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Measurements of Binary Diffusion Coefficients for Ferrocene and 1,1′-Dimethylferrocene in Supercritical Carbon Dioxide

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Binary diffusion coefficients D_{12} and retention factors k of ferrocene and 1,1′-dimethylferrocene at infinite dilution in supercritical (sc) carbon dioxide were measured by the chromatographic impulse response (CIR) method at temperatures from (308.2 to 323.2) K over a pressure range from (8.0 to 40.3) MPa for ferrocene and from (8.2 to 40.1) MPa for 1,1′-dimethylferrocene. The D_{12} data for ferrocene were also measured by the Taylor dispersion method with two injection procedures of ferrocene: ferrocene dissolved both in sc CO_2 and in liquid hexane. The D_{12} values of ferrocene were not affected by the injection methods and agreed with those measured by the CIR method. As has been seen for various organic compounds measured in our previous reports, the D_{12} data for both metal complexes were correlated with the hydrodynamic equation $D_{12}/T = \alpha\eta^{\beta}$, where η is the CO_2 viscosity and α and β are the constants determined by each solute. The retention factors were also correlated with CO_2 density.

Introduction

Metal complexes such as ferrocene and its derivatives have been investigated for a variety of applications in organic syntheses and biological systems, etc., due to the unique properties such as electrochemical and photoinduced electron transfer properties.[1] Recently, the behavior of metal complexes in supercritical (sc) carbon dioxide has become the focus of attention due to the compounds not only having relatively high solubility in sc fluids but also having the potential to control solvation and reaction behavior via changes in the physical conditions of the system.[2] Then, the estimation of mass transfer properties, such as diffusion coefficients, of metal complexes in sc CO_2 is essential for process design.

Measurements of diffusion coefficients of metal complexes in subcritical and sc fluids were mainly made by a voltammetric method. In fact, diffusion coefficients of ferrocene, as a simple and typical metal complex, have been measured by the voltammetric method in various subcritical and sc fluids: acetonitrile,[3,4] chlorodifluoromethane,[5] CO_2 containing water,[6,7] CO_2 in the presence of a water-in-CO_2 microemulsion,[8] and a dimethylformamide + CO_2 mixture.[9] As mentioned,[8] the voltammetric measurement for nonpolar fluid such as CO_2 is extremely difficult, and it requires an assistant electrolyte. As a result, the system is not binary and sometimes consists of two phases: gaseous and heavy electrolyte phases. The values of diffusion coefficients determined in the presence of an electrolyte cannot be regarded as binary diffusion coefficients, and the effect of the presence of an electrolyte is not clarified in most cases.

A number of experimental data on diffusion coefficients of various organic compounds in sc fluids have been measured by the transient response techniques, i.e., the Taylor dispersion method[10,11] and the chromatographic impulse response (CIR) method.[12,13] The Taylor dispersion method is suitable for the values at infinite dilution with relatively high accuracy and is less time consuming,[14] and the CIR method is more suitable for polar and/or high molecular weight compounds than the Taylor dispersion method.[12,13,15] However, the measurements for metal complexes in sc CO_2 by the transient response methods are extremely limited: the data are only available for copper(II) trifluoroacetylacetonate[16] and palladium(II) and cobalt(III) acetylacetonate complexes.[17] When these methods are applied, binary diffusion coefficients can be obtained in pure sc fluids in the absence of an electrolyte. Thus, the objectives of this study are to measure the diffusion coefficients of ferrocene and 1,1′-dimethylferrocene in sc CO_2 over a wide range of pressure by the CIR and the Taylor dispersion method and to compare the D_{12} data measured by both methods.

Theory

The theory was described for the Taylor dispersion method by Taylor[10] and Aris[11] and for the CIR method in our previous studies.[12,13] In both cases, when a tracer is pulse-injected into a fully developed laminar flow in a cylindrical diffusion column, the fundamental equation in terms of the tracer concentration $c(r, x, t)$ together with the initial and boundary conditions are given as eqs A1 to A4 in Table 1. Approximate solutions $C_a(t)$ for the cross-sectional average concentration of the tracer at the diffusion column exit are given by eqs A5a and A5b. The validity of both measurements can be evaluated in terms of root-mean-square (rms) relative difference δ between the measured curve $C_{a,meas}(t)$ and the calculated curve $C_a(t)$ using eq A6. The curve fit is considered good when $\delta < 1$ % and acceptable when $\delta <$ (2 to 3) %.[13,15]

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Table 1. Fundamental Equations of (a) the Taylor Dispersion and (b) the CIR Methods[a]

	(a) Taylor dispersion method	(b) CIR method
$c(r, x, t)$	$\frac{\partial c}{\partial t} = D_{12}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial x^2}\right\} - 2u_a\left\{1 - \left(\frac{r}{R}\right)^2\right\}\frac{\partial c}{\partial x}$ (A1)	
initial condition	$c = \frac{m}{\pi R^2}\delta(x)$ at $t = 0$ (A2a)	$c = \frac{m}{\pi R^2}\frac{\delta(x)}{1 + k}$ at $t = 0$ (A2b)
boundary condition	$\frac{\partial c}{\partial r} = 0$ at $r = 0$ and R (A3a)	$\frac{\partial c}{\partial r} = 0$ at $r = 0$ $k\frac{\partial c}{\partial t} = -\frac{2D_{12}}{R}\frac{\partial c}{\partial r}$ at $r = R$ (A3b)
	$c = 0$ at $x = \pm\infty$ (A4)	
$C_a(t)$	$C_a(t) = \frac{m/(\pi R^2)}{(4\pi at)^{1/2}}\exp\left\{-\frac{(L - u_a t)^2}{4at}\right\}$ $a = D_{12} + \frac{R^2u_a^2}{48D_{12}}$ (A5a)	$C_a(t) = \frac{m/(\pi R^2)}{(1 + k)(4\pi at)^{1/2}}\exp\left\{-\frac{\left(L - \frac{u_a}{1 + k}t\right)^2}{4at}\right\}$ $a = \frac{D_{12}}{1 + k} + \frac{1 + 6k + 11k^2}{(1 + k)^3}\frac{R^2u_a^2}{48D_{12}}$ (A5b)
δ	$\delta = [\int_{t_1}^{t_2}\{C_a(t) - C_{a,meas}(t)\}^2 dt/\int_{t_1}^{t_2}\{C_{a,meas}(t)\}^2 dt]^{1/2}$ (A6)	

[a] D_{12}: infinite-dilution binary diffusion coefficient of the tracer species in the fluid. R: column radius. u_a: average fluid velocity. t: time. r and x: radial and axial variables. m: injected amount of tracer species, L: distance between injection point and detection point. k: retention factor defined as the ratio of a solute amount in the polymer stationary phase to that in the supercritical fluid phase. t_1 and t_2 correspond to the times at the frontal and latter 10 % peak heights of $C_{a,meas}(t)$, respectively.

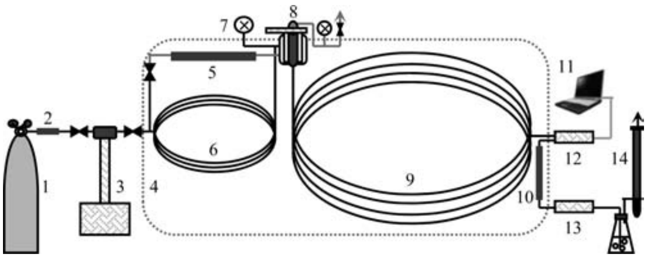

Figure 1. Schematic diagram of the apparatus. (1) CO_2 cylinder; (2) filter; (3) ISCO syringe pump; (4) water bath; (5) sample packed column; (6) preheating column; (7) Heise pressure gauge; (8) injector; (9) diffusion column; (10) packed column; (11) computer; (12) UV−vis multidetector; (13) back pressure regulator; (14) soap bubble flow meter.

Experimental Section

Chemicals. Ferrocene (purity of 98 %) and 1,1′-dimethylferrocene (97 %) were obtained from Aldrich Chemicals. Hexane was HPLC grade (96 %, Wako Pure Chemical Ind., Japan). These reagents were used as received without further purification. CO_2 with purity higher than 99.95 % was purchased from Air Gases Tokai Ltd., Japan.

Equipment and Procedure. A schematic diagram of the experimental apparatus is shown in Figure 1. A poly(ethylene glycol) coated capillary column (UACW-15W-1.0F, the Frontier Laboratories Ltd., Japan, thickness of 1 μm, R = 0.265 mm, L = 16.293 m, and R_{coil} = 0.155 m) and a stainless-steel column (bright annealed 316 stainless-steel, GL Science Inc., Japan, R = 0.416 mm, L = 20.675 m, and R_{coil} = 0.165 m) were used as a diffusion column in the CIR method and the Taylor dispersion method, respectively. A pulse of a solute dissolved in sc CO_2 or in hexane was injected through an injector (model 7520 equipped with a 0.5 μL rotor, Rheodyne, USA) into CO_2 flowing at a constant flow rate, fed by a syringe pump (260D, ISCO, USA) for both the CIR and Taylor dispersion measurements. The temperature of the water bath and the pressure of the system were controlled within 0.01 K and 5 kPa, respectively. After the prescribed temperature, pressure, and flow rate had become stabilized, the system was held under the same condition for at least 2 h prior to a sample injection. Response curves, as time change of the tracer concentration, in terms of absorbance spectra were monitored with a high-pressure multi-UV−vis detector by scanning at wavelengths from (195 to 550) nm with increments of 1 nm and time interval of 1.6 s for each measurement. Only a single pulse of each metal complex dissolved in sc CO_2 or in hexane was loaded for each run.

For determination of D_{12} values, as described in the previous study,[17] the wavelengths of 260 and 450 nm were employed for ferrocene and 1,1′-dimethylferrocene, respectively. The ranges of the measurement conditions were: (1) for the Reynolds number, $20 < Re < 71$; (2) for the Schmidt number, $2 < Sc < 17$; and (3) for a criterion of the secondary flow effect in terms of $DeSc^{1/2}$, mainly $2 < DeSc^{1/2} < 8$, where De is the Dean number.

Results and Discussion

The D_{12} values of ferrocene measured by the CIR method, together with the values of retention factor k, rms fitting relative

Table 2. Measured Values of D_{12} and Retention Factors k for Ferrocene, Together with δ and $DeSc^{1/2}$ by the CIR Method

	T	P	10^2k	10^9D_{12}	100δ	$DeSc^{1/2}$
	K	MPa	-	$m^2 \cdot s^{-1}$	-	-
ferrocene[a]	308.15	8.02	78.57	18.34	0.66	5.35
		8.23	31.42	15.79	0.43	6.49
		8.52	21.69	14.92	0.30	6.24
		8.52	21.81	15.05	0.29	6.09
		8.72	18.74	14.29	0.54	5.63
		11.02	10.34	11.87	0.11	4.53
		15.02	7.758	10.01	0.19	4.92
		17.02	6.550	9.437	0.23	4.75
		20.02	5.837	9.118	0.22	5.15
		22.02	5.735	8.898	0.29	5.13
		25.02	5.298	8.431	0.25	4.11
		30.02	4.701	7.702	0.26	5.23
		30.02	4.677	7.795	0.16	5.33
		35.02	4.184	7.294	0.24	3.67
		40.18	3.896	6.833	0.19	3.41
	313.15	8.02	436.2	29.08	0.73	12.86
		8.52	161.8	23.49	0.89	9.50
		8.72	97.16	20.61	0.61	6.19
		9.02	46.84	18.14	0.56	6.30
		9.22	34.38	17.19	0.24	7.70
		9.22	34.36	17.42	0.28	8.56
		9.22	35.08	17.30	0.60	3.21
		9.22	34.60	16.76	0.20	3.25
		9.51	25.21	16.24	0.37	5.41
		9.52	25.64	15.86	0.29	4.68
		9.52	25.03	16.06	0.34	8.99
		9.52	26.11	15.89	0.30	3.88
		9.52	25.16	15.77	0.27	5.60
		10.02	18.93	14.61	0.11	4.40
		11.02	14.00	13.84	0.44	4.42
		11.02	13.92	13.74	0.38	4.49
		11.02	13.95	13.79	0.23	4.08
		11.02	13.90	13.65	0.35	9.13
		11.02	13.96	13.76	0.37	7.04
		12.02	11.47	12.59	0.47	3.69
		15.02	8.119	11.05	0.39	3.40
		20.02	6.500	10.06	0.16	3.86
		25.03	5.605	9.257	0.22	3.85
		30.03	5.080	8.551	0.24	3.25
		35.08	4.600	8.237	0.20	3.28
		35.08	4.560	8.024	0.29	3.33
		40.06	4.077	7.456	0.17	3.16
	323.15	10.02	94.89	23.13	0.53	7.25
		10.02	95.73	23.50	0.91	7.20
		11.02	36.58	19.23	0.31	5.57
		11.02	35.75	18.82	0.31	5.48
		12.02	20.12	16.60	0.61	6.35
		13.02	15.47	15.37	0.18	4.66
		13.02	15.59	15.45	0.22	4.63
		13.02	15.65	15.82	0.30	4.63
		13.02	15.61	15.69	0.27	4.65
		15.02	10.48	13.69	0.28	5.53
		16.02	8.733	12.70	0.094	3.78
		20.02	6.831	11.57	0.15	4.57
		25.02	5.506	10.21	0.18	3.79
		30.03	4.898	9.484	0.24	3.47
		35.02	4.360	8.798	0.21	5.20
		40.34	3.689	8.250	0.20	4.55

[a] Ferrocene dissolved in sc CO_2 was injected.

Table 3. Measured Values of D_{12} for Ferrocene, Together with δ and $DeSc^{1/2}$ by the Taylor Dispersion Method

	T	P	10^9D_{12}	100δ	$DeSc^{1/2}$
solute	K	MPa	$m^2 \cdot s^{-1}$	-	-
ferrocene[a]	308.15	10.02	12.11	0.22	7.36
		10.52	11.61	0.17	6.86
		11.02	11.45	0.25	6.93
		12.02	10.94	0.11	7.35
		13.02	10.47	0.24	5.79
		16.02	9.844	0.11	7.23
		18.02	9.373	0.056	8.04
		20.02	8.955	0.076	6.22
		25.02	8.322	0.30	7.50
		30.02	7.783	0.072	6.22
		35.02	7.318	0.068	7.50
		40.02	7.084	0.060	6.57
ferrocene[a]	313.15	10.02	14.63	0.45	5.90
		11.02	13.06	0.081	7.12
		11.02	13.28	0.35	5.30
		11.02	13.30	0.14	6.74
		13.02	11.76	0.15	6.22
		16.02	10.80	0.10	6.68
		17.02	10.41	0.48	6.33
		18.02	10.20	0.36	6.34
		20.03	9.801	0.095	7.42
		22.02	9.356	0.29	6.38
		25.03	8.926	0.070	7.47
		30.03	8.375	0.081	6.97
		35.02	7.909	0.11	6.05
		40.02	7.437	0.12	6.06
		40.03	7.408	0.12	6.09
ferrocene[b]	313.15	10.02	14.46	0.34	6.38
		10.52	13.63	0.096	6.19
		12.02	12.42	0.28	6.40
		15.02	11.08	0.23	6.60
		19.02	10.13	0.19	7.64
		22.02	9.532	0.10	7.12
		28.02	8.637	0.19	7.01
		34.02	7.951	0.13	6.63
ferrocene[b]	323.15	20.02	11.25	0.21	7.15
		25.02	10.35	0.17	6.94
		30.02	9.572	0.17	8.50
		35.02	8.821	0.24	6.47
		40.03	8.465	0.20	6.23

[a] Ferrocene dissolved in hexane was injected. [b] Ferrocene dissolved in sc CO_2 was injected.

difference δ, and $DeSc^{1/2}$, are listed in Table 2. Those measured with the Taylor dispersion method by injecting ferrocene dissolved both in hexane and in sc CO_2 are also listed in Table 3. Those of 1,1′-dimethylferrocene measured by the CIR method were presented in Table 4. As has been seen for various organic compounds in our previous reports,[15,17,18] the D_{12} and k values decreased with increasing pressures. In all cases the measurements seemed to be quite accurate because the values of rms fitting relative difference δ were lower than 1 %. Moreover, the effects of the secondary flow due to column coiling were also negligible because mainly $DeSc^{1/2} < 8$. Note that according to the estimation of the effect of the secondary flow due to column coiling as a deviation of the second moment of the response curve by Alizadeh et al.[19] the relative difference was 1 % at $DeSc^{1/2} = 8$. The authors[20] also estimated the deviation and proposed a correction formula both in the Taylor dispersion and in the CIR method. The D_{12} value having the maximum $DeSc^{1/2}$ value of 12.9 with $k = 4.36$ was higher by 3 % than the intrinsic one determined from the estimation.[20] To minimize fluctuation in density, we injected only 0.5 μL volume of a solute into the system for each measurement, as mentioned above. The mole fractions of ferrocene in the diffusion column under our experimental conditions were of the order of 10^{-3} to 10^{-5}. Because the solubilities of ferrocene in sc CO_2 were of the order of 10^{-2} to 10^{-3} mole fraction,[21] the solute studied was considered to be at diluted concentration. In addition, the determined value of each datum in this study was the mean value of several measured values. The standard deviation values of D_{12} and k was within ± 2 %; the reproducibilities were within ± 2.5 %; and both decreased with increasing CO_2 density.

Figure 2 compares the response curves for ferrocene in sc CO_2 measured at 260 nm, 313.15 K, and 10.02 MPa with those

Table 4. Measured Values of D_{12} and Retention Factors k for 1,1′-Dimethylferrocene, Together with δ and $DeSc^{1/2}$ by the CIR Method

	T	P	10^2k	10^9D_{12}	100δ	$DeSc^{1/2}$
	K	MPa	-	$m^2 \cdot s^{-1}$	-	-
1,1′-dimethylferrocene[a]	308.15	8.22	18.02	14.57	0.84	5.35
		8.22	18.77	14.57	1.0	6.18
		8.22	18.52	14.62	0.92	6.35
		8.22	18.78	14.65	0.78	6.36
		8.51	12.61	13.79	0.29	6.78
		8.72	10.36	13.18	0.66	6.66
		9.02	9.006	12.45	0.78	6.12
		9.03	9.066	12.44	0.58	6.21
		9.52	7.787	11.81	0.53	6.33
		10.01	7.091	11.16	0.60	7.26
		10.02	7.106	11.44	0.50	7.12
		10.52	6.363	10.99	0.54	5.82
		10.52	6.207	11.05	0.51	5.53
		11.02	5.368	10.51	0.46	4.52
		12.02	4.861	10.16	0.45	6.21
		13.02	4.667	10.07	0.49	6.03
		15.02	3.953	9.271	0.57	5.09
		20.02	3.122	8.430	0.47	4.79
		25.02	2.757	7.712	0.35	4.81
		25.02	2.672	7.769	0.26	4.78
		40.12	2.059	6.629	0.18	4.71
		40.12	2.020	6.613	0.12	4.69
	313.15	9.71	12.31	14.36	0.20	4.47
		9.72	12.21	14.38	0.88	6.60
		9.72	11.94	13.93	0.72	6.66
		9.82	11.65	14.01	0.87	6.42
		9.82	12.05	14.07	0.97	6.52
		9.82	11.64	13.88	0.50	6.49
		10.01	10.39	13.14	0.77	5.32
		10.02	10.27	13.25	0.82	5.56
		11.02	7.382	12.11	0.68	5.24
		11.02	7.409	12.11	0.73	5.26
		11.02	7.138	11.98	0.67	5.12
		11.02	7.537	12.16	0.86	3.08
		12.02	6.079	10.95	0.79	4.74
		12.02	6.144	11.45	0.47	6.52
		13.02	5.458	10.52	0.75	4.07
		13.02	5.650	11.07	0.38	5.86
		14.02	5.016	10.75	0.70	4.91
		15.02	4.470	10.28	0.48	5.35
		15.02	4.565	10.24	0.51	4.94
		17.02	4.234	9.958	0.43	5.75
		20.02	3.530	9.021	0.43	5.11
		25.02	2.857	8.176	0.37	4.44
		30.02	2.607	7.653	0.23	5.20
		35.02	2.300	7.261	0.19	5.27
		40.02	2.151	7.002	0.19	4.55
	323.15	10.02	61.66	21.27	0.81	7.94
		10.52	33.86	19.54	0.71	6.81
		10.72	27.32	18.45	0.68	6.73
		11.02	20.59	17.04	0.64	6.69
		11.03	20.04	17.24	0.52	3.95
		11.52	15.40	16.45	0.96	7.77
		12.02	12.81	15.51	0.90	5.70
		12.50	10.37	14.57	0.80	5.00
		12.50	10.18	14.38	0.74	4.99
		12.50	10.54	14.34	0.73	5.59
		12.50	10.12	13.91	0.32	5.62
		12.50	10.02	14.10	0.14	5.62
		13.02	8.545	13.85	0.82	4.78
		14.02	7.700	13.05	0.82	6.00
		15.02	5.917	12.49	0.58	6.36
		16.02	5.502	11.76	0.66	5.41
		20.02	4.464	10.65	0.41	4.77
		25.02	3.396	9.498	0.28	6.09
		30.02	2.811	8.640	0.37	5.08
		35.02	2.700	8.055	0.39	5.03
		40.02	2.344	7.854	0.26	3.67

[a] 1,1′-Dimethylferrocene dissolved in sc CO_2 was injected.

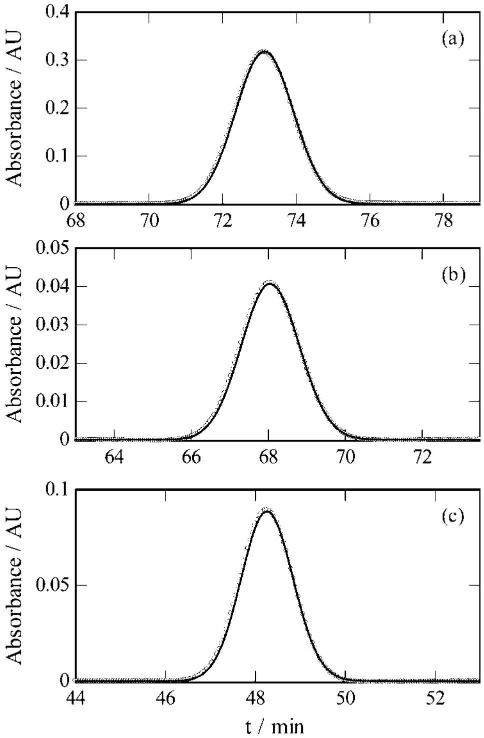

Figure 2. Comparison of response curves for ferrocene in supercritical CO_2 measured (○) at 260 nm, 313.15 K and 10.02 MPa with those predicated (—) by (a) the Taylor dispersion method with ferrocene dissolved in hexane before injection, (b) the Taylor dispersion method with ferrocene dissolved in CO_2 before injection, and (c) the CIR method with ferrocene dissolved in CO_2 before injection.

predicted by (a) the Taylor dispersion method with ferrocene dissolved in hexane (19 $mg \cdot cm^{-3}$) prior to an injection, (b) the Taylor dispersion method with ferrocene dissolved in CO_2 prior to an injection, and (c) the CIR method with ferrocene dissolved in CO_2 prior to an injection. The mole fraction at the top of the response curve was $1.2 \cdot 10^{-5}$ in the case of ferrocene dissolved in hexane in Figure 2(a) and corresponded to the value of $u_a \cdot$(peak area) which was $1.8 \cdot 10^{-1}$ AU·m. The mole fraction was far lower than the order of solubility of ferrocene.[21] The values of $u_a \cdot$(peak area) in the case of ferrocene dissolved in sc CO_2 in Figures 2(b) and 2(c) were ($2.3 \cdot 10^{-2}$ and $5.1 \cdot 10^{-2}$) AU·m, respectively, which were obviously smaller than that in Figure 2(a). Consequently, the measured D_{12} values in all cases were considered to be at infinite dilute conditions.

The values of D_{12} and δ obtained from above the three cases were (a) $1.463 \cdot 10^{-8}$ $m^2 \cdot s^{-1}$ and 0.0045, (b) $1.446 \cdot 10^{-8}$ $m^2 \cdot s^{-1}$ and 0.0034, and (c) $1.461 \cdot 10^{-8}$ $m^2 \cdot s^{-1}$ and 0.0011, respectively. The diffusion coefficients were almost consistent in the three cases. As presented in Figure 2, all the measured curves showed the Gaussian like ones and were well represented by the predicted curves with $\delta < 0.01$ for all cases. Note that in comparison with the D_{12} values of vitamin K_3 measured by the CIR method and the Taylor dispersion method in the near critical region of carbon dioxide the D_{12} values by the Taylor dispersion method were found to be much less accurate than those in the CIR method.[22] In the present study, however, the pressure range for the D_{12} data in the Taylor dispersion was higher than 10 MPa, far from the critical region, and the D_{12} values measured by both methods were consistent.

The hydrodynamic equation shown in eq 1 was found to be effective for ferrocene at the three measurement conditions mentioned above, and 1,1′-dimethylferrocene measured in the CIR method (not shown in figure), as has been seen for various organic compounds.[15,17,18,23]

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

where T is the temperature; η is the CO_2 viscosity; and α and β are the constants, which were determined for each solute−solvent system. Figure 3 plots D_{12}/T vs CO_2 viscosity for ferrocene measured with the CIR method by injecting ferrocene dissolved in sc CO_2 and with the Taylor dispersion by injecting ferrocene dissolved both in liquid hexane and in sc CO_2, together with deviation between $D_{12,\mathrm{meas}}$ and $D_{12,\mathrm{crrl}}$ values. In the use of a hexane solution, the system was not binary but ternary (even hexane was not detected with a UV−vis absorption detector), and hexane and ferrocene were hardly separated in the Taylor dispersion. However, in the Taylor dispersion method the D_{12} values by injecting ferrocene dissolved in sc CO_2 were fully consistent with those by injecting ferrocene dissolved in liquid hexane. Moreover, the D_{12} values with the CIR method also agreed with those in the Taylor dispersion method by injecting both the sc CO_2 and hexane solution. The D_{12} data were represented well by the hydrodynamic equation, but the data deviated slightly near critical region, as depicted in Figure 3(b). The determined values for both solutes were listed in Table 5, together with AAD and the number of data points N. As seen for other organic compounds in sc CO_2, the values of β were not equal to minus unity, which is the case for the Stokes−Einstein equation.

The retention factors k for ferrocene and 1,1′-dimethylferrocene were plotted against CO_2 density in Figure 4. The k values were nearly represented by a function of CO_2 density in eq 2, similar to those for various organic compounds.[12,17]

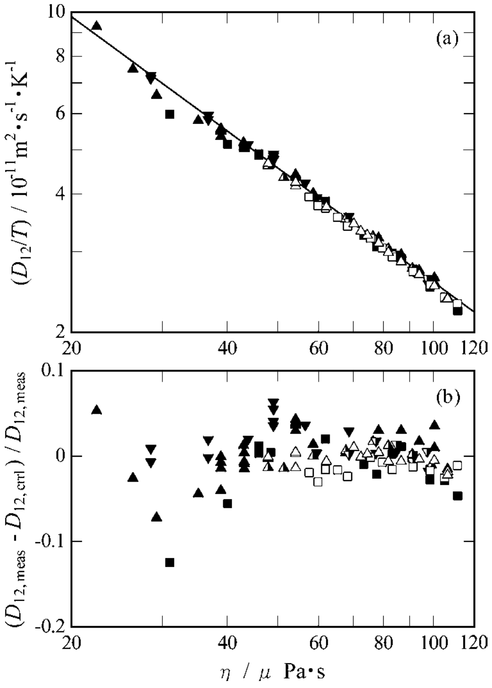

Figure 3. Plots of (a) D_{12}/T and (b) deviation between $D_{12,\mathrm{meas}}$ and $D_{12,\mathrm{crrl}}$ values vs CO_2 viscosity η for ferrocene measured by the CIR method and the Taylor dispersion method. CIR method by injecting ferrocene dissolved in sc CO_2: ■, 308.15 K; ▲;, 313.15 K;▼, 323.15 K. The Taylor dispersion: □, 308.15 K; and Δ, 313.15 K by injecting ferrocene dissolved in hexane; ▲, 313.15 K; and ▼, 323.15 K by injecting ferrocene dissolved in sc CO_2. The solid line in (a) was obtained with the values of the parameters α and β listed in Table 5.

$$\ln(k) = \sum_{i=0}^{n} b_i\{\ln(\rho/\mathrm{kg}\cdot\mathrm{m}^{-3})\}^i \tag{2}$$

where ρ is the CO_2 density and b_i is the constant. The determined b_i values for ferrocene and 1,1′-dimethylferrocene are listed in Table 6. In this case the slopes were almost the same at the three temperatures, but the intercepts were affected by temperature. Note that the accuracy was slightly improved when $n = 2$ rather than $n = 1$ in eq 2.

Conclusions

Infinite dilution binary diffusion coefficients of ferrocene and 1,1′-dimethylferrocene in sc CO_2 were measured by the CIR method at temperatures from (308.15 to 323.15) K and pressures from (8.0 to 40.3) MPa for ferrocene and from (8.2 to 40.1) MPa for 1,1′-dimethylferrocene. The D_{12} values of ferrocene were also measured with the Taylor dispersion method by injecting ferrocene dissolved in hexane and in sc CO_2. The D_{12} values of ferrocene by the two injection methods in the Taylor dispersion were consistent and agreed with those in the CIR method. This resulted in almost no effect of the presence of hexane as the third component on the D_{12} values in the Taylor dispersion method. The values of root-mean-square fitting

Table 5. Determined α and β for Ferrocene and 1,1′-Dimethylferrocene in Equation 1[a]

	α	β	100·AAD[b]	N[c]	
			1.88	98	for all data
ferrocene	$1.243\cdot10^{-14}$	−0.8279	2.41	58	by the CIR method
			1.07	40	by the Taylor dispersion method
1,1′-dimethylferrocene	$1.286\cdot10^{-14}$	−0.8158	1.56	68	by the CIR method

[a] Constants α and β were determined when units of D_{12} and CO_2 viscosity η were in $\mathrm{m}^2\cdot\mathrm{s}^{-1}$ and Pa·s, respectively. [b] AAD = $(1/N)\sum_{i=1}^{N}|1 - (D_{12,\mathrm{corr}})/(D_{12,\mathrm{meas}})|$. [c] Number of data points.

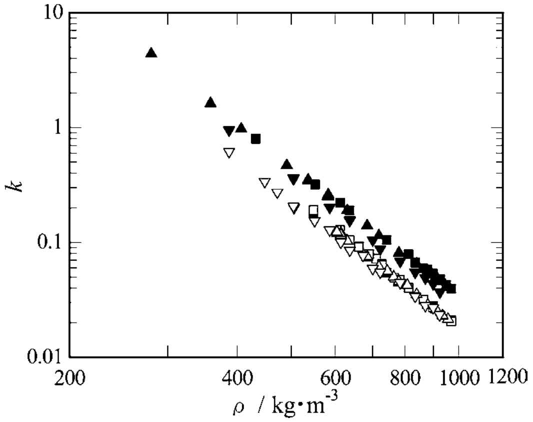

Figure 4. k vs CO_2 density ρ for ferrocene and 1,1′-dimethylferrocene measured at ■, □, 308.15 K; ▲, Δ, 313.15 K; and ▼, ∇, 323.15 K by the CIR method. The solid and open keys designate ferrocene and 1,1′-dimethylferrocene, respectively.

Table 6. Determined b_i Values in Equation 2

	T	b_0	b_1	100 AAD	N[a]
ferrocene	308.15	22.306946	−3.713313	1.56	15
	313.15	22.488981	−3.745424	2.30	27
	323.15	22.053137	−3.708058	2.58	16
1,1′-dimethylferrocene	308.15	22.990336	−3.908791	2.09	22
	313.15	22.210642	−3.797727	1.95	25
	323.15	21.373705	−3.682419	3.38	21

[a] N: number of data points.

relative difference between the measured curve and the calculated curve for all measurements were lower than 1 %. The hydrodynamic equation well represented D_{12} values of ferrocene and 1,1′-dimethylferrocene measured in this study, and the constants involved in the equation were determined for each compound. In the CIR method the retention factors k were also determined, and those values were correlated with CO_2 density.

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