_2 density for all solutes and seem to become large and negative values at the critical points.

Conclusions

The chromatographic impulse response method was employed to measure infinite dilution binary diffusion coefficients and retention factors for three long-chain triglycerides having molecular weights around 1000 in supercritical carbon dioxide. The measured diffusion coefficients were separately expressed with two correlations proposed previously by the authors, the D_{12}/T as a function of viscosity and the Schmidt number correlation. The partial molar volumes of the solutes were also determined by the retention factor-density correlations.

Literature Cited

(1) Funazukuri, T.; Nishiumi, H. In *Supercritical Fluids*; Arai, Y., Sako, T., Takebayashi, Y., Eds.; Springer: Berlin, 2002; Chapter 3.3.

(2) Funazukuri, T.; Kong, C. Y.; Kagei, S. Impulse response techniques to measure binary diffusion coefficients under supercritical conditions. *J. Chromatogr. A* **2004**, *1037*, 411−429.

(3) Wakeham, W. A.; Nagashima, A.; Sengers, V. J. *Measurement of the Transport Properties of Fluids*; Blackwell Scientific Publishers: Oxford, U.K., 1991; p 233.

(4) Knaff, G.; Shlünder, E. U. Diffusion coefficients of naphthalene and caffeine in supercritical carbon dioxide. *Chem. Eng. Process*. **1987**, *21*, 101−105.

(5) 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.

(6) Higashi, H.; Iwai, Y.; Takahashi, Y.; Uchida, H.; Arai, Y. Diffusion coefficients of naphthalene and dimethylnaphthalene in supercritical carbon dioxide. *Fluid Phase Equilib*. **1999**, *144*, 269−278.

(7) Higashi, 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.

(8) 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.

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

(10) 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.

(11) 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.

(12) Kong, C. Y.; Funazukuri, T.; Kagei, S. Chromatographic impulse response technique with curve fitting to measure binary diffusion coefficients and retention factors using polymer-coated capillary columns. *J. Chromatogr. A* **2004**, *1035*, 177−193.

(13) 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.

(14) Pitzer, K. S.; Schreiber, D. R. Improving equation-of-state accuracy in the critical region; equations for carbon dioxide and neopentane as examples. *Fluid Phase Equilib*. **1988**, *41*, 1−17.

(15) Fenghour, A.; Wakeham, W. A.; Vesovic, V. The viscosity of carbon dioxide. *J. Phys. Chem. Ref. Data* **1998**, *27*, 31−44.

(16) Funazukuri, T.; Kong, C. Y.; Kagei, S. Infinite dilution binary diffusion coefficients of benzene in carbon dioxide by the Taylor dispersion technique at temperatures from 308.15 to 328.15 K and pressures from 6 to 30 MPa. *Int. J. Thermophys*. **2001**, *22*, 1643−1660.

(17) 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.

(18) 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.

(19) Funazukuri, T.; Kong, C. Y.; Kagei, S. Measurements of binary diffusion coefficients for some low volatile compounds in supercritical carbon dioxide by input-output response technique with two diffusion columns connected in series. *Fluid Phase Equilib*. **2002**, *194*−*197*, 1169−1178.

(20) Bondi, A. van der Waals volumes and radii. *J. Phys. Chem*. **1964**, *68*, 441−451.

(21) Špicka, B.; Cortesi, A.; Fermeglia, M.; Kikic, I. Determination of partial molar volumes at infinite dilution using SFC technique. *J. Supercrit. Fluids* **1994**, *7*, 171−176.

Received for review March 16, 2005. Accepted June 7, 2005. The authors are grateful to the Ministry of Education, Sports, Culture, Science and Technology of Japan for support through Grant-in-aid 15560658. This research was also financially supported by a special program for the promotion of graduate research and a project research from Chuo University and by a cooperative research project from Faculty of Environment and Information Sciences of Yokohama National University.

JE050101I