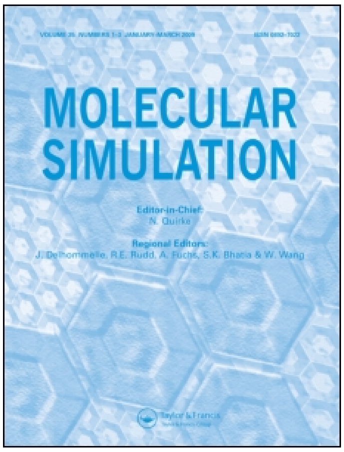

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Calculation of diffusion coefficient for supercritical carbon dioxide and carbon dioxide+naphthalene system by molecular dynamics simulation using EPM2 model

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Calculation of diffusion coefficient for supercritical carbon dioxide and carbon dioxide + naphthalene system by molecular dynamics simulation using EPM2 model

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NVT ensemble molecular dynamics (MD) simulation has been applied to calculate the self-diffusion coefficients of carbon dioxide and the tracer diffusion coefficients of naphthalene in supercritical carbon dioxide. The simulation was carried out in the pressure range from 8 to 40 MPa. The elementary physical model proposed by Harris and Yung was adopted for carbon dioxide and some approximation models were used for naphthalene. The systems of MD simulation for carbon dioxide consist of 256 particles. One naphthalene molecule was added for carbon dioxide + naphthalene system. The system can be assumed to be an infinite dilution condition for carbon dioxide + naphthalene system and the mutual diffusion coefficients are equal to the tracer diffusion coefficients of naphthalene. The self-diffusion coefficients of carbon dioxide and the tracer diffusion coefficients of naphthalene in supercritical carbon dioxide can be calculated by mean square displacement. The calculated results of diffusion coefficients showed good agreement with the experimental data without adjustable parameters.

Keywords: diffusion coefficient; molecular dynamics simulation; supercritical carbon dioxide

Nomenclature

D	diffusion coefficient, $m^2 s^{-1}$
k	angle potential parameter
k_B	Boltzman constant (1.38×10^{-23}), $J K^{-1}$
P	pressure, Pa
q	charge, $\|e\|$
r_{ij}	distance, m
r	position of molecule, m
t	time, s
U_{angle}	angle potential function, $J mol^{-1}$
$U_{non\text{-}bond}$	non-bond (van der Waals) interaction potential, $J mol^{-1}$
v	molar volume, $m^3 mol^{-1}$

Greek Letters

ε	relative dielectric constant
ε_{ij}	energy parameter, J
σ	size parameter, m
π	circle ratio
θ	angle, degree
ρ	molar density, $mol m^{-1}$

Subscripts

i, j	sites i and j
1	carbon dioxide

1. Introduction

One of the important physical properties necessary for the design of supercritical extractor, separator and reactor is the diffusion coefficient of solutes in supercritical fluids. However, measurement of diffusion coefficients under the supercritical conditions is difficult so that the diffusion

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coefficient data in the supercritical region are quite limited. Computer simulation would be feasible and helpful to obtain thermodynamic data for mixtures under high pressure.

In previous works [1–3], the authors applied single-site model molecular dynamics (MD) simulation to calculate the tracer diffusion coefficients of aromatic compounds, such as naphthalene and dimethylnaphthalene isomers, in supercritical carbon dioxide under the infinite dilution condition. The calculated results showed fairly good correlation. However, the calculated diffusivities were smaller than the experimental results, as the molecular weight increases. As a result, the assumption of sphere, such as single-site model, was not suitable for the complicated compounds. More accurate models for complicated compounds are necessary to represent the diffusion coefficients of solute in supercritical fluid. In a previous work [4], the tracer diffusion coefficients of naphthalene and dimethylnaphthalene isomers in supercritical carbon dioxide were calculated by MD simulation and the influence of molecular models on diffusion coefficients was discussed. The simulations by the united atom model and those by the all atom model for naphthalene and dimethylnaphthalene isomers are carried out and the calculated results of diffusion coefficients show good agreement with the experimental data.

In this work, as an extension, the MD simulation using the elementary physical model (EPM2) potential [5] for carbon dioxide was performed and the self-diffusion coefficients of carbon dioxide and the tracer diffusion coefficients of naphthalene in supercritical carbon dioxide were calculated.

2. Simulation methods

2.1 Models and potential functions

Carbon dioxide

Carbon dioxide was treated as a rigid and flexible model of EPM2. The Lennard-Jones (12–6) potential function with electrical term was used for all sites in the simulation,

$$U_{\text{non-bond}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r_{ij}}, \quad (1)$$

where ε_{ij} is the energy parameter, σ the size parameter, r_{ij} is the distance, q is the charge, ε is the relative dielectric constant, and i and j denote the sites i and j, respectively. The Ewald sum method was used to calculate the electrical interaction.

The angle potential shown in Equation (2) was used for the flexible model,

$$U_{\text{angle}}(\theta) = k\{1 - \cos(\theta - \theta_0)\}. \quad (2)$$

Naphthalene

Naphthalene was treated as a single-site model, a rigid model of multi-sites (united atom models) and a rigid model of all atoms (all atom model). The potential functions for naphthalene were the same as those of carbon dioxide. The schematic images of the naphthalene molecule are shown in Figure 1.

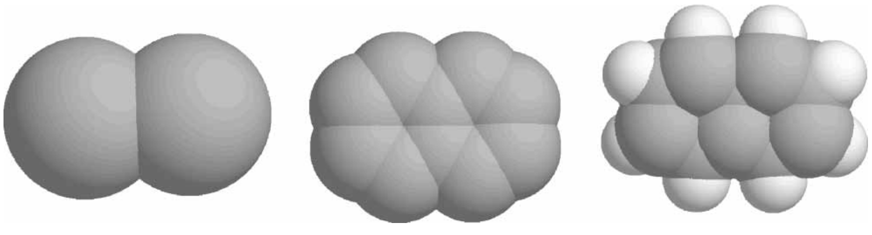
2.2 Parameters

Carbon dioxide

The potential parameters of EPM2 for carbon dioxide were referred from the model proposed by Harris and Yung [5]. These parameters were determined by the critical locus of pure carbon dioxide. The angle potential for the flexible model was determined by adjusting the *PVT* relationship of carbon dioxide in this work. The parameters of carbon dioxide used in the present study are listed in Table 1.

Naphthalene

The energy and size parameters of naphthalene for single-site model were determined by the critical temperature and pressure, the procedure being the same as that reported by the previous works [1]. The parameters for other models were obtained from literature [4,6,7]. The parameters of solute used in the present study are listed in Table 2. The interaction parameters between unlike molecules were calculated by the Lorenz–Berthelot rule.



Two-site model Ten-site model All atom model

Figure 1. Schematic images of naphthalene molecule.

Table 1. EPM2 potential parameters of carbon dioxide [5].

Atom site	σ (nm)	ε/k_B (K)	Q ($\lvert e\rvert$)	k (kJ/mol)	θ (°)
Non-bond					
C	0.2757	28.129	−0.3256		
O	0.3033	80.507	+0.6512		
Angle[a]					
O=C=O				50	0[b]

Notes: C=O bond length, $l = 0.1149$ nm.[a] Angle potential was used by flexible model and k was adjusted to *PVT* relationship. [b] The angle was defined by external angle in OCTA.

Table 2. Potential parameters of naphthalene.

Atom or site	σ (nm)	ε/k_B (K)
Single-site [1]		
Naphthalene	0.6547	554.4
Two-site [4]		
Benzene ring	0.4480	322.4
Ten-site [6]		
CH	0.3246	89.42
C	0.3246	37.72
All atom [7]		
C	0.3430	52.9
H	0.2570	22.2

2.3 Simulation conditions and analysis

Pure carbon dioxide system

Fujitsu Materials Explorer V3.0 and COGNAC 6.0.4 in OCTA2007 (http://www.octa.jp/) were used to simulate the rigid model and flexible model, respectively. *NVT* ensemble MD simulation was applied in this work. The simulations were performed at 308.2 and 323.2 K. The time step of the calculations was set to 1 fs. The time step, 1 fs, was short enough to prevent the particle from overlapping, also for the model. After more than 2×10^4 equilibration steps (20 ps), 2×10^6 production steps (2 ns) were performed. The system consists of 256 molecules. The cut-off length was set to be the half-cell. The diffusion coefficients were calculated by mean square displacement (MSD) of the centre of mass for carbon dioxide using the Einstein relationship,

$$D_{11} = \lim_{t\to\infty} \frac{1}{6t} \langle [r_1(t) - r_1(0)]^2 \rangle, \tag{3}$$

where r is the position of molecules and t is the time. The diffusion coefficients could be calculated by the slope of MSD.

Carbon dioxide+naphthalene system

COGNAC 6.0.4 in OCTA2007 was used for the simulation. *NVT* ensemble MD simulation was also applied to this system. The simulations were performed at 308.2 K. The time step of the calculations was set to 1 fs. The SHAKE algorithm was used to maintain the shape of molecules. One naphthalene molecule was added in the 256 carbon dioxide system. The systems are assumed to be at the infinite dilution condition of naphthalene and the cut-off length was set to be the half-cell. The calculated diffusion coefficients are considered to correspond to the infinite dilution diffusion coefficients of naphthalene in supercritical carbon dioxide. The diffusion coefficients were calculated by MSD of the centre of mass for naphthalene.

3. Results and discussion

3.1 Carbon dioxide system

The calculated result of *PVT* relationship at 308.2 and 323.2 K is shown in Figure 2. The calculated results of MD simulation by rigid and flexible models are in good agreement with the EOS [8] calculation. The simulated results with 80% confidence interval for the self-diffusion

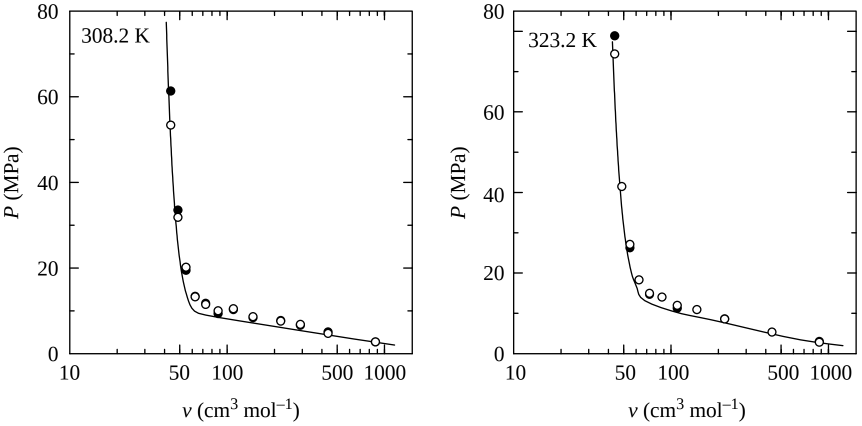


Figure 2. *PVT* relationship of pure carbon dioxide. —, calculated by EOS [8]; ●, simulated by rigid model and ○, simulated by flexible model.

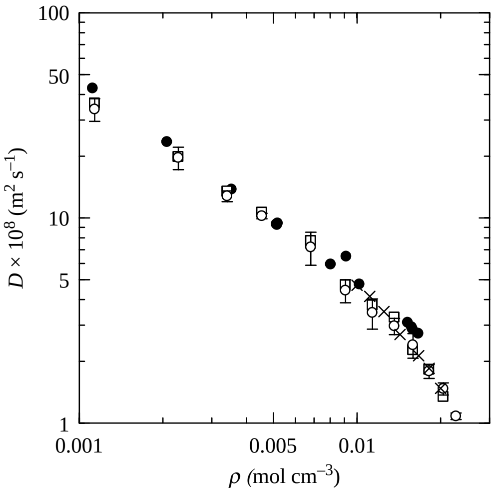


Figure 3. Self-diffusion coefficient of carbon dioxide at 308.2 K. ●, experimental data [9]; □, simulated by rigid model, ○, simulated by flexible model and ×, simulated by single-site model [1].

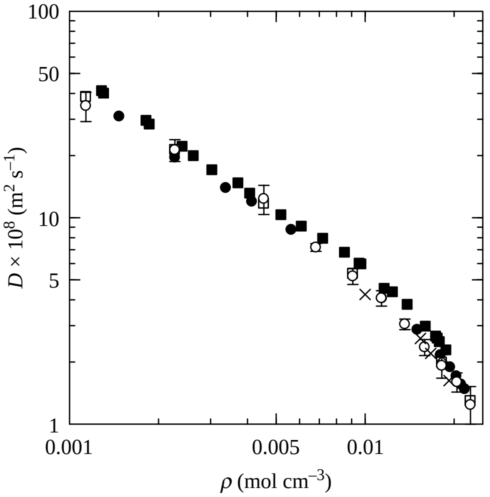


Figure 4. Self-diffusion coefficient of carbon dioxide at 323.2 K. ●, ■, experimental data [10,11]; □, simulated by rigid model; ○, simulated by flexible model and ×, simulated by single-site model [1].

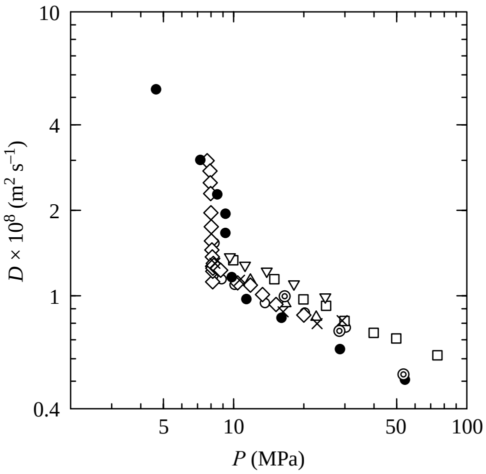


Figure 5. Diffusion coefficient of naphthalene in supercritical carbon dioxide at 308.2 K (single-site model of naphthalene). ○, △, □, ▽, ◇, experimental data [12–16]; ●, simulated by single-site model of naphthalene (original size parameters); ◎, simulated by single-site model of naphthalene (adjusted size parameters) and ×, simulated by single-site model for all components [1].

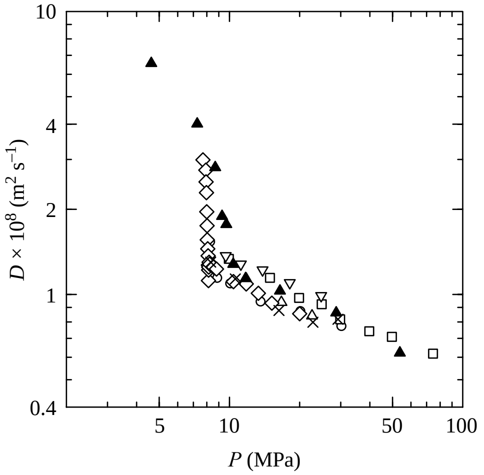


Figure 6. Diffusion coefficient of naphthalene in supercritical carbon dioxide at 308.2 K (two-site model of naphthalene). ○, △, □, ▽, ◇, experimental data [12–16]; ▲, simulated by two-site model of naphthalene and ×, simulated by single-site model for all components [1].

coefficient of carbon dioxide as a function of molar volume are shown in Figures 3 and 4. The simulated results by single-site model of carbon dioxide [1] are also plotted in the figures. The calculated results by the MD simulation of this work show good agreement with the experimental data under a wide range of densities.

3.2 Carbon dioxide + naphthalene system

The calculated results for the diffusion coefficient for naphthalene in supercritical carbon dioxide by each model are shown in Figures 5–8. The experimental results and the simulated results by the single-site model of carbon dioxide are cited from the previous work [1]. Although the adjustable parameters determined by the solubility data were used for the simulations by the single-site atom models in the previous work [1], no adjustable parameters were adopted in the simulations of this work. The simulated results of naphthalene by the single-site model and the all atom model are slightly smaller than those of the united atom models (two-site model and 10-site model). The estimated molecular size for the single-site model will be larger than the real molecular

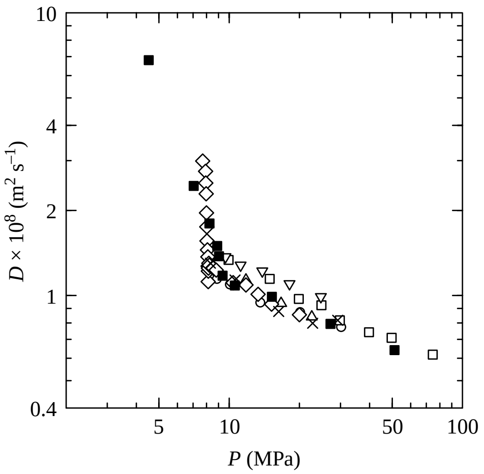


Figure 7. Diffusion coefficient of naphthalene in supercritical carbon dioxide at 308.2 K (10-site model of naphthalene). ○, △, □, ▽, ◇, experimental data [12–16]; ■, simulated by 10-site model of naphthalene and ×, simulated by single-site model for all components [1].

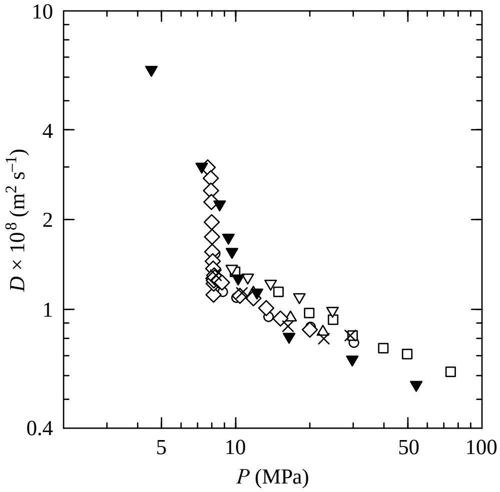


Figure 8. Diffusion coefficient of naphthalene in supercritical carbon dioxide at 308.2 K (all atom model of naphthalene). ○, △, □, ▽, ◇, experimental data [12–16]; ▼, simulated by all atom model of naphthalene and ×, simulated by single-site model for all components [1].

size. The Lennard-Jones parameters for the all atom model were determined, except the electric interaction and the parameters for the united atom models, which were determined by containing the electric interaction. Although the difference among the diffusion coefficients of naphthalene calculated by the MD in the present study was not remarkable for each model, the united atom models are well applicable to estimate the diffusion coefficient of naphthalene in supercritical carbon dioxide.

Since the deviation of calculated diffusion coefficients by single-site model is large in the range of high pressure, the size parameter of naphthalene for single-site model was adjusted to the diffusion coefficient. The size parameters between carbon and naphthalene and between oxygen and naphthalene were set to 0.9 times as long as the original values. The calculated results are also shown in Figure 5. The calculated results of diffusion coefficients at high pressure region improve using the adjusted size parameters. However, the results over 50 MPa did not improve. It is difficult to represent the diffusion coefficients under a wide pressure range by the single-site model of solute.

4. Conclusions

The MD simulations using the EPM2 model of carbon dioxide were performed to calculate the self-diffusion coefficients of carbon dioxide and the tracer diffusion coefficients of naphthalene in supercritical carbon dioxide. Some approximation models were used for naphthalene. The calculated results of diffusion coefficients were compared with the experimental results. The calculated results show that the united atom models are well applicable to estimate the diffusion coefficient of naphthalene in supercritical carbon dioxide. The calculated results of diffusion coefficient at high pressure by single-site model for naphthalene improve by adjusting the size parameters.

Acknowledgements

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