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Calculation of Diffusion Coefficients for Carbon Dioxide + Solute System near the
Critical Conditions by Non-Equilibrium Molecular Dynamics Simulation

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ABSTRACT

A non-equilibrium molecular dynamics simulation was adopted to calculate the diffusion coefficients for a pseudo binary system of carbon dioxide and for a carbon dioxide + solute system at 308.2 and 318.2 K. The calculated results were compared with the self- and tracer diffusion coefficients calculated by an equilibrium molecular dynamics simulation. The simulated results for the pseudo binary system of carbon dioxide by the non-equilibrium molecular dynamics simulation are in good agreement with the results of self-diffusion coefficients for pure carbon dioxide by the equilibrium molecular dynamics simulation. The simulated results of mutual diffusion coefficients for the carbon dioxide + solute system by the non-equilibrium molecular dynamics simulation are slightly lower than the results of the tracer diffusion coefficients by the equilibrium molecular dynamics simulation. The anomalous behavior of diffusion coefficients near the critical concentration was represented by the results of the non-equilibrium molecular dynamics simulation.

INTRODUCTION

Recently, the use of supercritical fluid in extraction and fractionation processes is remarked, because of its various advantages. The fundamental data, such as equilibrium and transport properties, are essential to design the supercritical extractors, separators and reactors. However, the diffusion coefficient data in supercritical region have been limited. Computer simulations may be feasible and helpful to obtain thermodynamic data for mixtures under high pressure.

Anomalous behaviors of diffusion coefficient in the vicinity of critical point have been reported experimentally[1-8] and have been discussed theoretically[9-12]. In previous works[13-15], *NVT* ensemble single-site model equilibrium molecular dynamics simulation has been applied to calculate the self-diffusion coefficients for pure carbon dioxide and the tracer diffusion coefficients for the carbon dioxide + aromatic compound systems. As a result, the calculated results of self- and tracer diffusion coefficients show a good agreement with the experimental results in a high pressure region. However, the anomalous decrease of diffusion coefficients at the vicinity of critical point reported experimentally is not represented by the results of the equilibrium molecular dynamics simulation. Because the self- and tracer diffusion coefficients are essentially different from a mutual diffusion coefficient, it was concluded that a non-equilibrium molecular dynamics simulation for the mutual diffusion coefficients was required to explain the anomalous decrease of diffusion coefficients near the critical point.

Non-equilibrium molecular dynamics simulation is effective to calculate the transport properties

and have been mainly applied to investigate a heat transfer. Non-equilibrium molecular dynamics simulation was adopted to calculate the thermal conductivity and the thermal diffusion in a single phase region[16-20] and also to calculate the heat transfer across the vapor-liquid interface[21-25]. It was also applied to ionic systems[26]. Non-equilibrium molecular dynamics simulation enables to calculate the mutual diffusion coefficients directly. Wang and Cummings[27] adopted the non-equilibrium molecular dynamics simulation to calculate the diffusion coefficient of carbon dioxide. Arya et al.[28] investigate the applicability of equilibrium and non-equilibrium molecular dynamics simulation to calculate the transport properties. In this work, the non-equilibrium molecular dynamics simulation was applied to calculate the mutual diffusion coefficients for a pseudo binary system of carbon dioxide and for the carbon dioxide + model solute system at 308.2 and 318.2 K.

METHOD

1. Non-equilibrium Molecular Dynamics Simulation

The snapshot of a simulation for pseudo binary system of carbon dioxide is shown in **Fig.1(a)**. The simulation cell consisted of some regions, as shown in **Fig.1(b)**. The concentration in regions A and B was controlled and flux calculation regions C_I and C_{II} were prepared. The simulation cell consisted of the three unit cubic cells and the length of x-axis was three times longer than those of y- and z-axis. As the 108 particles consisted in a unit cubic cell, the simulation cell consisted of 324

particles. The volume of the unit cubic cell was determined by the density of the simulated conditions. The width of the concentration control regions and of the diffusion regions were set to be half of a side of the unit cubic cell. In the case of a simulation for the pseudo binary system of carbon dioxide, the particles were colored with white and black, and the conditions of each concentration control regions A and B were adjusted by the ratio of white and black carbon dioxide as shown in **Fig.1(a)**. The mole fractions of the component 2 in the concentration control regions, y_2^A and y_2^B , were adjusted to the given values of mole fraction, y_{20}^A and y_{20}^B , by replacing the particles when a particle came in to the concentration control region. In the present work, the change of potential energy by replacing the particles of solute with carbon dioxide is negligible to the deviation of the calculated potential energies, because of the size of solute is the same as that of carbon dioxide and the energy parameters of solute is not so different to that of carbon dioxide.

NVT ensemble single-site model molecular dynamics simulation was performed. The equations of motion were solved with a Leap-Frog algorithm with a constraint method to maintain constant temperature[29]. The time step of the calculation was 5 fs. After more than 1×10^5 of the equilibration steps, 2×10^6 of the production steps were performed. It was checked that the center of mass of the system did not move.

The fluxes of each component were calculated from the center of gravity for the components in the regions C_I and C_{II} . The diffusion coefficients were determined by the calculated fluxes and concentration gradients for the regions C_I and C_{II} , and then they were averaged. The calculation

procedure for the region C_1 is as follows.

The cell-fixed fluxes N_1 and N_2 in the region C_1 can be calculated by the following equations.

$$N_1^{C_1} = \frac{m_1}{V^{C_1}} \sum_{i=1}^{n_1^{C_1}} v_{xi} \quad (1)$$

$$N_2^{C_1} = \frac{m_2}{V^{C_1}} \sum_{i=1}^{n_2^{C_1}} v_{xi} \quad (2)$$

where m_1 and m_2 are the mass of particles, and n_1 and n_2 are the number of particles of the components 1 and 2, respectively. V^{C_1} is the volume of the region C_1 . v_{xi} is the x -axis component of the velocity vector for particles. The mass-fixed fluxes J_1 and J_2 in the region C_1 can be represented by the following equations.

$$J_1^{C_1} = N_1^{C_1} - y_1^{C_1} (N_1^{C_1} + N_2^{C_1}) \quad (3)$$

$$J_2^{C_1} = N_2^{C_1} - y_2^{C_1} (N_1^{C_1} + N_2^{C_1}) \quad (4)$$

The mass-fixed diffusion coefficients were calculated by the following equations.

$$D_{12}^J = J_1^{C_1} \frac{v^{C_1}}{m_1} \frac{\Delta x}{n_1^{E_1} - n_1^{E_{II}}} \quad (5)$$

$$D_{21}^J = J_2^{C_1} \frac{v^{C_1}}{m_2} \frac{\Delta x}{n_2^{E_1} - n_2^{E_{II}}} \quad (6)$$

where Δx are the width of the flux calculation regions as shown in **Fig.1**, and $n_1^{E_1}$, $n_2^{E_1}$, $n_1^{E_{II}}$

and $n_2^{E_{II}}$ are the number of particles of the components 1 and 2 in zones E_I and E_{II} .

The volume-fixed diffusion coefficients (mutual diffusion coefficients) D_{12}^V and D_{21}^V were calculated by the following equations.

$$D_{12}^V = \frac{\bar{v}_2}{v} D_{12}^J \quad (7)$$

$$D_{21}^V = \frac{\bar{v}_1}{v} D_{21}^J \quad (8)$$

where v is the molar volume of this system. \bar{v}_1 and \bar{v}_2 are the partial molar volume of the components 1 and 2, respectively. The partial molar volumes were calculated as follows.

$$\bar{v}_1 = \frac{V^E \left\{ \left(\frac{n_2^{E_{II}}}{n_2^{E_I}} \right) - 1 \right\}}{n_1^{E_I} \left(\frac{n_2^{E_{II}}}{n_2^{E_I}} \right) - n_1^{E_{II}}} N_{AV} \quad (9)$$

$$\bar{v}_2 = \frac{V^E \left\{ \left(\frac{n_1^{E_I}}{n_1^{E_{II}}} \right) - 1 \right\}}{n_2^{E_{II}} \left(\frac{n_1^{E_I}}{n_1^{E_{II}}} \right) - n_2^{E_I}} N_{AV} \quad (10)$$

where V^E is a volume of the region $E_I \sim E_{IV}$ and N_{AV} is the Avogadro number.

As shown in eqs. (5) and (6), the diffusion coefficient was determined by the relationship of the flux and the difference of the number of particles in zones E_I and E_{II} . The diffusion coefficients were calculated under several conditions by changing the concentration profiles and were described as a function of the difference of mole fractions in the regions A and B. The diffusion coefficients

calculated in the regions C_I and C_{II} were averaged in each simulation.

2. Equilibrium Molecular Dynamics Simulation

The equilibrium molecular dynamics simulation to calculate the self- and tracer diffusion coefficients was performed. *NVT* ensemble single-site model molecular dynamics simulation was applied. The equations of motion were solved with a Leap-Frog algorithm with a constraint method to maintain constant temperature[29]. The cubic simulation cell consisted of 256 particles was adopted and the volume of the cell was determined by the density of the simulated conditions. The time step of the calculation was 5 fs. After more than 1×10^5 of the equilibration steps, 1×10^6 of the production steps were performed.

The self-and tracer diffusion coefficients for carbon dioxide and solute were calculated by the Einstein equation as follows.

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle \quad (11)$$

where t is the elapsed time and \mathbf{r} is the position of a particle for each component.

3. Intermolecular Potential Function

For all particles, in the preset study, the Lennard-Jones(12-6) potential function was used.

$$\phi_{ij} = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \quad (12)$$

where i and j are components i and j , respectively. ϕ is the intermolecular potential, ε is the energy parameter, σ is the size parameter, and r is the molecular distance.

The interaction parameters between solvent (1) and solute (2) are given by using the following combining rules.

$$\varepsilon_{12} = (\varepsilon_{11} \times \varepsilon_{22})^{0.5} \quad (13)$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \quad (14)$$

4. Determination of Potential Parameters

In this work, the potential parameters ε and σ of carbon dioxide were determined from the data of the critical point of carbon dioxide by Nicolas method[30]. Based on the corresponding state principle, the volume V , the absolute temperature T and pressure P of the Lennard-Jones fluid of a pure substance can be reduced as follows.

$$\rho^r = n\sigma^3/V, \quad T^r = kT/\varepsilon, \quad P^r = \sigma^3 P/\varepsilon \quad (15)$$

where ρ is the number density. Nicolas et al. proposed the reduced value at the critical point.

$$\rho_c^r = 0.35, \quad T_c^r = 1.35, \quad P_c^r = 0.1418 \quad (16)$$

The energy parameter of solute was set to be 1.1 times larger than that of carbon dioxide. The size parameter and molecular weight of solute were set to the same values to those of carbon dioxide.

The parameters determined for carbon dioxide and solute are listed in **Table 1**.

RESULTS AND DISCUSSION

1. Pseudo Binary System of Carbon Dioxide

Fig.2 shows the simulated results of diffusion coefficients by the non-equilibrium molecular dynamics simulation for the pseudo binary system of carbon dioxide at 308.2 K as a function of difference of mole fractions in the region A and B. In this case, the concentration gradients between two control regions were set to be large, because the diffusion coefficients for this system will not show the concentration dependence. The diffusion coefficients were determined by extrapolating the difference of mole fractions in the regions A and B to zero. The diffusion coefficients by the non-equilibrium molecular dynamics simulation are compared with the self-diffusion coefficients by an equilibrium molecular dynamics simulation[15] in **Fig.3**. The simulated results by the non-equilibrium molecular dynamics simulation are in good agreement with the results of self-diffusion coefficients by the equilibrium molecular dynamics simulation.

2. Carbon Dioxide + Solute System

The simulation was also performed by adjusting the difference of mole fractions in the region A and B for this system. In this case, the concentration gradients between two control regions were set to be less than 0.3, because the diffusion coefficients for this system will indicate the concentration

dependence. The diffusion coefficients were determined by extrapolating the difference of mole fractions in the regions A and B to zero. The simulated results for carbon dioxide + solute system at 308.2 and 318.2 K are shown in **Figs.4** and **5**. The simulated results of self- and tracer diffusion coefficients of this system are also shown in **Figs.4** and **5**. The calculated pressures are shown in **Fig.6**. The diffusion coefficients by non-equilibrium molecular dynamics simulation are slightly lower than the self- and tracer diffusion coefficients by the equilibrium molecular dynamics simulations. The diffusion coefficients calculated by the non-equilibrium molecular dynamics simulation denote the mutual diffusion coefficients. The mutual diffusion coefficient is essentially different from the tracer diffusion coefficient. Mutual and tracer diffusion coefficients coincide with each other at the infinite dilution condition and don't coincide at the finite concentration, especially in the non-ideal system. The anomalous decrease of diffusion coefficients is represented at the vicinity of the mole fraction of 0.9 at 308.2 K and of 0.55 at 318.2 K. These points would be critical points of the simulated system at the given temperature.

The vapor-liquid equilibria of the carbon dioxide + solute system were calculated by the Soave-Redlick-Kwong (SRK) equation of state[32]. The SRK equation of state is shown as follows.

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \quad (17)$$

where a , α and b are parameters which can be determined from the critical properties and the acentric factors of the pure components.

$$a = 0.42747R^2T_C^2 / P_C \quad (18)$$

$$\alpha = [1 + m\{1 - (T/T_C)^{0.5}\}]^2 \quad (19)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (20)$$

$$b = 0.08664RT_C / P_C \quad (21)$$

The critical temperature and pressure of the solute were calculated by the size and energy parameters. The acentric factor of the solute was assumed to be the same to that of carbon dioxide. The values of these properties are listed in **Table 1**. The following mixing and combining rules were adopted.

$$(a\alpha) = \sum_i \sum_j x_i x_j (a\alpha)_{ij}, \quad (a\alpha)_{ij} = \{(a\alpha)_i \times (a\alpha)_j\}^{0.5} \quad (22)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = (b_i + b_j) / 2 \quad (23)$$

The calculated results of vapor-liquid equilibria of this system by the SRK equation of state are shown in **Fig.6**. It shows that the critical mole fraction and the critical pressure are about 0.9 and 7.5 MPa at 308.2 K and are 0.6 and 8.0 MPa at 318.2 K. Therefore, it is noted that the simulations were carried out in a single phase region.

The mutual diffusion coefficient can be represented by the Darken equation[33].

$$D_{21} = (y_2 D_1^* + y_1 D_2^*) \left(\frac{\partial \ln f_2}{\partial \ln y_2} \right) \quad (24)$$

where f_2 is the fugacity of the solute and D^* is the tracer diffusion coefficient. The tracer diffusion coefficients were smoothed by a cubic equation. The SRK equation of state was adopted to calculate the fugacity of the solute.

The calculated results of diffusion coefficients by the Darken equation are also shown in **Figs.4** and **5**. The results of mutual diffusion coefficients by the equations are slightly lower than the self- and tracer diffusion coefficients. It corresponds with the simulated results. The anomalous decreases of diffusion coefficients at the vicinity of the mole fraction of 0.9 at 7.5 MPa and 308.2 K and of 0.6 at 8.0 MPa and 318.2 K were represented by the equation. The anomalous behavior can be observed in very narrow regions of concentration and pressure and the calculated critical points by the SRK equation of state coincide with the critical points for the simulated system. More detailed simulations would be necessary to discuss the anomalous decrease of diffusion coefficient near the critical point.

CONCLUSION

The non-equilibrium molecular dynamics simulation was adopted to calculate the diffusion coefficients for a pseudo binary system of carbon dioxide and for a carbon dioxide + solute system near the critical condition. The simulated results for the pseudo binary system of carbon dioxide by the non-equilibrium molecular dynamics simulation are in good agreement with the results of self-diffusion coefficients for pure carbon dioxide by the equilibrium molecular dynamics simulation. The simulated results of mutual diffusion coefficients for the carbon dioxide + solute system by the

non-equilibrium molecular dynamics simulation are slightly lower than the results of the tracer diffusion coefficients by the equilibrium molecular dynamics simulation. The anomalous behavior of diffusion coefficients near the critical concentration can be represented by the simulation. It is noted that an estimation method of transport properties based on the non-equilibrium molecular dynamics simulation seems effective to calculate the mutual diffusion coefficients near the critical regions. More detailed simulations and applications for several real systems should be necessary to explain quantitatively the anomalous phenomena of diffusion coefficients near the critical point.

NOMENCLATURE

D	diffusion coefficient
f	fugacity
J	mss-fixed flux
k	Boltzmann constant
m	mass of particle
N	cell-fixed flux
N_{AV}	Avogadro number
n	number of particles
P	pressure
R	gas constant

r	distance between molecules
\mathbf{r}	position of a particle
T	temperature
t	time
v	molar volume
\bar{v}	partial molar volume
v_{xi}	x -axis component of velocity vector for particle i
V	volume
Δx	width of flux calculation region
x	mole fraction of liquid phase
y	mole fraction of vapor phase

Greek Letters

σ	size parameter
ε	energy parameter
ϕ	potential energy
ρ	density
ω	acentric factor

Subscripts

0	adjusted value
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1	component 1 (white carbon dioxide)
2	component 2 (black carbon dioxide or solute)
C	critical value
i, j	particles i and j
*	tracer diffusion

Superscripts

A, B, C, E	regions A, B, C and E
J	mass-fixed
r	reduced value
V	volume-fixed

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Figure captions

Fig.1 Snap shot and simulation cell.

Fig.2 Simulated results for diffusion coefficients of pseudo binary system of carbon dioxide at 308.2 K. () 200 cm³/mol; () 150 cm³/mol; () 100 cm³/mol; () 75 cm³/mol; () 60 cm³/mol.

Fig.3 Comparison between self-diffusion coefficients and mutual diffusion coefficients of pseudo binary system of carbon dioxide at 308.2 K. () Equilibrium molecular dynamics simulation[15]; () Non-equilibrium molecular dynamics simulation.

Fig.4 Simulated results for diffusion coefficients of carbon dioxide + solute system at 308.2 K. Equilibrium MD: () Tracer diffusion coefficient of carbon dioxide; () Tracer diffusion coefficient of solute; () Self-diffusion coefficient. Non-equilibrium MD: () Mutual diffusion coefficient. Darken equation: () 7.5 MPa; () 7.7 MPa; () 7.9 MPa.

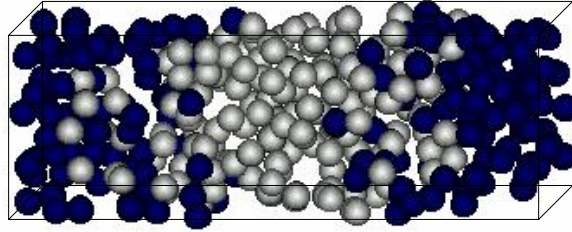
Fig.5 Simulated results for diffusion coefficients of carbon dioxide + solute system at 318.2 K. Equilibrium MD: () Tracer diffusion coefficient of carbon dioxide; () Tracer diffusion coefficient of solute; () Self-diffusion coefficient. Non-equilibrium MD: () Mutual diffusion coefficient. Darken equation: () 8.0 MPa; () 8.5 MPa; () 9.0 MPa.

Fig.6 Calculated results of vapor-liquid equilibria for carbon dioxide + solute system. SRK equation of state: (—) 308.2 K; () 318.2 K. Simulated condition of non-equilibrium molecular dynamics simulation: () 308.2 K; () 318.2 K.

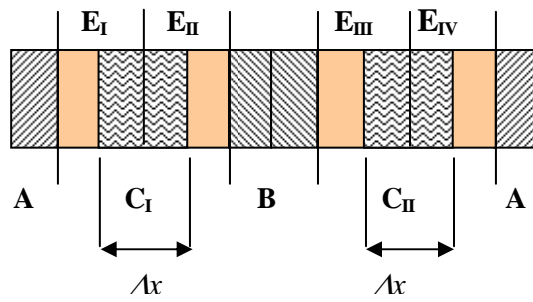
Table 1 Physical properties and potential parameters


Component	T_C [K]	P_C [MPa]	ω [-]	σ [nm]	ϵ/k [K]
Carbon dioxide(1)	304.1 *)	7.37 *)	0.225	0.391	225.3
Solute(2)	334.5	8.11	0.225	0.391	247.8


*) Poling et al.[31]



(a) Snap shot



 Concentration control region, A

 Concentration control region, B

 Flux calculation regions, C_I , C_{II}

(b) Simulation cell

Fig.1 Higashi et al.

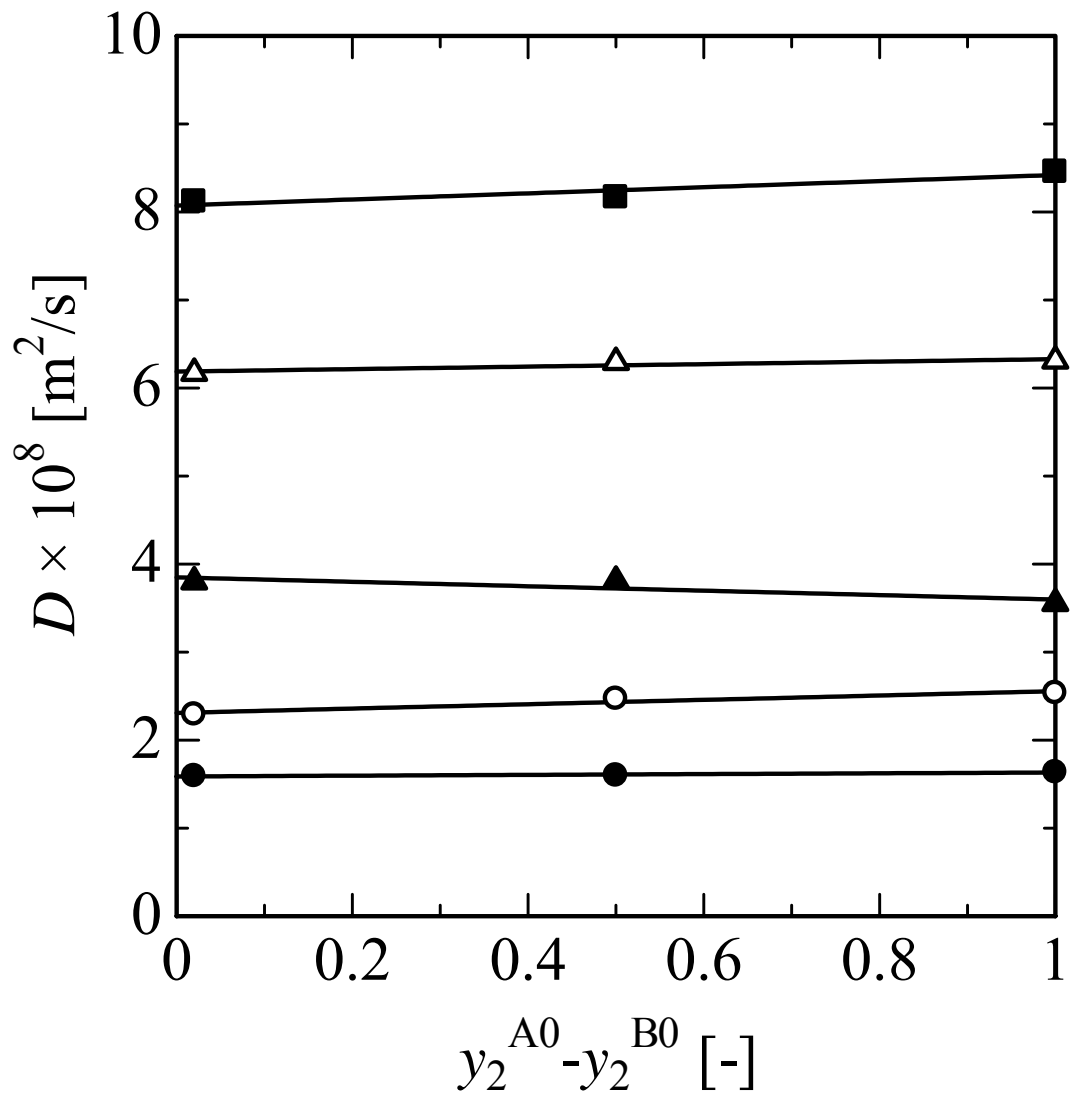


Fig.2 Higashi et al.

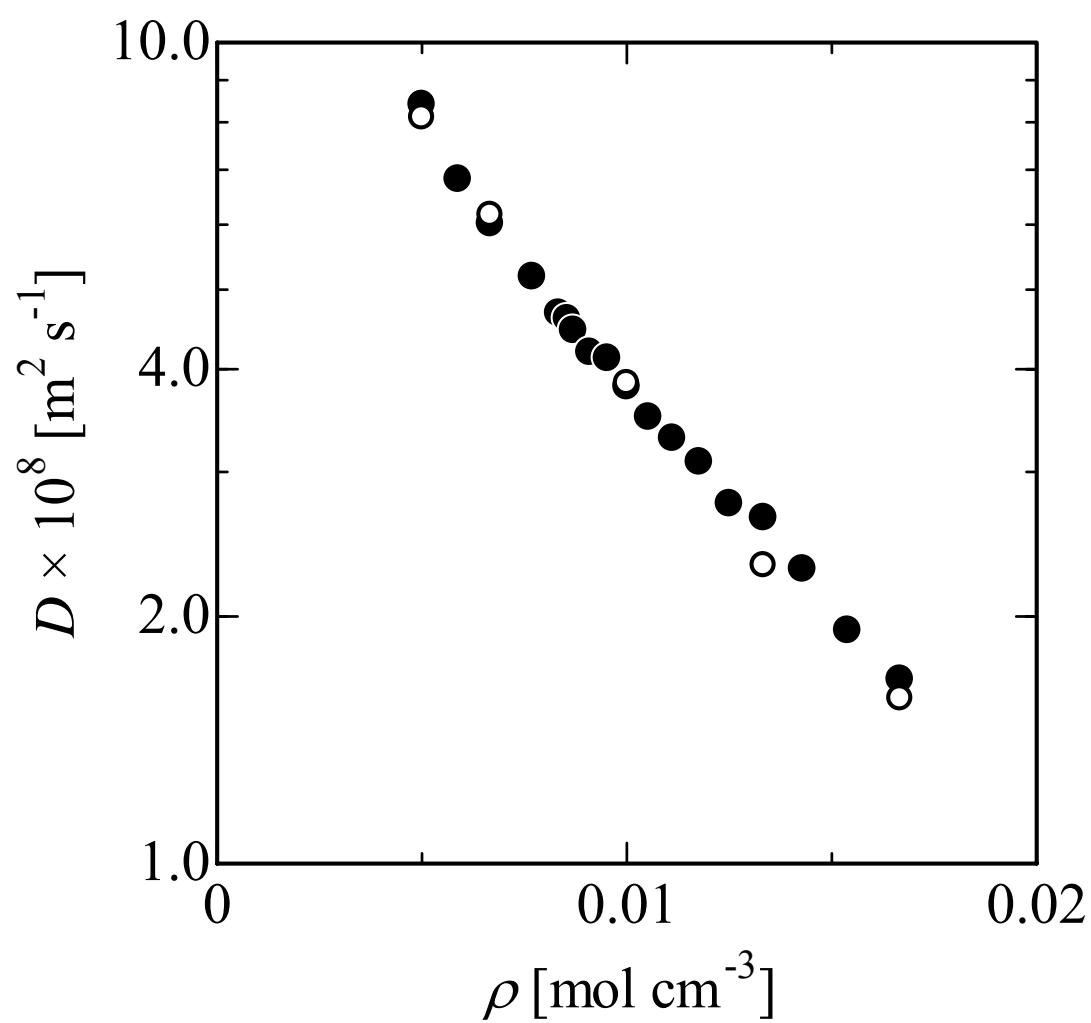


Fig.3 Higashi et al.

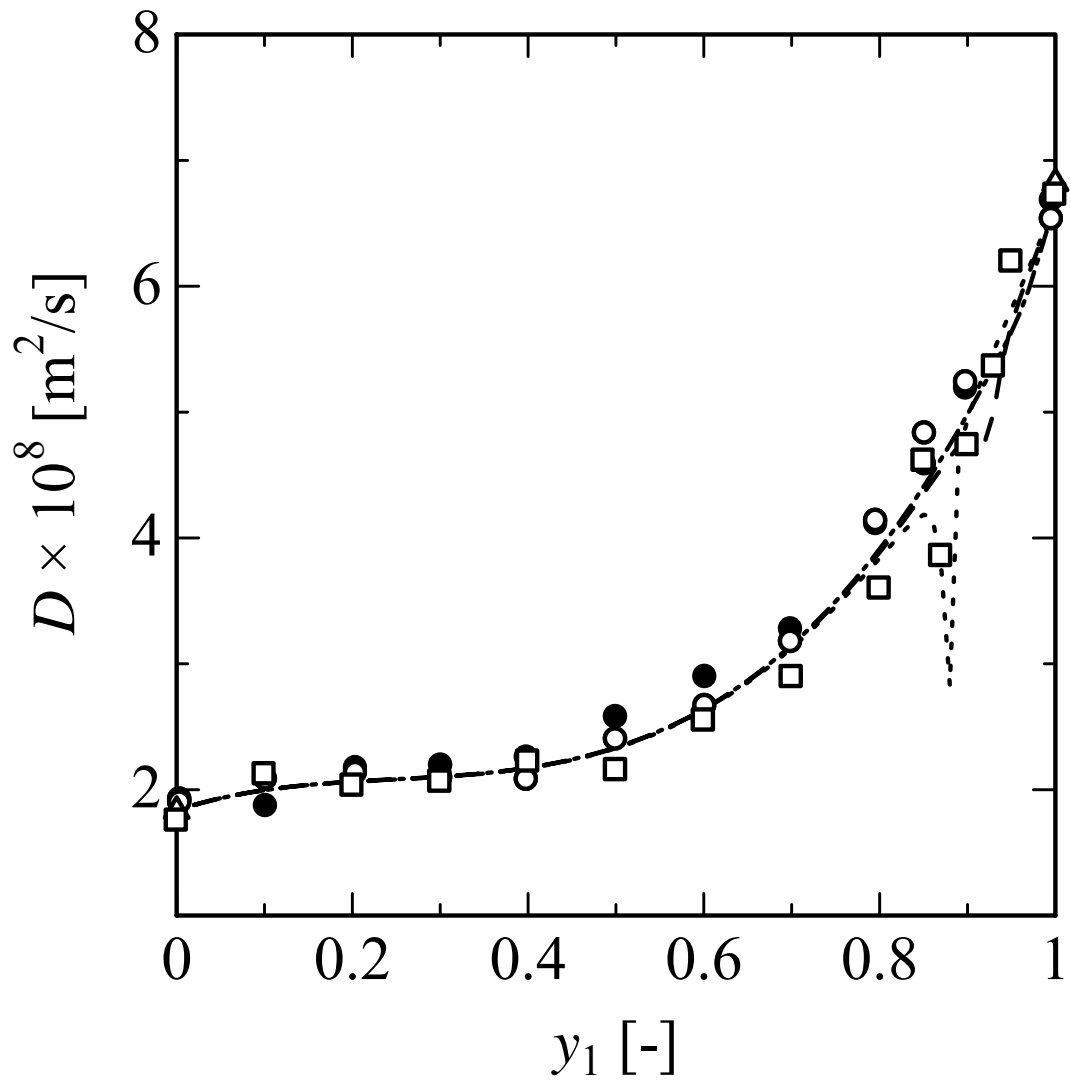


Fig.4 Higashi et al.

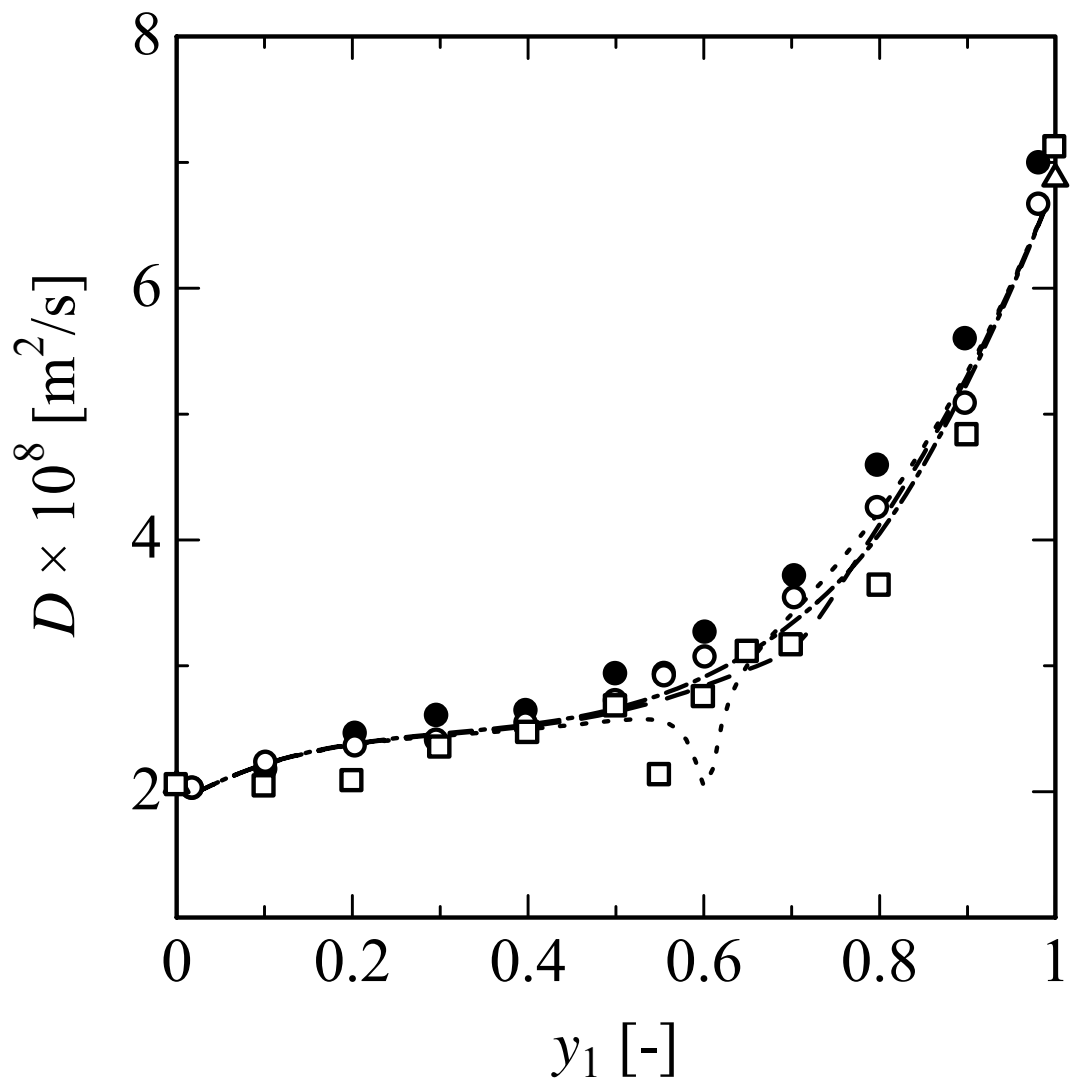


Fig.5 Higashi et al.

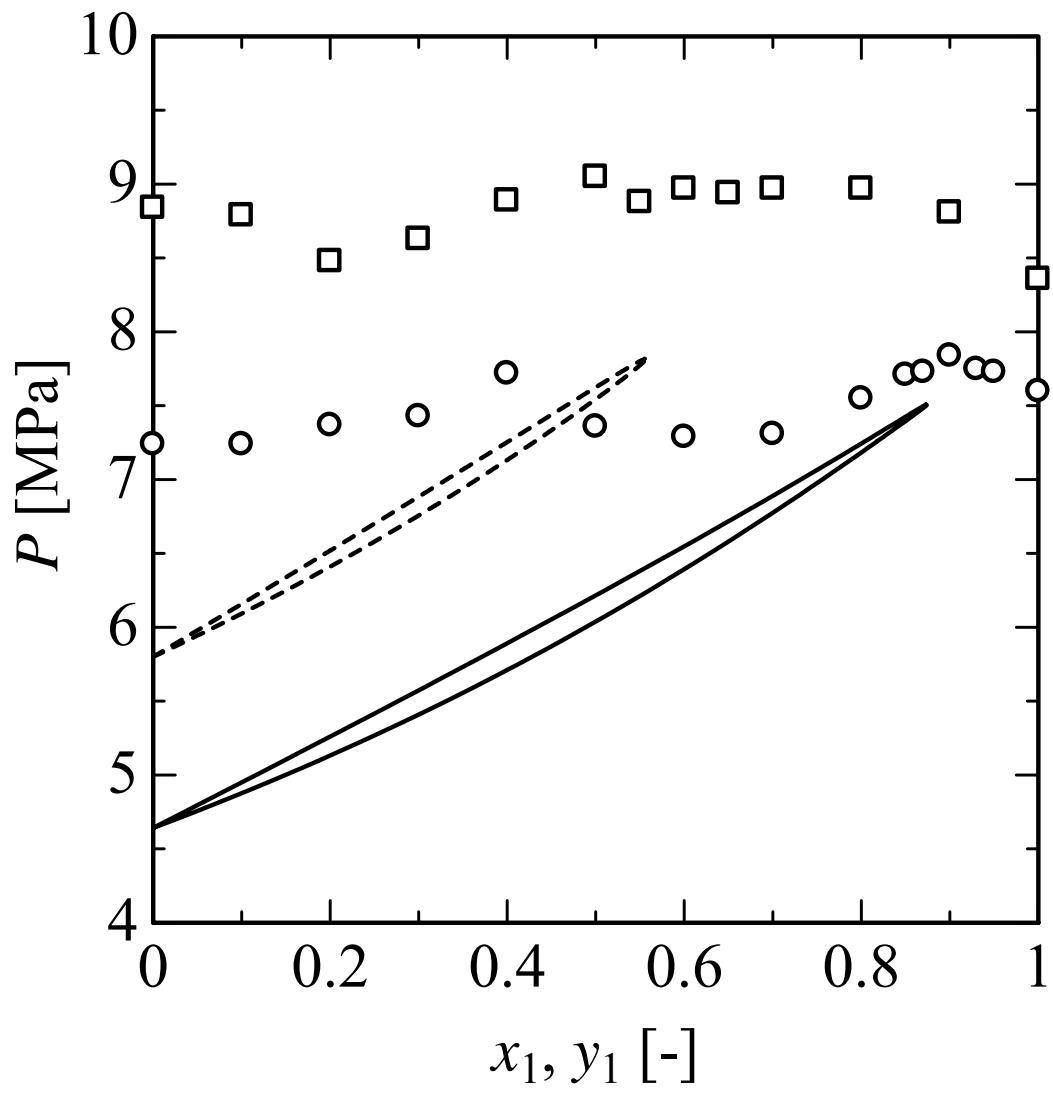


Fig.6 Higashi et al.