Measurements of Binary Diffusion Coefficients for Ferrocenes in Supercritical Carbon Dioxide

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ABSTRACT

The binary diffusion coefficients of ferrocene and 1,1'-dimethylferrocene at infinite dilution in supercritical carbon dioxide, D_{12}, were measured by the chromatographic impulse response (CIR) method at temperatures from 308.2 to 323.2 K and pressures from 9 to 40 MPa. The D_{12} data for ferrocene were also measured by the Taylor dispersion method. The diffusion data of ferrocene measured by the Taylor disperion method were consistent with those measured by the CIR method. In addition, it was found that all the measured D_{12} data were well represented by the correlation of $(D_{12}/T)M^{0.5}$ as a function of carbon dioxide viscosity.

INTRODUCTION

The organometallic compounds such as ferrocene and its derivatives have been investigated for a variety of applications in organic synthesis and biological systems, etc, due to the unique properties such as electrochemical and photoinduced electron transfer properties [1]. Recently, the behavior of organometallic compounds in supercritical carbon dioxide has become focus of attention due to the compounds not only having relatively high solubility in supercritical 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 of the organometallic compounds in supercritical carbon dioxide are essential for process design. So far, considerable experimental data have been reported regarding the diffusion coefficients of organic compounds in supercritical carbon dioxide [3,4]. Unfortunately, the diffusion data for organometallic compounds in supercritical carbon dioxide have not been reported except for copper(II) trifluoroacetylacetonate [5], at the limited conditions, which were measured by the Taylor dispersion method [6]. On the other hand, the authors [7] have demonstrated that the diffusion coefficients measured by the CIR method are more reliable than those by the Taylor dispersion method, especially in the near critical region.

The application of supercritical fluids is usually carried out at higher pressures in order to achieve higher solvent power. Thus, the objectives of this study are (1) to measure the diffusion coefficients of ferrocene and its dirrevative in supercritical carbon dioxide at pressures up to 40 MPa, and (2) to examine the effectiveness of the Taylor dispersion method for measuring the diffusion coefficients in the system of carbon dioxide and ferrocenes.

THEORY

The detail theories for the Taylor dispersion and the CIR methods have been described by Alizadeh et al. [6] and in our previous study [8], respectively. When a tracer is pulse-injected into a fully developed laminar flow in a cylindrical diffusion column, the continuity equation in terms of the tracer concentration $c(r, x, t)$ together with the initial and boundary conditions are given as Eqs (1), (2a), (2b), (3a) and (3b) in Table 1. Approximate solutions $C_a(t)$ for the cross-sectional average concentration of the tracer at diffudion column exit are given by Eqs (4a) and (4b). The validity of both measurements can be evaluated in terms of root-mean-square (r-m-s) error ε between measured curve $C_{a,meas}(t)$ and calculated curve $C_a(t)$ using Eq. (5). The curve fitting is considered good when $\varepsilon < 1\%$, and acceptable when $\varepsilon < 2 \sim 3\%$ [8].

Table 1. Fundamental equations of the Taylor dispersion and the CIR methods

	Taylor dispersion method	CIR method
$c(r, x, t)$	$$\frac{\partial c}{\partial t} = D_{12}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial x^2}\right) - 2u_a\left(1 - \left(\frac{r}{R}\right)^2\right)\frac{\partial c}{\partial x} \qquad (1)$$ $$c = 0 \qquad \text{at} \qquad x = \pm\infty$$	
Initial condition	$c = \dfrac{m}{\pi R^2}\delta(x) \qquad \text{at } t = 0 \qquad (2a)$	$c = \dfrac{m}{\pi R^2}\dfrac{\delta(x)}{1+k} \qquad \text{at } t = 0 \qquad (2b)$
Boundary condition	$\dfrac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \text{ and } R \qquad (3a)$	$\dfrac{\partial c}{\partial r} = 0 \qquad \text{at } r = 0$ $k\dfrac{\partial c}{\partial t} = -\dfrac{2D_{12}}{R}\dfrac{\partial c}{\partial r} \qquad \text{at } r = R \qquad (3b)$
$C_a(t)$	$C_a(t) = \dfrac{m/(\pi R^2)}{(4\pi a t)^{1/2}}\exp\left\{-\dfrac{(L - u_a t)^2}{4at}\right\} \qquad (4a)$ $a = D_{12} + \dfrac{R^2 u_a^2}{48 D_{12}}$	$C_a(t) = \dfrac{m/(\pi R^2)}{(1+k)(4\pi a t)^{1/2}}\exp\left\{-\dfrac{\left(L - \dfrac{u_a}{1+k}t\right)^2}{4at}\right\} \qquad (4b)$ $a = \dfrac{D_{12}}{1+k} + \dfrac{1 + 6k + 11k^2}{(1+k)^3}\dfrac{R^2 u_a^2}{48 D_{12}}$
ε	$\varepsilon = \left[\displaystyle\int_{t_1}^{t_2}\{C_a(t) - C_{a,meas}(t)\}^2 dt \middle/ \displaystyle\int_{t_1}^{t_2}\{C_{a,meas}(t)\}^2 dt\right]^{1/2} \qquad (5)$	

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, and k : retention factor defined as the ratio of a solute amount in the polymer phase to that in the 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.

EXPERIMENTAL

Chemicals

Ferrocene (purity of 98%) and 1,1'-dimethylferrocene (97%) were obtained from Aldrich Chemicals. CO_2 with purity higher than 99.95% was purchased from Ltd. Air Gases Tokai, Japan

Equipment and procedure

A schematic 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 colmun (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 solute dissolved in supercritical 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 at least more 2 hours 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 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 single pulse was loaded for each run.

For determination of D_{12} values, as described in the previous study [8], the wavelengths of 260 nm 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 the Dean number, $2 < DeSc^{1/2} < 8$.
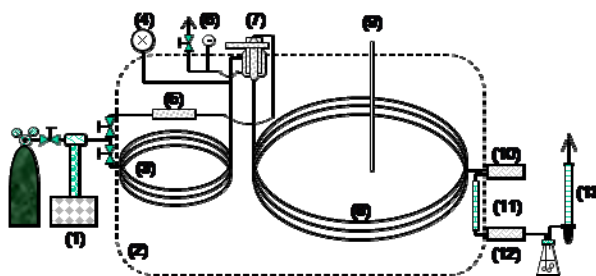

Figure 1. Schematic diagram of the apparatus
(1) ISCO syringe pump; (2) water bath; (3) preheating column; (4) Heise pressure gauge; (5) sample packed column; (6) pressure gauge; (7) injector; (8) diffusion column; (9) thermometer ; (10) UV-Vis multi-detector; (11) packed column; (12) back pressure regulator; (13) soap bubble flow meter.

RESULTS

Figure 2 compares the response curves for ferrocene in supercritical CO_2 measured at 260 nm, 313.15 K and 10.00 MPa with those predicted by (a) the Taylor dispersion method with ferrocene predissolved in hexane prior to an injection, (b) the Taylor dispersion method with ferrocene predissolved in CO_2 prior to an injection, and (c) the CIR method with ferrocene predissolved in CO_2 prior to an injection. The values of D_{12} and ε obtained from above the three cases were (a) 1.422×10^{-8} m^2/s and 0.1%, (b) 1.425×10^{-8} m^2/s and 0.2%, and (c) 1.447×10^{-8} m^2/s and 0.2%, 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 $\varepsilon < 1\%$ for all cases.

The effect of pressure P for ferrocene in supercritical CO_2 at 313.15 K and 9.7 - 40.04 MPa on the values of (a) D_{12} and (b) ε obtained from the three cases are shown in Figure 3. In the whole range of pressure, the values of ε were less than 1% for each case, and all D_{12} data decreased gradually with increasing pressure. Moreover, no difference in the D_{12} values obtained from the three cases was seen under the studied conditions, which were

far from the ciritical point. Note that the authors [7] have demonstrated that the D_{12} values determined by the CIR method are more reliable in the near critical region.
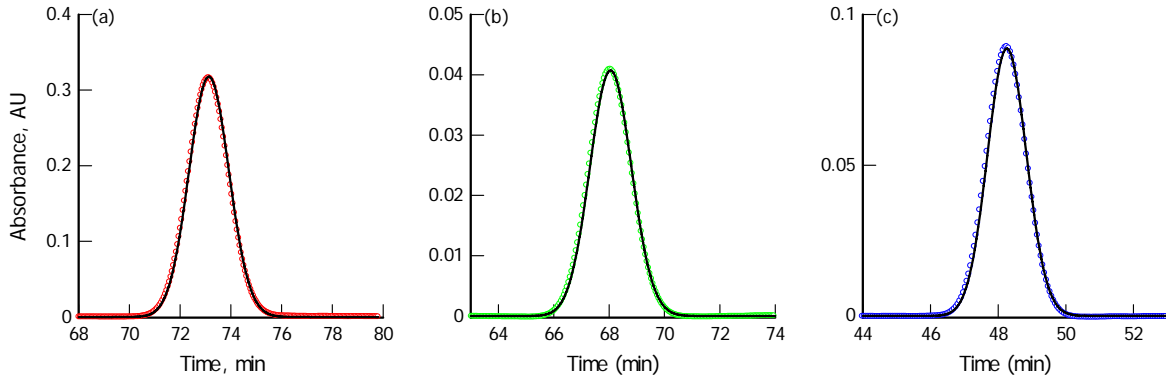

Figure 2. Comparison of response curves for ferrocene in supercritical CO_2 measured (○) at 260 nm, 313.15 K and 10.00 MPa with those predicated (—) by (a) the Taylor dispersion method with ferrocene predissolved in hexane before injected, (b) the Taylor dispersion method with ferrocene predissolved in CO_2 before injected, and (c) the CIR method with ferrocene predissolved in CO_2 before injected.
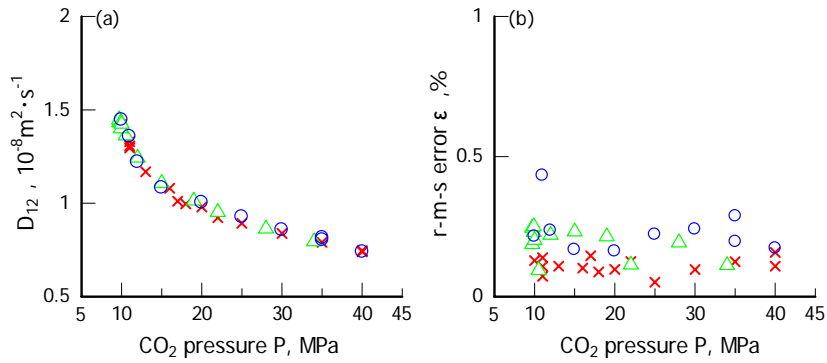

Figure 3. Comparison of (a) D_{12} and (b) ε vs. CO_2 pressure P for ferrocene in supercritical CO_2 at 313.15 K measured by the Taylor dispersion method with ferrocene predissolved in hexane before injected (cross), the Taylor dispersion method with ferrocene predissolved in CO_2 before injected (triangle), and the CIR method with ferrocene predissolved in CO_2 before injected (circle).

Figure 4 shows the CO_2 density dependence of D_{12} for ferrocene and 1,1'-dimethylferrocene at (a) 308.15 K and 8.70 - 40.16 MPa, (b) 313.15 K and 9.70 - 40.04 MPa, and (c) 323.15 K and 13.00 - 40.32 MPa in supercritical CO_2. In this study, all D_{12} data for ferrocene in supercritical CO_2 were measured both by the the CIR method with ferrocene predissolved in CO_2 before injected and by the Taylor dispersion method with ferrocene predissolved in hexane and in CO_2 before injected, respectively. On the other hand, 1,1'-dimethylferrocene was mesured only by the CIR method with 1,1'-dimethylferrocene predissolved in CO_2 prior to an injection. As seen in Figure 4, the D_{12} values decreased gradually as density increasing for both ferrocenes at each temperature, and well correlated to CO_2 density in the limited region studied. It was also observed that the D_{12} data of ferrocene having smaller molecular weight (M=186.0) were higher than those of 1,1'-dimethylferrocene having slightly larger molecular weight (M=214.1) at all temperatures.

Figure 5 denotes the plot of $(D_{12}/T)M^{0.5}$ vs. CO_2 viscosity for all measured D_{12} data of ferrocene and 1,1'-dimethylferrocene in this study, together with the curve fitting error

values ε. All ε values were smaller than 1%. This indicates that the measured response curves were well reproduced by the calculated response curves, and all D_{12} data for ferrocene and 1,1'-dimethylferrocene in supercritical CO_2 were accurately measured by the methods. It is known that D_{12}/T can be correlated with CO_2 viscosity [9,10]. As shown in Figure 5(a), the present data were also predicted by the correlation $(D_{12}/T)M^{0.5}$ as a function of CO_2 viscosity. On the other hand, it was observed that the D_{12} data slightly deviated from a dashed line with the slope = -1, corresponding to the Stokes-Einstein relationship.
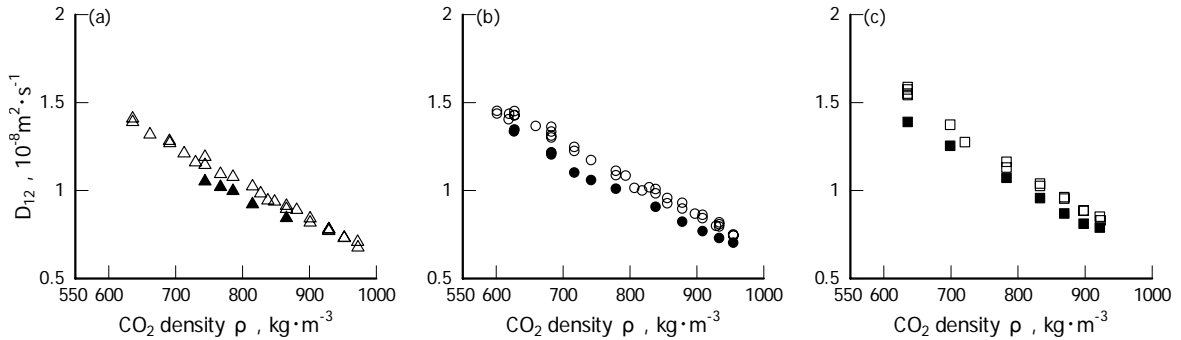

Figure 4. Comparison of D_{12} vs. CO_2 density ρ at (a) 308.15 K and 8.70 - 40.16 MPa (triangle), (b) 313.15 K and 9.70 - 40.04 MPa (circle), and (c) 323.15 K and 13.00 - 40.32 MPa (square) for ferrocene (blank key) and 1,1'-dimethylferrocene (solid key) in supercritical CO_2.
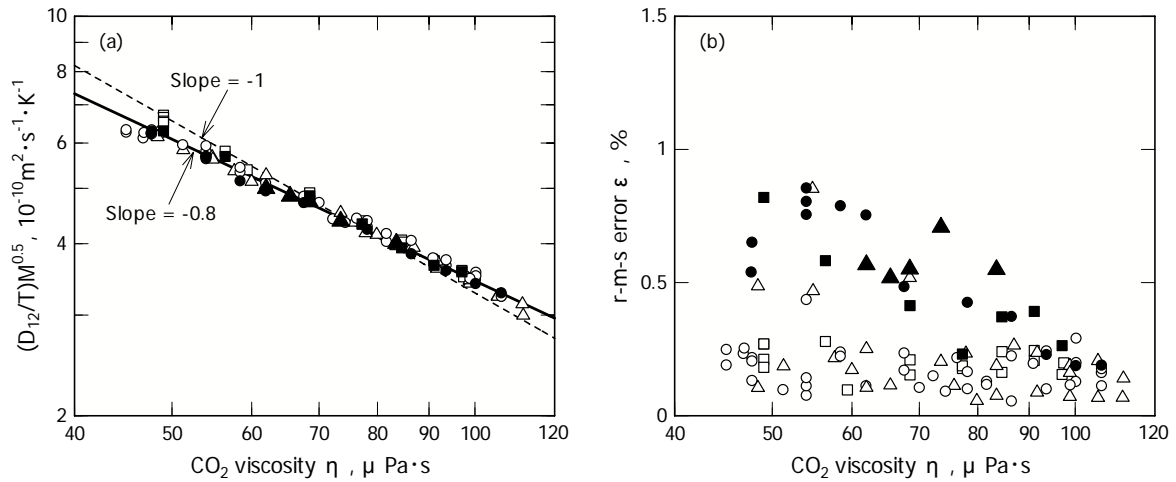

Figure 5. Plots of (a) $(D_{12}/T)M^{0.5}$ and (b) ε vs. CO_2 viscosity η for all measured D_{12} data of ferrocene and 1,1'-dimethylferrocene in this study (the key is the same as in Figure 4).

CONCLUSION

Infinite dilution binary diffusion coefficients of ferrocene and 1,1'-dimethylferrocene in supercritical carbon dioxide were measured at temperatures from 308.15 to 323.15 K and pressures from 8.70 to 40.32 MPa by the CIR method. Some D_{12} data for ferrocene were also measured by the Taylor dispersion method. The values of root-mean-square fitting error for all measurements were lower than 1%. It was found that the Taylor dispersion mehtod was applicable for measuring the diffusion data for ferrocene in supercritical carbon dioxide under the conditions away from the critical point. Furthermore, all the measured D_{12} data were well represented by the correlation of $(D_{12}/T)M^{0.5}$ as a function of carbon dioxide viscosity.

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