

Calculation of Self-Diffusion and Tracer Diffusion Coefficients near the Critical Point of Carbon Dioxide Using Molecular Dynamics Simulation

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An *NVT* ensemble single-site model molecular dynamics simulation using a leapfrog algorithm with a constraint method for constant temperature has been applied to calculate the self-diffusion coefficients for pure carbon dioxide and the tracer diffusion coefficients for the carbon dioxide + naphthalene system at 308.2 K in the pressure range from 7 to 20 MPa. The simulation results of the self-diffusion and tracer diffusion coefficients are compared with the experimental data. The calculated tracer diffusion coefficients of carbon dioxide for the carbon dioxide + naphthalene system are slightly smaller than the self-diffusion coefficients for pure carbon dioxide at the same pressures near the critical point of carbon dioxide. However, the anomalous decrease of diffusion coefficients observed in the experimental data for mixture systems is not shown in the present simulation results.

Introduction

The diffusion coefficient in the supercritical region is one of the important properties for the design of supercritical fluid extraction and reaction processes. Some experimental results have reported an anomalous decrease of diffusion coefficients at the vicinity of the critical point.^{1–4} The restriction to thermal motion of the solute molecule by formation of clusters near the critical region is considered to be one of the reasons for the anomalous diffusivity. The self-diffusion coefficient is an index of the thermal motion. Katagiri et al.⁵ calculated the self-diffusion coefficients of carbon dioxide and naphthalene in their mixture by molecular dynamics (MD) simulation with the Lennard-Jones potential. They pointed out the restriction of the diffusive motion of naphthalene by the formation of the solvation structure. In our previous works,^{6,7} MD simulation was adopted to calculate the diffusion coefficients for supercritical carbon dioxide + aromatic hydrocarbon systems. However, the diffusivity near the critical point has not yet been discussed in detail. In this work, an *NVT* ensemble single-site model MD simulation with a Lennard-Jones potential has been applied to calculate the self-diffusion coefficients for pure carbon dioxide and the tracer diffusion coefficients for the carbon dioxide + naphthalene system at 308.2 K in the pressure range from 7 to 20 MPa.

Methods

Potential Function and Parameters. The Lennard-Jones (12–6) potential function was used as the intermolecular potential. The corresponding state principle provides that all Lennard-Jones fluids for pure components obey the same reduced equation of state by using the reduced variables. The reduced critical con-

Table 1. Critical Properties and Potential Parameters

molecule	T_C [K] ⁹	P_C [MPa] ⁹	σ [nm] ¹⁰	ϵ/k_B [K] ¹⁰
(1) carbon dioxide	304.2	7.37	0.391	225.3
(2) naphthalene	748.4	4.05	0.645	554.4

stant values proposed by Nicolas et al.⁸ were used to determine the Lennard-Jones energy and size parameters of pure compounds. The values of these parameters are listed in Table 1.

The combining rules shown by eqs 1 and 2 were used

$$\epsilon_{12} = (1 - k_{12})(\epsilon_{11}\epsilon_{22})^{1/2} \quad (1)$$

$$\sigma_{12} = (1 - l_{12})(\sigma_{11} + \sigma_{22})/2 \quad (2)$$

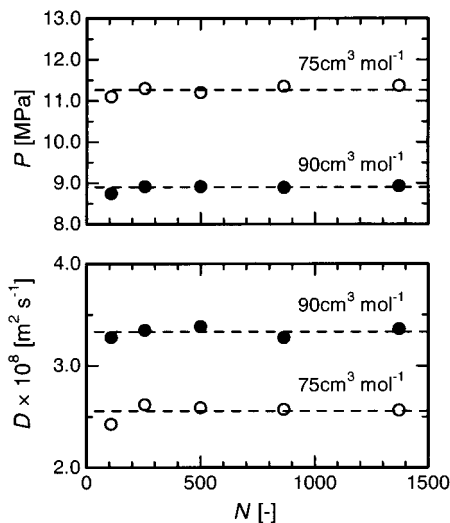
to calculate the Lennard-Jones parameters between unlike molecules, where k_{12} and l_{12} are the intermolecular interaction parameters which were adjusted to give a good representation for the solubilities of naphthalene in supercritical carbon dioxide at 308.2 K by using a Monte Carlo simulation. The values of k_{12} and l_{12} are given as -0.01 and $+0.05$, respectively.¹⁰

Calculation of the Diffusion Coefficient. An *NVT* ensemble single-site model MD simulation using a leapfrog algorithm with a constraint method for constant temperature¹¹ has been applied to calculate the self-diffusion coefficients for pure carbon dioxide and the tracer diffusion coefficients for the carbon dioxide + naphthalene system at 308.2 K in the pressure range from 7 to 20 MPa. To consider the effect of the number of particles and the concentration of naphthalene, the systems consist of 108, 256, 500, 864, and 1372 particles. The details of the simulation conditions are listed in Table 2. The time step of the calculation was 5 fs. After more than 2×10^3 equilibration steps, 2×10^6 production steps for 108–500 particle systems and 1×10^6 for 864 and 1372 particle systems were performed. The self-diffusion and tracer diffusion coefficients for carbon

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Table 2. Simulation Conditions for Particle Number and Concentration

molar volume [cm ³ mol ⁻¹]	mole fraction of naphthalene, y_2 (no. of naphthalenes/total number of particles)				
75	0 (0/108) ^a	0 (0/256) ^a	0 (0/500) ^a	0 (0/864) ^a	0 (0/1372) ^a
	0.00926 (1/108)	0.00391 (1/256)	0.00200 (1/500)	0.00116 (1/864)	0.00073 (1/1372)
		0.00781 (2/256)	0.00400 (2/500)		
		0.0156 (4/256)	0.00800 (4/500)	0.00463 (4/864)	0.00292 (4/1372)
90	0 (0/108) ^a	0 (0/256) ^a	0 (0/500) ^a	0 (0/864) ^a	0 (0/1372) ^a

^a Pure carbon dioxide.**Figure 1.** Particle number dependence of the calculated pressure and self-diffusion coefficient for pure carbon dioxide at 308.2 K.

dioxide and naphthalene can be calculated by the Einstein equation as

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle \quad (3)$$

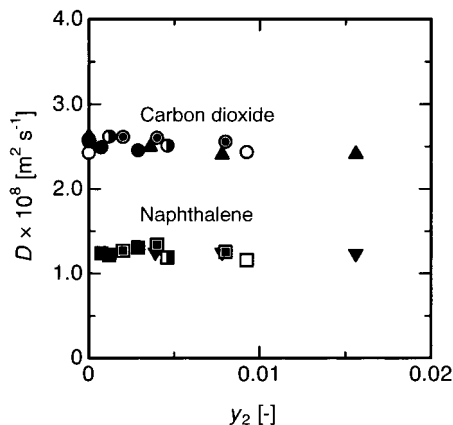
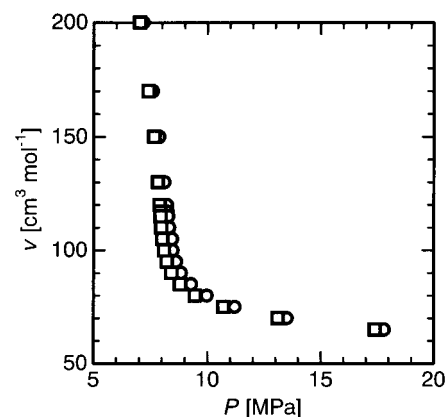
where t is the elapsed time and \mathbf{r} is the position of a particle for each component.

Results and Discussion

The self-diffusion and tracer diffusion coefficients were determined as an average value obtained from several simulation results. The reproducibilities are within 10%. The calculated results of the pressures and self-diffusion coefficients for pure carbon dioxide versus the number of particles are plotted in Figure 1. The calculated results for the concentration dependence of the tracer diffusion coefficients are shown in Figure 2.

The particle number does not affect the simulation results for the self-diffusion coefficients at the same molar volumes except for the 108-particle system. The concentration also does not affect the calculated tracer diffusion coefficients. Therefore, the 256-particle system was adopted in the present simulations. For the carbon dioxide + naphthalene system, one of them is naphthalene and others are carbon dioxide.

Figure 3 shows the molar volume versus the calculated pressure for pure carbon dioxide and for the carbon dioxide + naphthalene system. The calculated pressures for the carbon dioxide + naphthalene system are slightly smaller than those for pure carbon dioxide at the vicinity of the critical point of carbon dioxide. Figure 4

**Figure 2.** Concentration dependence of the tracer diffusion coefficient at 308.2 K and 75 cm³ mol⁻¹: (○, □) $N = 108$; (▲, ▼) $N = 256$; (◊, □) $N = 500$; (●, ■) $N = 864$; (●, ■) $N = 1372$.**Figure 3.** Molar volume vs. calculated pressure at 308.2 K: (○) pure carbon dioxide; (□) carbon dioxide + naphthalene.

shows the partial molar volumes of naphthalene calculated by the equation

$$\bar{v}_2 = \left(\frac{256v_{1+2} - 255v_1}{1 - 0} \right)_{T,P} \quad (4)$$

where v_{1+2} and v_1 are the molar volumes of the carbon dioxide + naphthalene system and pure carbon dioxide at the same temperature and pressure, respectively. The calculated partial molar volumes of naphthalene are negative and show a minimum near 8 MPa. Eckert et al.^{12,13} showed the unusual behavior of the partial molar volumes experimentally. It is considered to be due to the formation of a solvation structure caused by the increase in the correlation length near the solvent's critical point. The results of the present simulation are very close to their experimental results. Hence, the box size of the simulated systems is large enough for the correlation length.

The simulation results of the self-diffusion and tracer diffusion coefficients for carbon dioxide and naphthalene

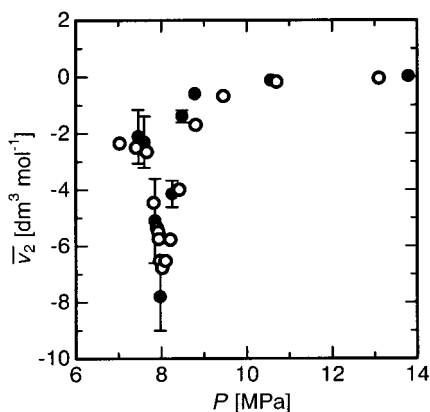


Figure 4. Partial molar volume of naphthalene in the carbon dioxide + naphthalene system: (●) experimental data at 308.38 K, Eckert et al.;¹³ (○) calculated results at 308.2 K, this work.

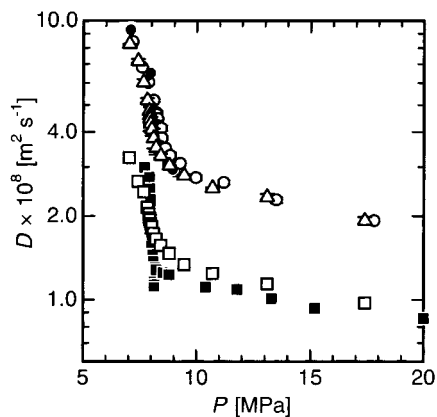


Figure 5. Diffusion coefficient vs pressure at 308.2 K. Experimental data: (●) carbon dioxide in pure carbon dioxide, O'hern and Martin;¹⁴ (■) binary diffusion coefficient for carbon dioxide + naphthalene, Higashi et al.⁴ Calculated results: (○) carbon dioxide in pure carbon dioxide; (△) carbon dioxide in carbon dioxide + naphthalene; (□) naphthalene in carbon dioxide + naphthalene.

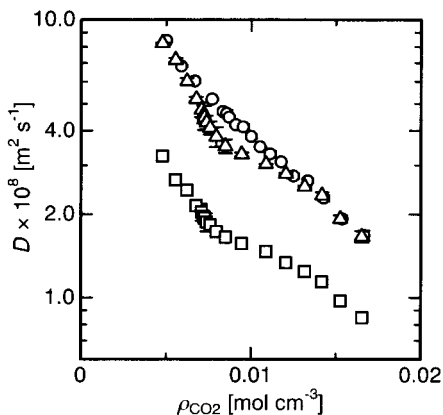


Figure 6. Diffusion coefficient vs mole density of pure carbon dioxide at 308.2 K: (○) carbon dioxide in pure carbon dioxide; (△) carbon dioxide in carbon dioxide + naphthalene; (□) naphthalene in carbon dioxide + naphthalene.

are plotted in Figures 5–7 as a function of pressure, molar density of pure carbon dioxide, and reduced density defined by

$$\rho^* = \frac{N_1 \sigma_1^3 + N_2 \sigma_2^3}{V} \quad (5)$$

where N_1 and N_2 are the number of molecules for carbon

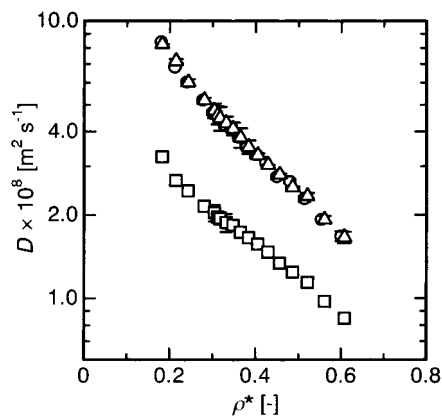


Figure 7. Diffusion coefficient vs reduced density at 308.2 K: (○) carbon dioxide in pure carbon dioxide; (△) carbon dioxide in carbon dioxide + naphthalene; (□) naphthalene in carbon dioxide + naphthalene.

Table 3. Simulated Results of Self-Diffusion and Tracer Diffusion Coefficients at 308.2 K

v [cm ³ mol ⁻¹]	pure carbon dioxide		carbon dioxide (1) + naphthalene (2)		
	P [MPa]	$D \times 10^8$ [m ² s ⁻¹]	P [MPa]	$D_1 \times 10^8$ [m ² s ⁻¹]	$D_2 \times 10^8$ [m ² s ⁻¹]
200	7.17	8.41 ± 0.07	7.03	8.25 ± 0.02	3.24 ± 0.06
170	7.59	6.82 ± 0.06	7.41	7.18 ± 0.12	2.66 ± 0.08
150	7.87	6.02 ± 0.09	7.66	6.02 ± 0.16	2.44 ± 0.05
130	8.11	5.19 ± 0.06	7.82	5.20 ± 0.10	2.15 ± 0.01
120	8.22	4.68 ± 0.10	7.90	4.76 ± 0.30	2.04 ± 0.14
117	8.24	4.61 ± 0.14	7.93	4.59 ± 0.34	1.97 ± 0.10
115	8.28	4.46 ± 0.03	7.94	4.47 ± 0.44	1.94 ± 0.10
110	8.32	4.20 ± 0.07	7.97	4.29 ± 0.24	1.88 ± 0.14
105	8.45	4.13 ± 0.09	8.02	4.09 ± 0.22	1.84 ± 0.08
100	8.47	3.81 ± 0.06	8.10	3.81 ± 0.31	1.73 ± 0.07
95	8.62	3.50 ± 0.01	8.21	3.52 ± 0.20	1.65 ± 0.06
90	8.84	3.30 ± 0.09	8.42	3.29 ± 0.05	1.57 ± 0.03
85	9.28	3.09 ± 0.01	8.80	3.03 ± 0.01	1.47 ± 0.01
80	9.97	2.75 ± 0.06	9.45	2.79 ± 0.03	1.34 ± 0.03
75	11.2	2.64 ± 0.05	10.7	2.52 ± 0.02	1.24 ± 0.01
70	13.5	2.29 ± 0.06	13.1	2.34 ± 0.06	1.14 ± 0.02
65	17.8	1.92 ± 0.01	17.4	1.93 ± 0.06	0.97 ± 0.04
60	25.9	1.68 ± 0.07	25.8	1.66 ± 0.08	0.85 ± 0.02

dioxide and naphthalene and V is the volume of the system.

The calculated results of self-diffusion and tracer diffusion coefficients are listed in Table 3. Figure 5 shows the calculated results of the self-diffusion and tracer diffusion coefficients versus pressure with the experimental data.^{4,14} The experimental binary diffusion coefficients for the carbon dioxide + naphthalene system show an anomalous decrease near 8 MPa. However, the anomalous decrease is not shown in the simulation results. The calculated diffusion coefficients of carbon dioxide are 2–3 times larger than those of naphthalene. The tracer diffusion coefficients of carbon dioxide for the carbon dioxide + naphthalene system are slightly smaller than the self-diffusion coefficients in pure carbon dioxide at the same pressure near the critical point of carbon dioxide.

To make clear the difference of the simulation results between pure carbon dioxide and the carbon dioxide + naphthalene system, the calculated pressures were converted to the densities of pure carbon dioxide in Figure 6. The calculated results of the self-diffusion coefficients for the pure carbon dioxide system decrease linearly as shown in Figure 6. On the other hand, a small deviation from the linearity is observed for the tracer diffusion coefficients for the carbon dioxide +

naphthalene system at $0.008 \text{ mol cm}^{-3}$. This may be due to the effect of the negative partial molar volume of naphthalene. The molar density of the carbon dioxide + naphthalene system becomes smaller than that of pure carbon dioxide at the same pressure because of a volume contraction. The results of the calculated diffusion coefficients are plotted as a function of the reduced density in Figure 7. The simulation results of self-diffusion coefficients for carbon dioxide in pure carbon dioxide and the tracer diffusion coefficients for carbon dioxide in the carbon dioxide + naphthalene system are very close at the same reduced density. The calculated self-diffusion and tracer diffusion coefficients for each system decrease as a linear function of the reduced density.

Conclusions

An *NVT* ensemble single-site model molecular dynamics simulation has been applied to calculate the self-diffusion coefficients for pure carbon dioxide and the tracer diffusion coefficients for carbon dioxide + naphthalene systems at 308.2 K. The particle number and concentration do not affect the simulation results of the pressure and the self-diffusion and tracer diffusion coefficients when the systems consist of more than 256 particles. The calculated results of the tracer diffusion coefficients of carbon dioxide for the carbon dioxide + naphthalene system are slightly smaller than the self-diffusion coefficients for pure carbon dioxide at the same pressure near the critical point of carbon dioxide. This fact is considered to be due to a local density augmentation. The calculated diffusion coefficients do not show the anomalous decrease obtained by the experiment near the critical point of a mixture, because the calculated results are the self-diffusivity or tracer diffusivity of carbon dioxide and naphthalene. A simulation containing the solute-solute interactions of the mutual diffusion coefficients is required in future work to explain the anomalous diffusivity near the mixture's critical point.

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Nomenclature

D = diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
 k, l = binary interaction parameters
 k_B = Boltzmann constant, J K^{-1}
 N = number of particles
 P = pressure, Pa
 \mathbf{r} = position of a particle, m
 T = temperature, K
 t = time, s
 v = molar volume, $\text{m}^3 \text{ mol}^{-1}$
 \bar{v} = partial molar volume, $\text{m}^3 \text{ mol}^{-1}$

V = volume, m^3
 y = mole fraction

Greek Letters

σ = Lennard-Jones size parameter, m
 ϵ = Lennard-Jones energy parameter, J
 ρ = density, mol m^{-3}

Subscripts

1 = carbon dioxide
 2 = naphthalene
 C = critical property

Superscript

* = reduced value

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