# CHANG YI KONG

EDITOR

# RESEARCH INTEREST

- Thermodynamic property in fluid.
- Supercritical Fluid.
- Carbon Nanomaterials.

# BIOGRAPHY

- C. Y. Kong is associate professor in the Department of Applied Chemistry and Biochemical Engineering at Shizuoka University, Japan. He received his Ph.D in chemical engineering in 2001 from Graduate School of Engineering at Yokohama National University, Japan. And then he joined the Graduate School of Environment and Information Science at Yokohama National University. In 2008 moved to the Department of Applied Chemistry and Biochemical Engineering at Shizuoka University. His current research interests focus on synthesis of carbon nanomaterials (such as graphene and nanocomposite etc.) with environmentally-friendly chemical processes and measurements of thermodynamic properties in the fluids from liquid state to supercritical state.

# Measurements of Binary Diffusion Coefficients and Partial Molar Volumes of Polar Compounds at Infinite Dilution in Supercritical Carbon Dioxide by Chromatographic Impulse Response (CIR) Method

**Diffusion & partial molar volume desired**

- ❖ in near-critical region
- ❖ in high pressure region ( $P > 50$ MPa )
- ❖ for high molecular weight compounds ($M > 1000$)
- ❖ for polar compounds

# DIFFUSION

- A flow of fluid always diffuses from one with higher concentration to lower one.
- It is hoped that the process is progressed effectively by reasonably employing the flow in a chemical reactor.
- Then, it is important to understand diffusion (mass transfer) in the reactor design and operation with the demand performance.

$$J = \frac{D}{\delta} \cdot A \cdot \Delta c$$

$J$ [mol·s$^{-1}$] : mass transfer rate
$D$ [m$^2$/s] : diffusion
δ[m]: thickness
A: area
Δc: deviation in concentration

# VARIOUS METHODS OF MEASURING DIFFUSION COEFFICIENTS

- Capillary Evaporation
- Impulse Response Method
- Dynamic Light Scattering
- NMR
- Solid Dissolution
- Steady State Diffusion

Measurements of infinite dilution binary diffusion coefficients in SC CO2: > 100 papers (1964~)

| | | |
|---|---|---|
| Non- or weakly polar compounds | M < 400 | 8 < P < 30 MPa<br>308 < T < 333 K |

# IMPULSE RESPONSE METHODS

Relatively accurate and less time consuming

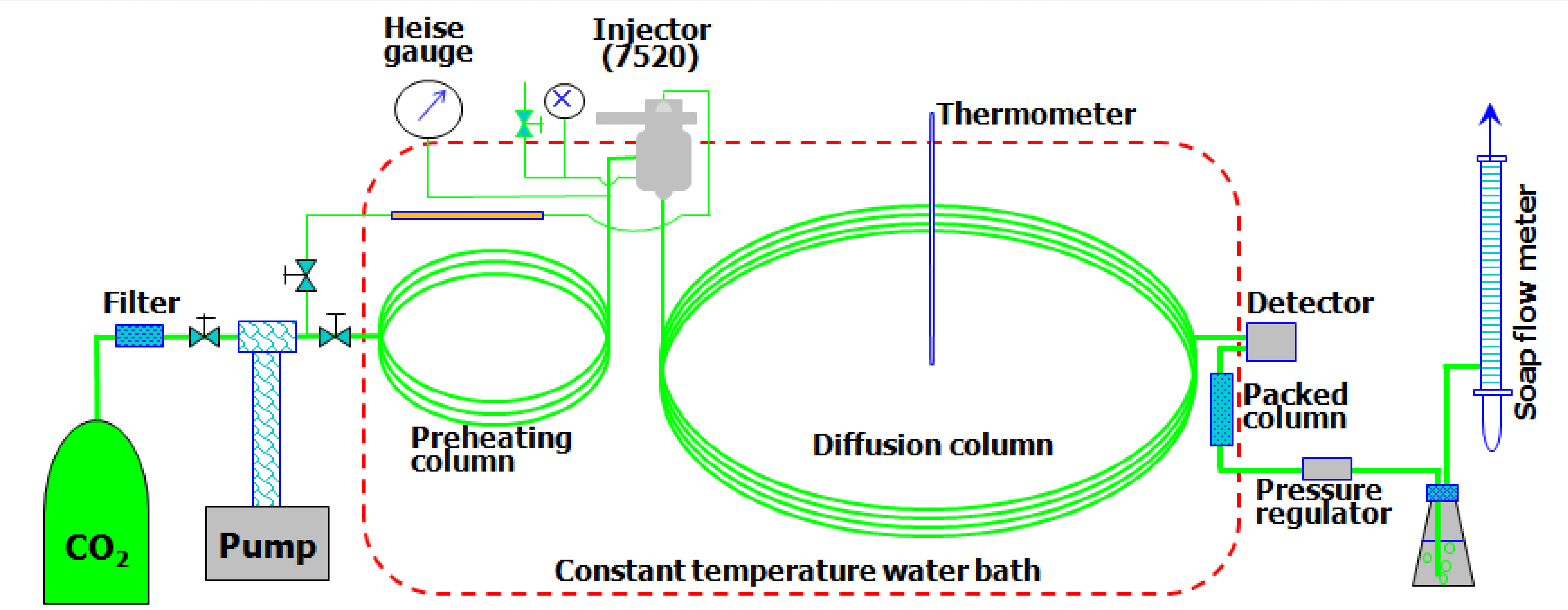

In a typical experiment using the technique a small amount of solute is pulse-injected into the fully developed laminar solvent flowing in a cylindrical diffusion column, and the concentration at the end of the diffusion column can be obtained. The variance of the concentration profile (response curve) is used to determine diffusion coefficients.

Coated and uncoated columns were often used as diffusion column in the chromatographic impulse response (CIR) method and the Taylor dispersion (TD) method, respectively.

# IMPULSE RESPONSE METHODS

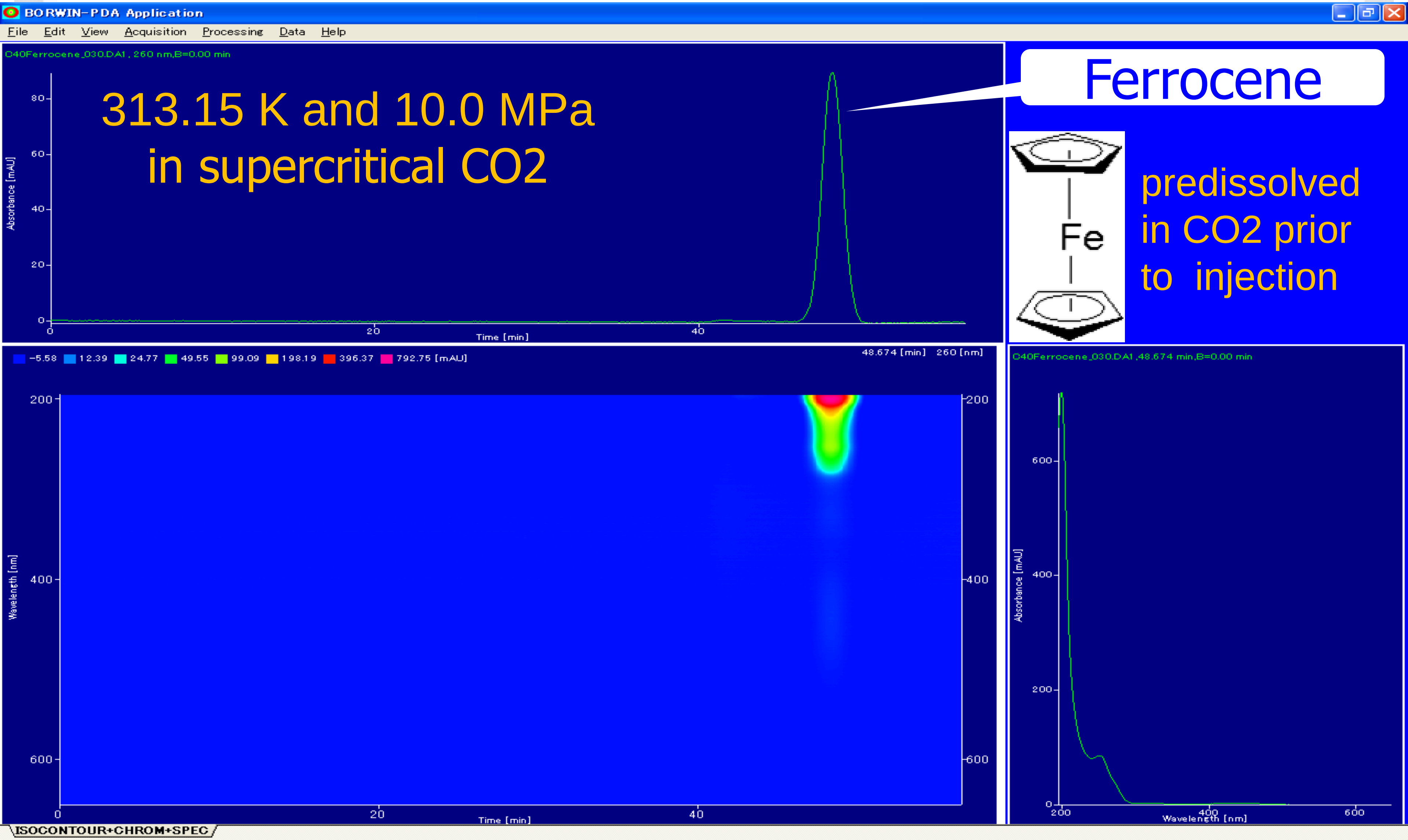
| Method | TD | CIR |
|---|---|---|
| $c(r, x, t)$ | $\frac{\partial c}{\partial t} = D_{12}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial x^2}\right) - 2u_a\left(1 - \left(\frac{r}{R}\right)^2\right)\frac{\partial c}{\partial x}$ <br> $\frac{\partial c}{\partial r} = \text{finite}$ at $r = 0$ <br> $c = 0$ at $x = \pm\infty$ | |
| $t = 0$ | $c = \frac{m}{\pi R^2}\delta(x)$ | $c = \frac{m}{\pi R^2}\frac{\delta(x)}{1+k}$ |
| $r = R$ | $\frac{\partial c}{\partial r} = 0$ | $k\frac{\partial c}{\partial t} = -\frac{2D_{12}}{R}\frac{\partial c}{\partial r}$ |
| $C_a(t)$ | $C_a(t) = \frac{m/(\pi R^2)}{(4\pi a t)^{1/2}}\exp\left(-\frac{(L - u_a t)^2}{4at}\right)$ <br> $a = D_{12} + \frac{R^2 u_a^2}{48 D_{12}}$ | $C_a(t) = \frac{1}{1+k}\frac{m/(\pi R^2)}{(4\pi a t)^{1/2}}\exp\left(-\frac{(L - \frac{u_a}{1+k}t)^2}{4at}\right)$ <br> $a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{(1+k)^3}\frac{R^2 u_a^2}{48 D_{12}}$ |

# EXPERIMENTAL APPARATUS




After the system temperature, pressure and flow rate had become stabilized, the flow system was held under the same condition at least more 2 hours. And then, after the equilibrium was completely established, the measurements could be started. Only single pulse of the tracer species was injected into the diffusion column each run.

# MEASURED RESPONSE CURVES



# WAVELENGTH DEPENDENCY

The wavelengths of 260 and 450 nm were employed for ferrocene and 1,1'-dimethylferrocene in this study, respectively.

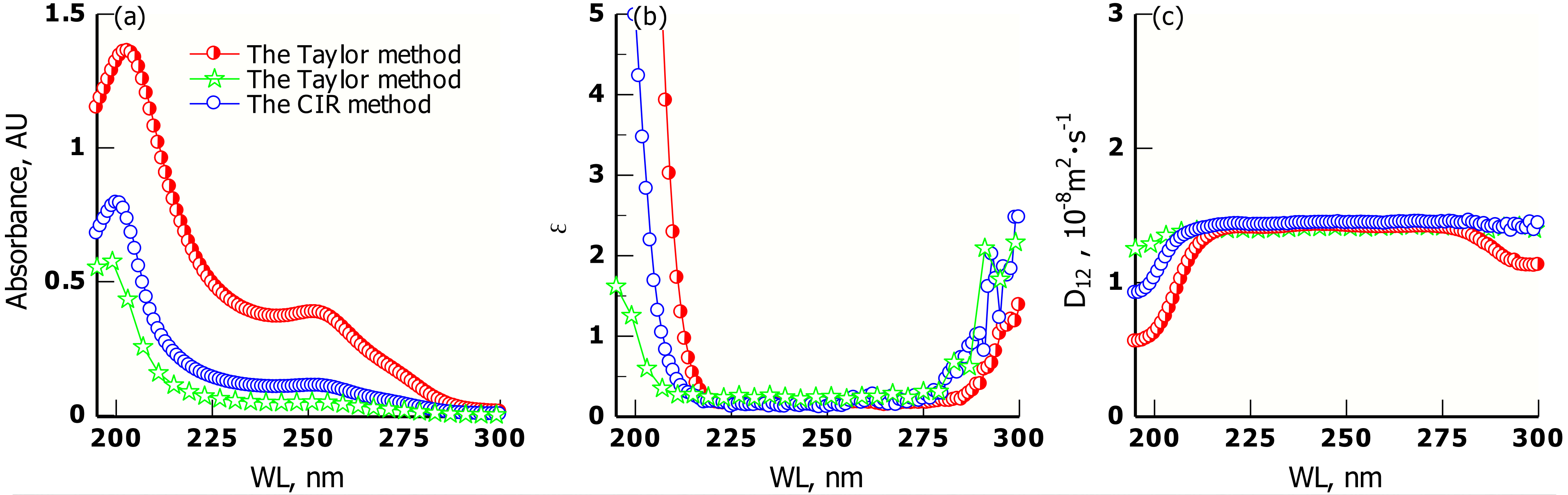
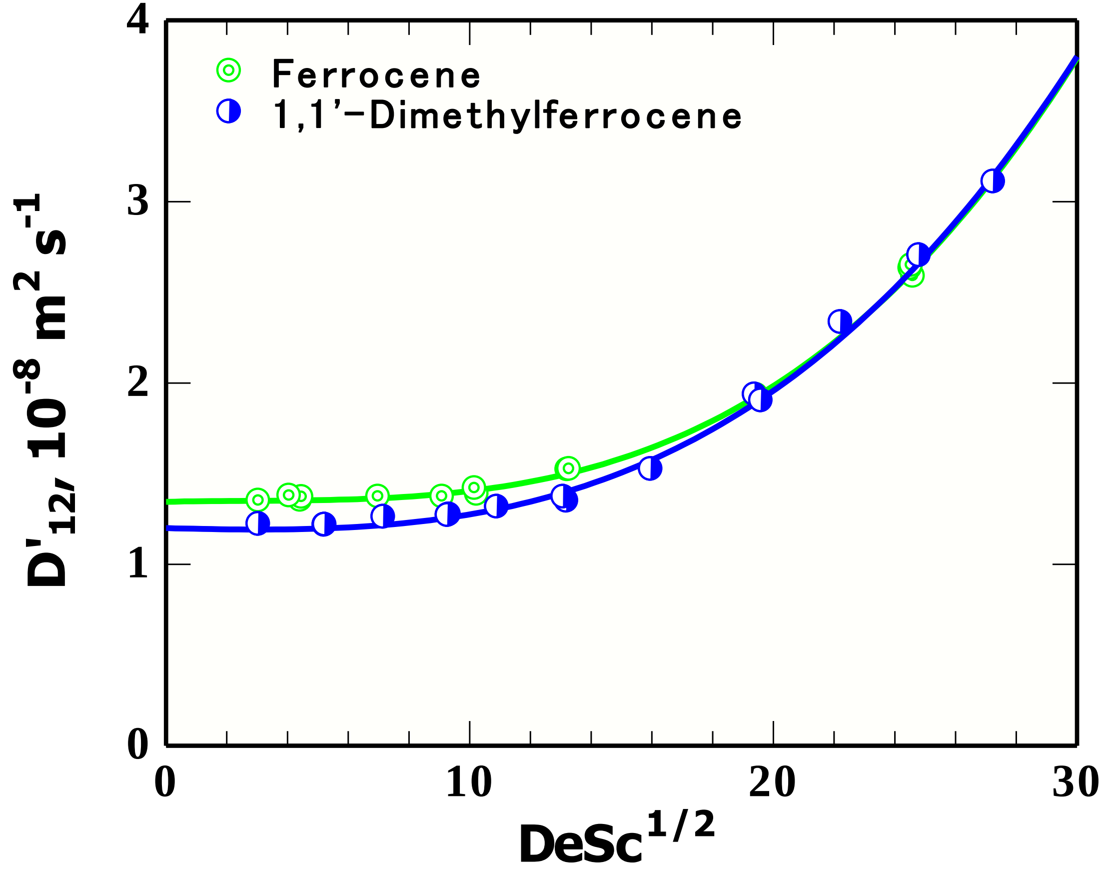



Figure Effects of wavelength on (a) peak absorbance, (b) ε, and (c) $D_{12}$ for ferrocene in SC $CO_2$ at 313.15 K and 10.0 MPa by the TD method with ferrocene predissolved in hexane before injected, the TD method with ferrocene predissolved in $CO_2$ before injected, and the CIR method with ferrocene predissolved in $CO_2$ prior to an injection.

# EFFECT OF THE SECONDARY FLOW




$$De = \frac{2Ru_a\rho\sqrt{R/R_{coil}}}{\eta}$$

$$Sc = \frac{\eta}{\rho D_{12}}$$

Figure Effect of the secondary flow on $D'_{12}$ for ferrocene and 1,1'-dimethylferrocene in SC $CO_2$ at 313.15 K and 11.0 MPa by the CIR method with ferrocene and 1,1'-dimethylferrocene predissolved in $CO_2$ prior to an injection, respectively.

# EFFECT OF THE INJECTED AMOUNT

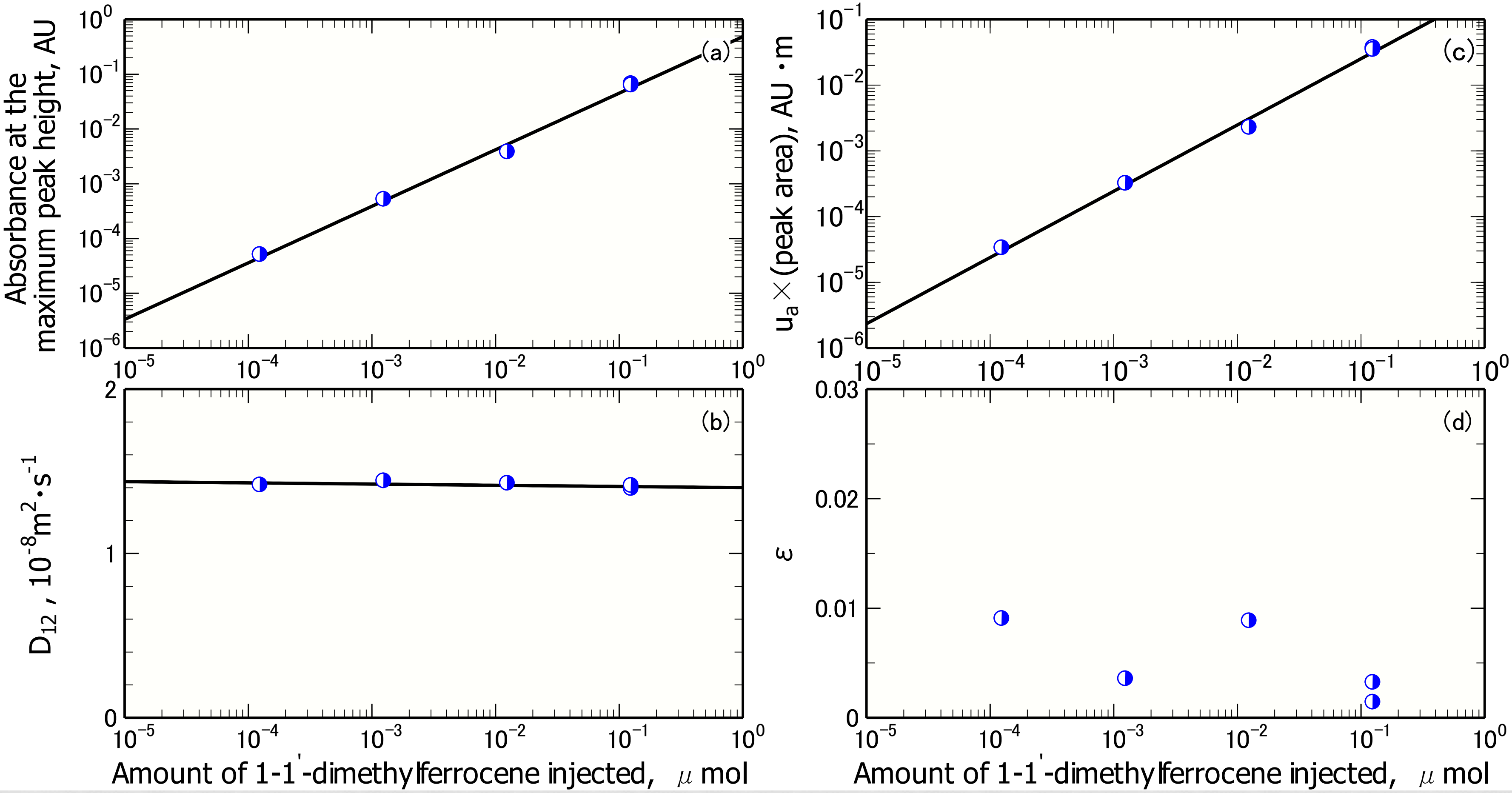



Figure The effects of the amount of injected 1,1-dimethylferrocene on (a) absorbance at the maxium peak height, (b) $D_{12}$, (c) $u_a \times$ (peak area), and (d) ε at various injected amounts of 1,1-dimethylferrocene dissolved in hexane at 323.15 K and 12.5 MPa by the CIR method.

# COMPARISON BETWEEN THE TD AND CIR METHODS

(a) the TD method with ferrocene predissolved in hexane

(b) the TD method with ferrocene predissolved in $CO_2$

(c) the CIR method with ferrocene predissolved in $CO_2$

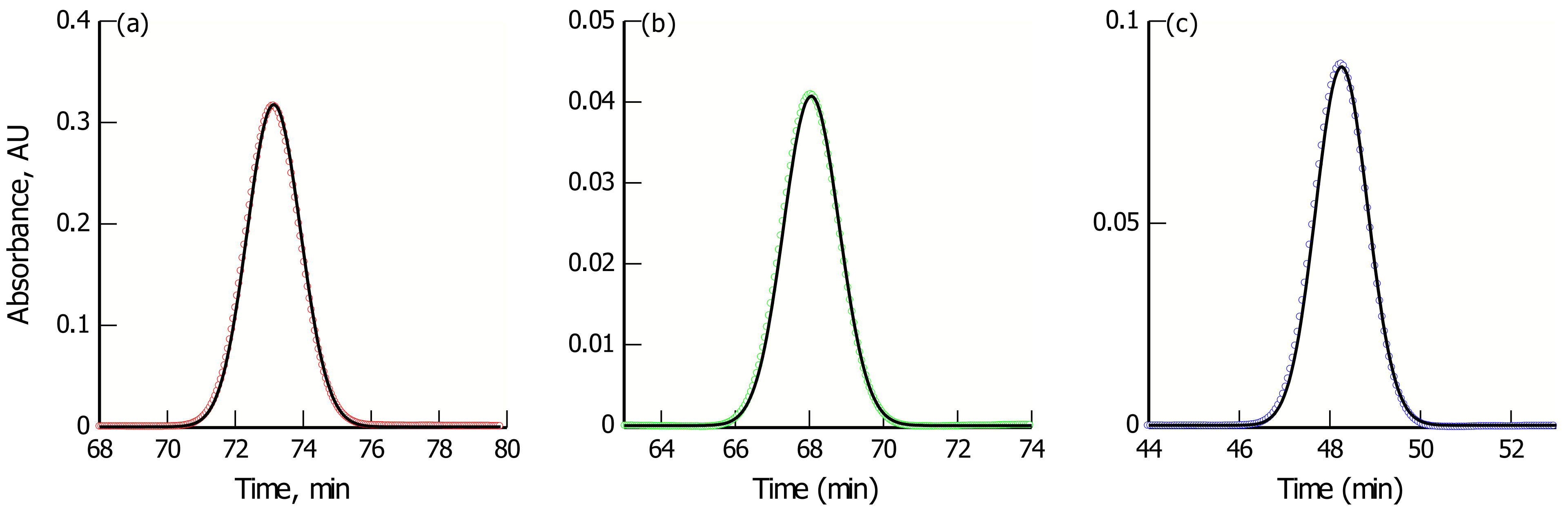



Figure Comparison of response curves for ferrocene in SC $CO_2$ measured (O) at 313.15 K, 10.0 MPa, and 260 nm with those predicted (—) .

# COMPARISON BETWEEN THE TD AND CIR METHODS

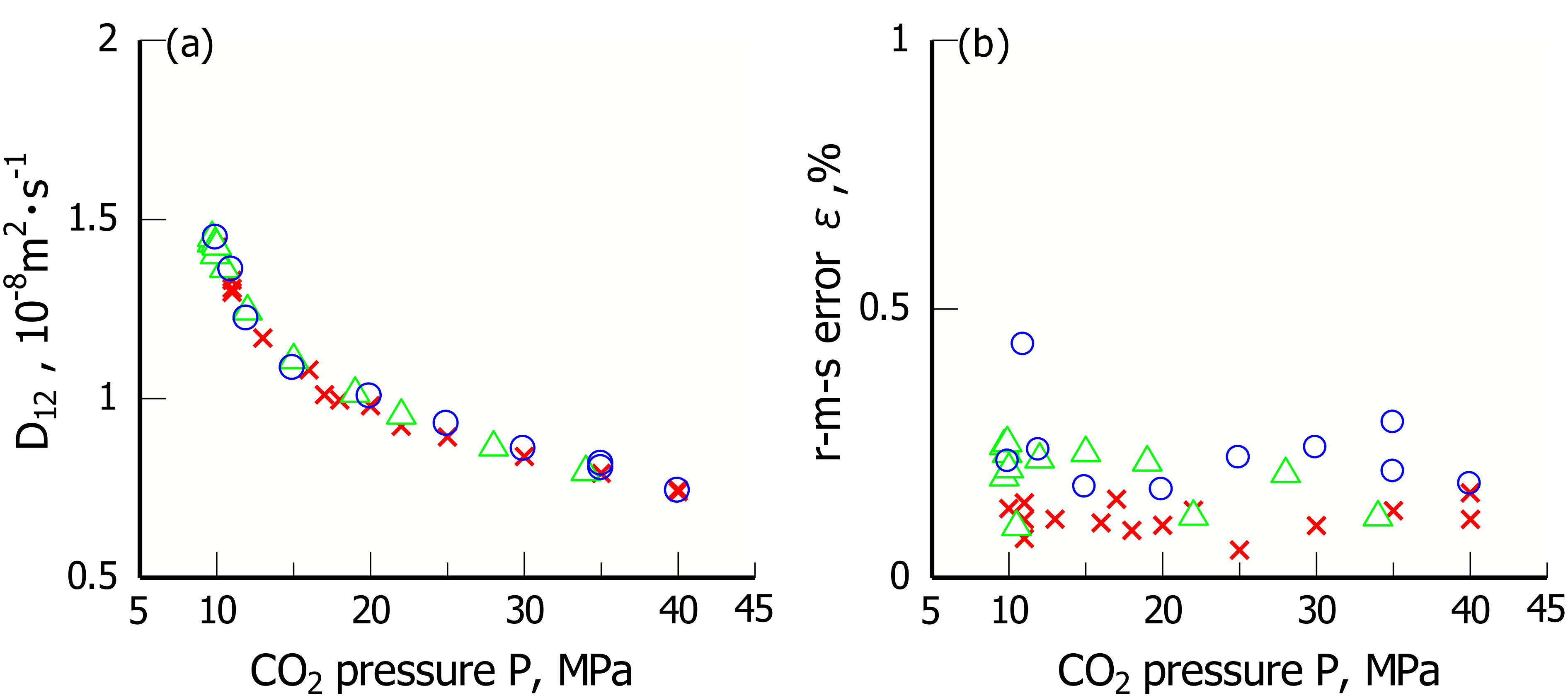



Figure Comparison of (a) $D_{12}$ and (b) $\varepsilon$ vs. $P$ for ferrocene in SC $CO_2$ at 313.15 K and 9.7 - 40.04 MPa measured by the TD method with ferrocene predissolved in hexane before injected (cross), the TD method with ferrocene predissolved in $CO_2$ before injected (triangle), and the CIR method with ferrocene predissolved in $CO_2$ before injected (circle).

# THE $D_{12}$ DATA OF 1,1′-DIMETHYLFERROCENE AND FERROCENE MEASURED

Ferrocene: M=186

1,1'-dimethylferrocene : M=214

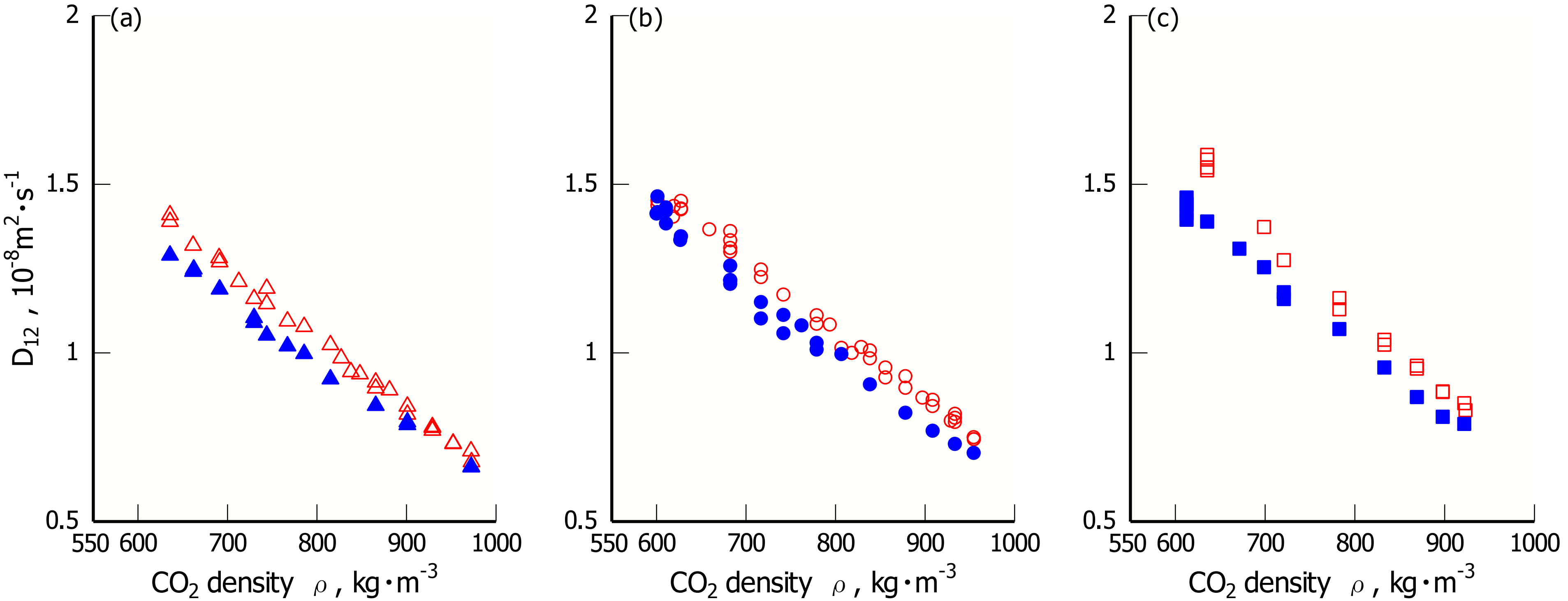



Figure $D_{12}$ vs. $CO_2$ density $\rho$ at (a) 308.15 K (triangle), (b) 313.15 K (circle), and (c) 323.15 K (square) for ferrocene (blank red key) and 1,1'-dimethylferrocene (solid blue key).

# THE CORRELATION AS FUNCTION OF VISCOSITY, TEMPERATURE AND SOLUTE MOLECULAR WEIGHT

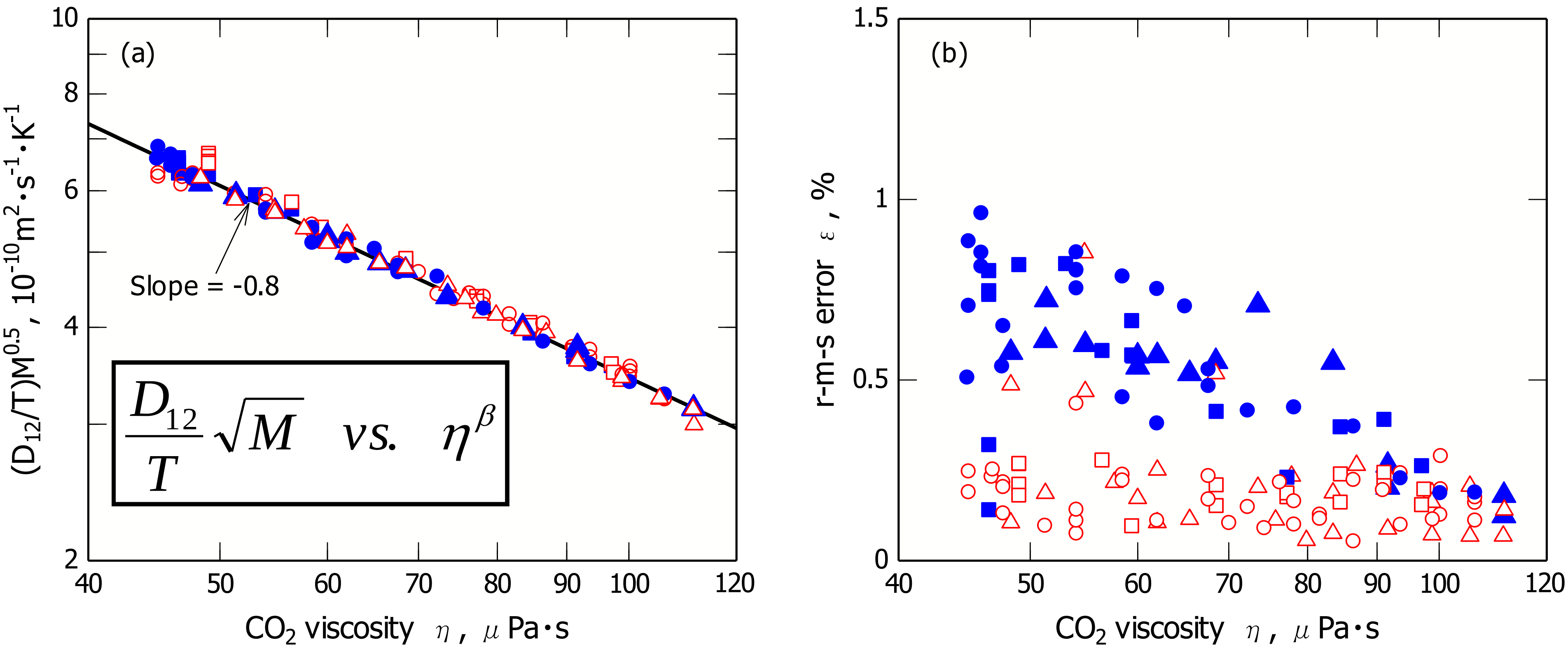



Figure Plots of $(D_{12}/T)M^{0.5}$ vs. $CO_2$ viscosity $\eta$ at 308.15 K (triangle), 313.15 K (circle), and 323.15 K (square) for ferrocene (blank red key) and 1,1'-dimethylferrocene (solid blue key) measured in this study.

# THE CORRELATION AS FUNCTION OF VISCOSITY, TEMPERATURE AND SOLUTE MOLECULAR WEIGHT

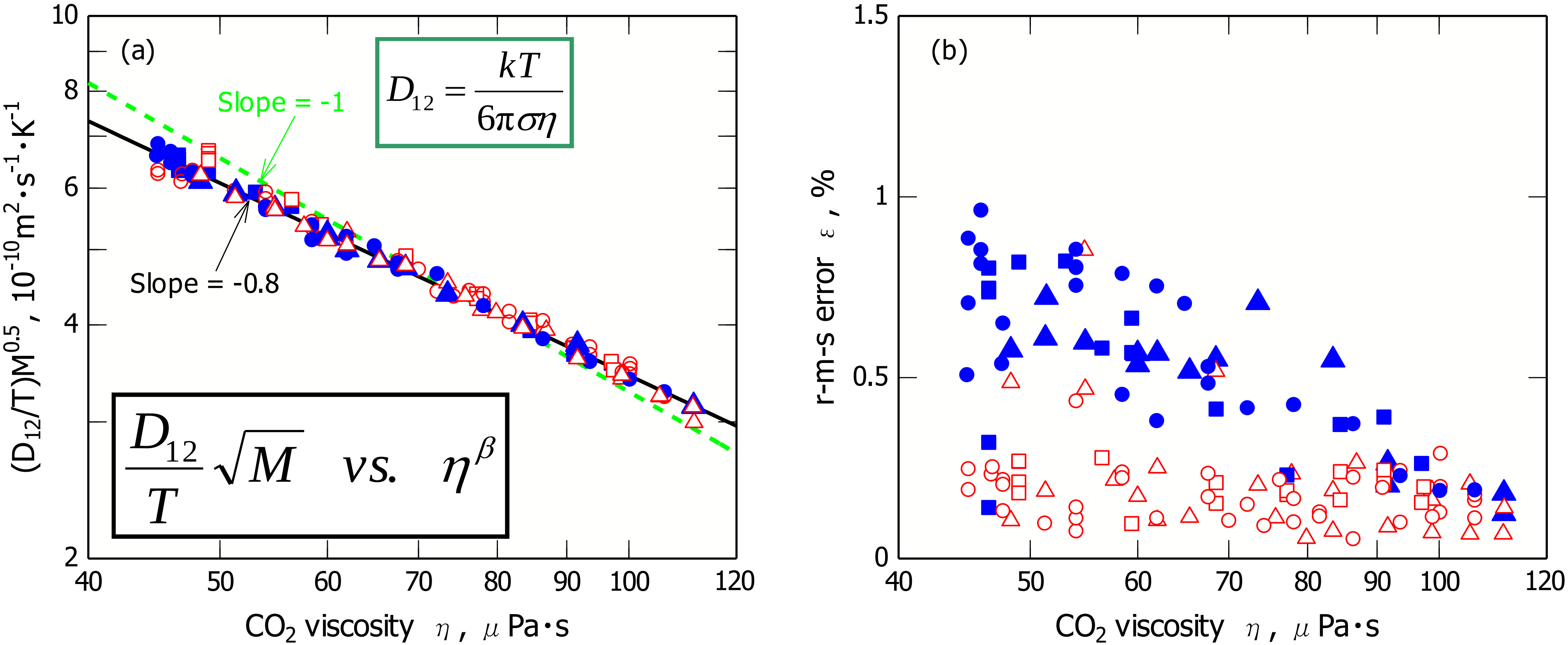
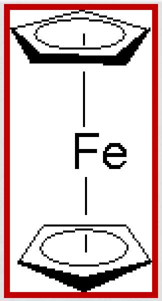
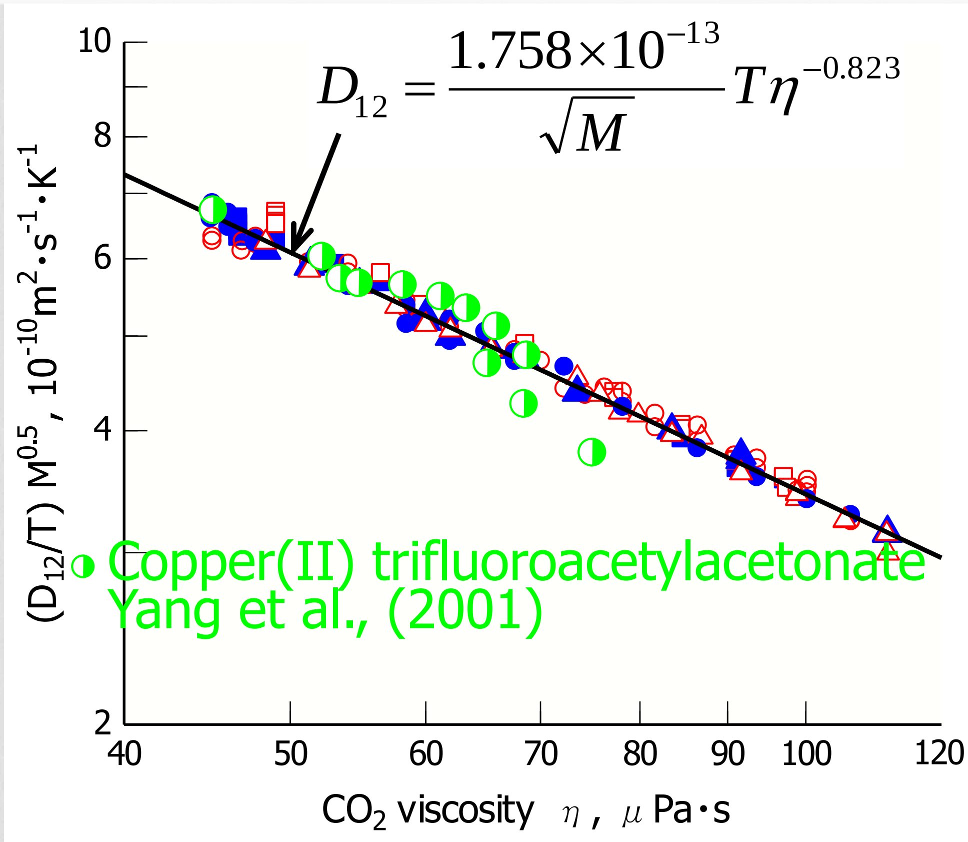


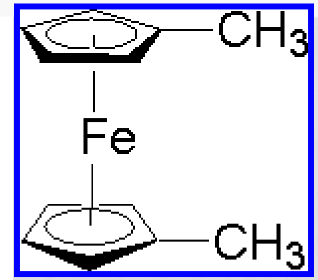

Figure Plots of $(D_{12}/T)M^{0.5}$ vs. $CO_2$ viscosity $\eta$ at 308.15 K (triangle), 313.15 K (circle), and 323.15 K (square) for ferrocene (blank red key) and 1,1'-dimethylferrocene (solid blue key) measured in this study.

# THE CORRELATION AS FUNCTION OF VISCOSITY, TEMPERATURE AND SOLUTE MOLECULAR WEIGHT

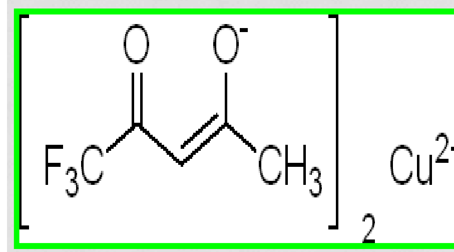



M=186




M=214




M=370

Figure Plots of $(D_{12}/T)M^{0.5}$ vs. $CO_2$ viscosity $\eta$ at 308.15 K (triangle), 313.15 K (circle), and 323.15 K (square) for ferrocene (blank red key) and 1,1'-dimethylferrocene (solid blue key) measured in this study.

# Thank You