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メタデータ	言語: English 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: Higashi, Hidenori, Iwai, Yoshio, Uchida, Hirohisa, Arai, Yasuhiko メールアドレス: 所属:
URL	http://hdl.handle.net/2297/6632

A paper submitted to Journal of Supercritical Fluids (S20)

revised manuscript

Diffusion Coefficients of Aromatic Compounds in Supercritical Carbon Dioxide Using Molecular Dynamics Simulation

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NVT ensemble molecular dynamics (MD) simulation using a leap-frog algorithm has been applied to calculate the diffusion coefficients of aromatic compounds in supercritical carbon dioxide under the infinite dilution condition. The Lennard-Jones (12-6) potential function was used as a intermolecular potential. The calculated results show good agreement with the experimental data, by using the intermolecular interaction parameters between unlike molecules which are determined by Monte Carlo (MC) simulation to give good representation for the solubility data of aromatic compounds in supercritical carbon dioxide.

Keywords : computer simulation, molecular dynamics, diffusion coefficient,
aromatic compound, supercritical carbon dioxide

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Introduction

One of important physical properties needed for the design of supercritical extractor, separator and reactor is the diffusion coefficients of solutes in supercritical fluids. However, measurement of diffusion coefficients under the supercritical conditions are very difficult so that the diffusion coefficient data in the supercritical region are quite limited. Computer simulation may be feasible and helpful to obtain thermodynamic data for mixtures under high pressure. In a previous work [1], the authors have applied molecular dynamics (MD) simulation to calculate the diffusion coefficients of naphthalene and 2-naphthol in supercritical carbon dioxide under the infinite dilution condition. In this work, as an extension, the diffusion coefficients of dimethylnaphthalene isomers, phenol, phenanthrene, and pyrene in supercritical carbon dioxide were calculated by the same method.

Methods

Intermolecular Potential Function.

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

$$\phi\left(r_{ij}\right) = 4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} \tag{1}$$

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

The interaction parameters between supercritical carbon dioxide(1) and aromatic compound(2) are given as

$$\varepsilon_{12} = \left(1 - k_{12}\right)\left(\varepsilon_{11}\varepsilon_{22}\right)^{1/2} \tag{2}$$

and

$$\sigma_{12} = \left(1 - l_{12}\right)\left(\sigma_{11} + \sigma_{22}\right) / 2 \tag{3}$$

where k_{12} and l_{12} are the intermolecular interaction parameters between unlike molecules.

Intermolecular Potential Parameters.

In this work, the potential parameters of carbon dioxide were determined to represent the *PVT* data of pure carbon dioxide proposed by Angus *et al*. [2]. *NVT* ensemble MD simulation using a leap-frog algorithm with the constraint method for constant temperature proposed by Brown and Clark [3] was applied to calculate the pressure of pure carbon dioxide. The pressures P can be calculated from

$$P = \frac{NkT}{V} - \frac{1}{3V}\left\langle \sum_{i}^{N}\sum_{j>i}^{N} \frac{\mathrm{d}\phi(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \right\rangle \tag{4}$$

where V is the volume of the cell, N is the number of molecules in the cell, T is the temperature, and k is the Boltzmann constant. The values of potential parameters adopted are listed in Table 1. The potential parameters of aromatic compounds were calculated by the method proposed by Nicolas *et al*. [4] using T_C and P_C of those compounds [5]. The values of the potential parameters are also listed in Table 1.

Intermolecular Interaction Parameters.

The intermolecular interaction parameters k_{12} and l_{12} were determined to give good representation of the solubilities of aromatic compounds in supercritical carbon dioxide by using Monte Carlo simulation. Details of the calculation procedure were reported previously [6]. The systems consist of 108 particles of carbon dioxide in a cubic cell with a periodic boundary conditions. The standard Metropolis importance sampling method [7] was used to obtain new configurations. Widom's test particle method [8] was adopted to calculate the residual chemical potentials for aromatic compounds in supercritical carbon dioxide. After 2.0 $\times 10^5$ configurations of carbon dioxide were generated to reach equilibrium condition, a test

particle was tried to place at random locations 50 times for 50 configurations of carbon dioxide. The length of calculations were 5.0×10^6 to 1.8×10^7 configurations of carbon dioxide. The values of intermolecular interaction parameters at 308.2 K are listed in Table 1. The calculated results of solubilities for aromatic compounds in supercritical carbon dioxide at 308.2 K are shown Fig.1.

Calculation of Diffusion Coefficients.

NVT ensemble MD simulation using a leap-frog algorithm with the constraint method for constant temperature proposed by Brown and Clark [3] was applied to calculate the diffusion coefficients of aromatic compounds in supercritical carbon dioxide. The time step of the calculations was 10 fs. The number of equilibriation steps was more than 3.0×10^3 steps and that of the production steps was 1.0×10^6 steps. These systems consist of 256 particles. One is an aromatic compound, and the others (255) are carbon dioxide. So the systems may be at the infinite dilution condition, and the calculated diffusion coefficients may be considered as the infinite dilution diffusion coefficients of the aromatic compounds in supercritical carbon dioxide. They were calculated by mean square displacement (MSD) and velocity auto-correlation function (VAF),

$$D_{21} = \lim_{t\to\infty}\frac{1}{6t}\left\langle\left[\boldsymbol{r}_2(t)-\boldsymbol{r}_2(0)\right]^2\right\rangle \tag{5}$$

$$D_{21} = \frac{1}{3}\int_0^\infty\left\langle\boldsymbol{v}_2(t)\cdot\boldsymbol{v}_2(0)\right\rangle\mathrm{d}t \tag{6}$$

where $\boldsymbol{r}_2$ is the position, $\boldsymbol{v}_2$ is the velocity of aromatic compound, and t is the time. The diffusion coefficients calculated by these two methods have been essentially the same.

Results and Discussion

The calculated diffusion coefficients of aromatic compounds in supercritical carbon dioxide at 308.2 K are shown in Table 2 and Figs.2-5. The 68% confidence intervals of calculated values are also represented by vertical lines. The 68% confidence intervals were calculated by the ten samples of diffusion coefficients from every 1.0×10^5 steps. By using the intermolecular interaction parameters determined to represent the solubilities of aromatic compounds in supercritical carbon dioxide, the calculation results show good agreement with the experimental data. The shapes of aromatic compounds are different from spheres and are rather planer. It should be noted that the planner molecules can be assumed to Lennard-Jones particles for calculation of diffusion coefficients for the systems studied here.

Conclusions

In this work, molecular dynamics simulation was performed to calculate the diffusion coefficients of aromatic compounds in supercritical carbon dioxide under the infinite dilution condition. By using the intermolecular interaction parameters fitted to the solubilities, the diffusion coefficients of aromatic compounds in supercritical carbon dioxide can be calculated by molecular dynamics simulations with a good agreement with the experimental data. The planner molecules studied here can be approxmated by Lennard-Jones potential model for calculation of diffusion coefficients.

Acknowledgments

We gratefully acknowledge the financial support provided by "Research for the Future" Program (96P00401), The Japan Society for the Promotion of Science. The authors thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes for the use of the NEC HSP and the Supercomputer Center, Institute for Solid State Physics, University of Tokyo for the use of the FACOM VPP500. H.U. is the Research Fellow of the

Japan Society for the Promotion of Science (JSPS) for Young Scientists.

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Table 1 Potential and intermolecular interaction parameters for carbon dioxide(1)-aromatic compound(2) systems

Molecule	ε / k [K]	σ [nm]	k_{12}	l_{12}

Carbon dioxide	236.1	0.372	-	-
2,6-Dimethylnaphthalene	570.8	0.727	0.10	0.05
2,7-Dimethylnaphthalene	571.1	0.727	0.10	0.05
Phenol	514.2	0.547	-0.07	0.05
Phenanthrene	650.4	0.764	0.05	0.10
Pyrene	693.0	0.804	0.09	0.10

Table 2 Calculated results of diffusion coefficients for aromatic compound in supercritical carbon dioxide at 308.2 K.

Aromatic Compounds	P [MPa]	$D_{21} \times 10^8$ [m^2s^{-1}]
2,6-Dimethylnaphthalene	23.0	0.71
	16.3	0.79
	10.6	0.98
	8.0	1.07
2,7-Dimethylnaphthalene	23.0	0.67
	16.4	0.73
	10.5	0.92
	8.2	0.99
Phenol	16.0	1.10
	10.7	1.41
	8.4	1.48
Phenanthrene	25.4	0.62
	19.7	0.69
	15.8	0.76
	10.2	0.92
	7.8	1.03
Pyrene	25.6	0.63
	19.9	0.70
	15.9	0.76
	10.0	0.83
	7.8	0.94

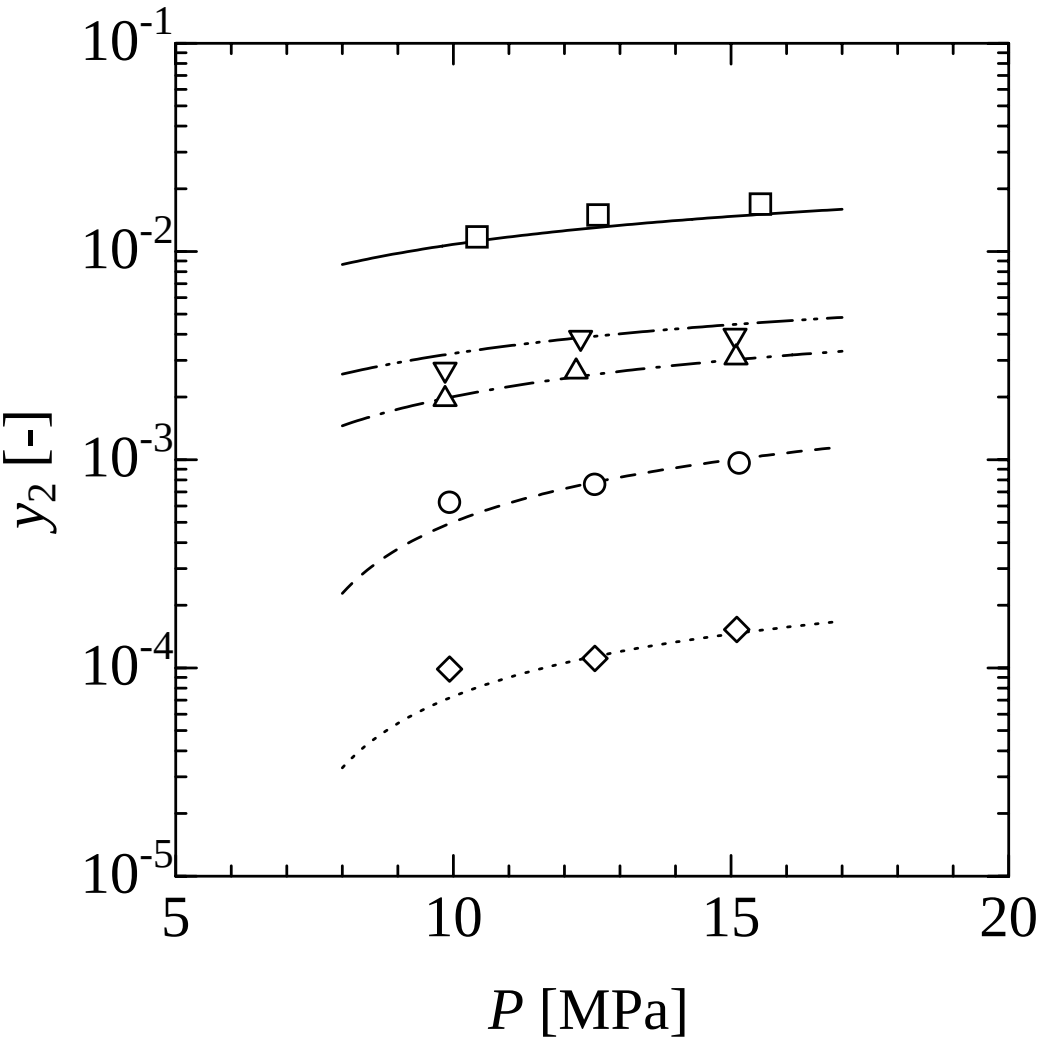
Fig.1 Solubilities of aromatic compounds in supercritical carbon dioxide at 308.2 K. Experimental: (- - - - -) 2,6-dimethyl-naphthalene, Iwai et al. [9] and Kurnik et al. [10]; (- · - · -) 2,7-dimethylnaphthalene, Iwai et al. [9]; (——) 309.2 K, phenol, Leer and Paulaitis [11]; (- - - - -) phenanthrene, Bartle et al. [12]; (· · · · · ·) pyrene, Johnston et al. [13]. MC calculations: (△) 2,6-dimethyl-naphthalene; (▽) 2,7-dimethylnaphthalene; (□) 309.2 K, phenol; (○) phenanthrene; (◇) pyrene.

Fig.2 Diffusion coefficients of 2,6-dimethyl-naphthalene and 2,7-dimethylnaphthalene in supercritical carbon dioxide at 308.2 K. Experimental: (▲) 2,6-dimethylnaphthalene; (▼) 2,7-dimethylnaphthalene, Higashi et al. [14]. MD calculations: (△) 2,6-dimethyl-naphthalene; (▽) 2,7-dimethylnaphthalene; vertical lines represent fluctuations in calculated results.

Fig.3 Diffusion coefficients of phenol in supercritical carbon dioxide at 308.2 K. Experimental: (●) Lai and Tan [15]. MD calculations: (○); vertical lines represent fluctuations in calculated results.

Fig.4 Diffusion coefficients of phenanthrene in supercritical carbon dioxide. Experimental: (■) 308.2 K, Smith et al. [16]; (◆) 308.2 K, Akgerman et al. [17]; (□) 303.2 K; (□) 313.2 K, Sassiat et al. [18]. MD calculations: (□) 308.2 K; vertical lines represent fluctuations in calculated results.

Fig.5 Diffusion coefficients of pyrene in supercritical carbon dioxide. Experimental: (▲) 303.2 K; (▼) 313.2 K, Sassiat et al. [18]. MD calculations: (△) 308.2 K; vertical lines represent fluctuations in calculated results.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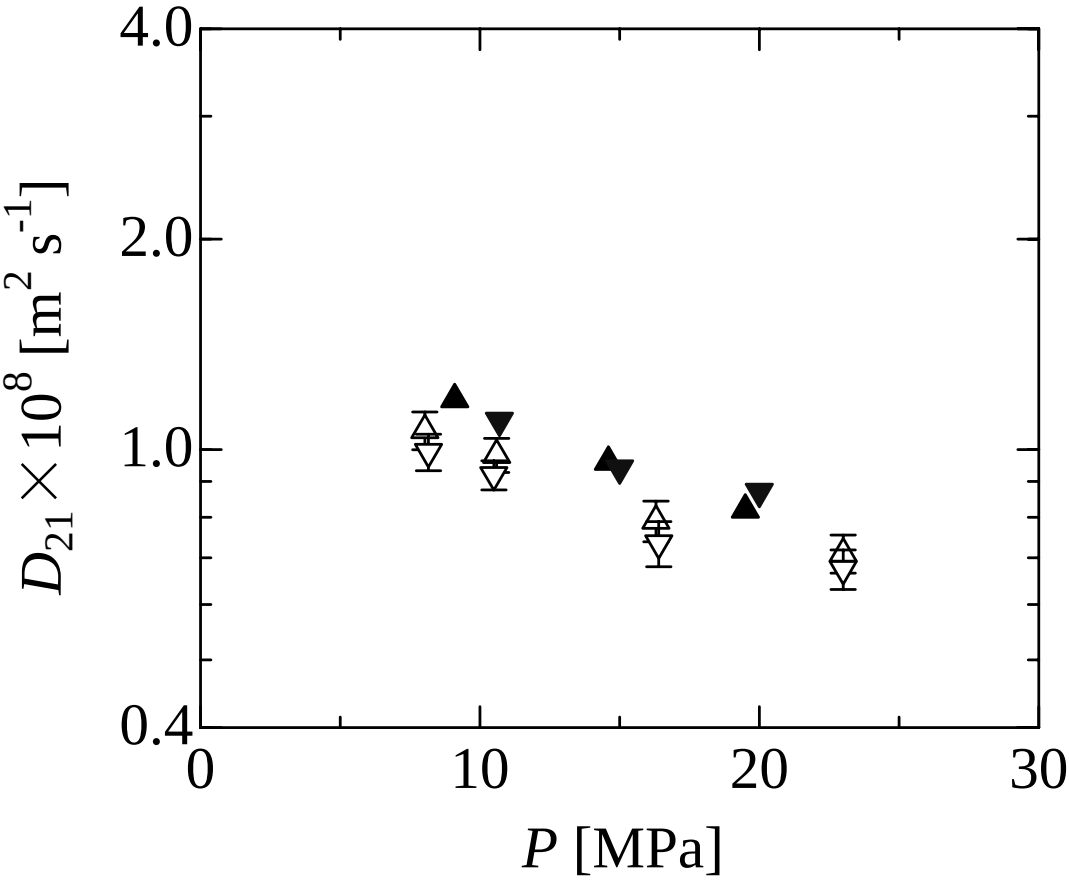
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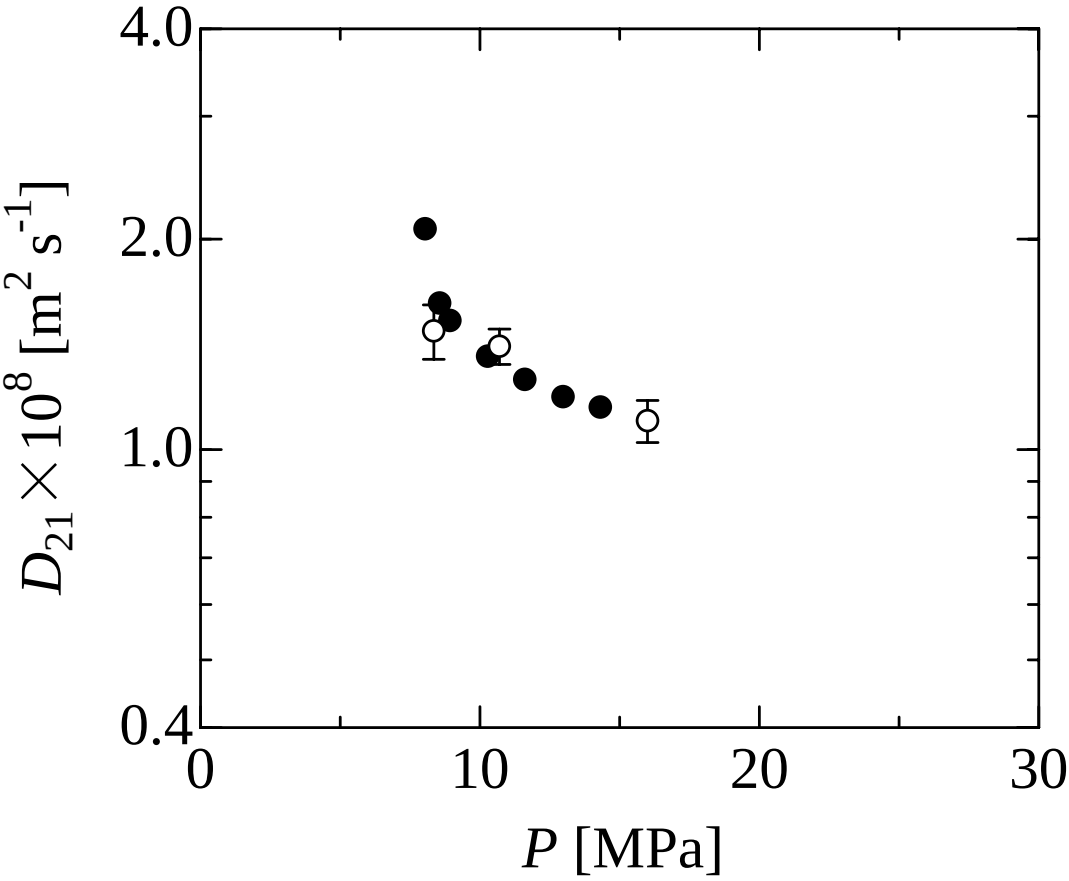
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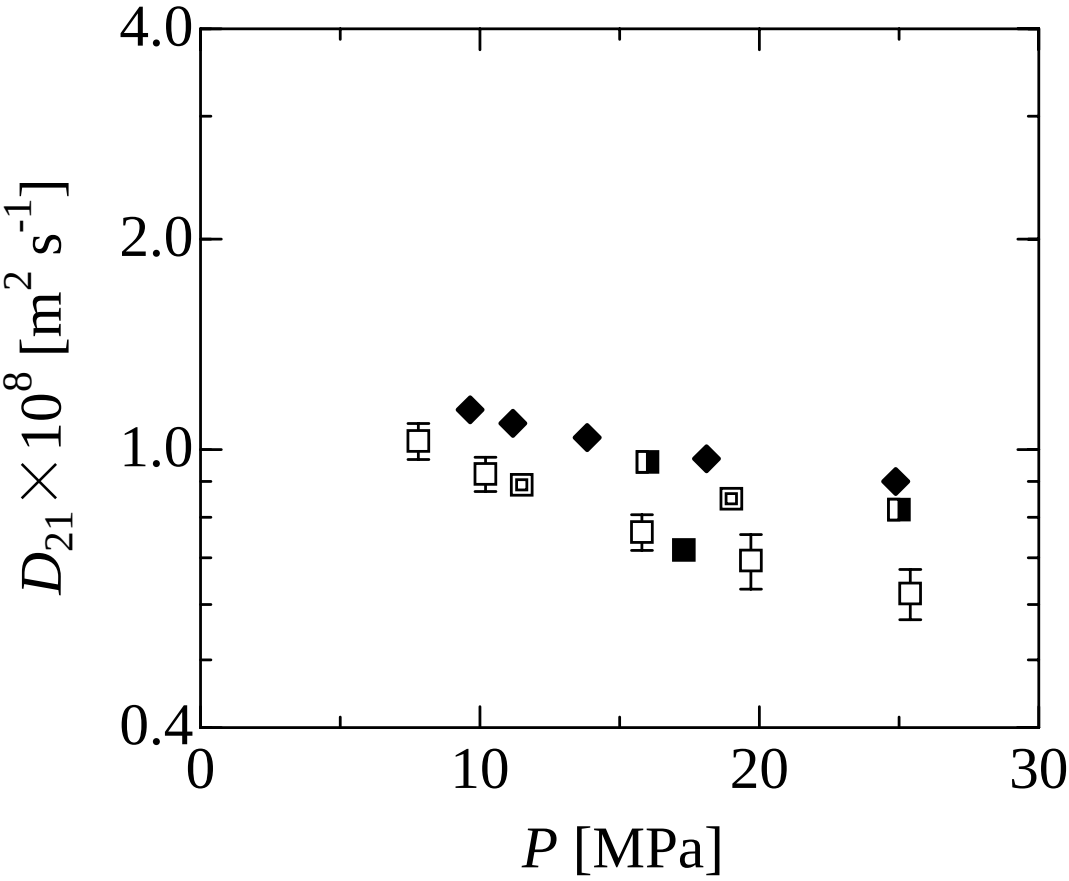
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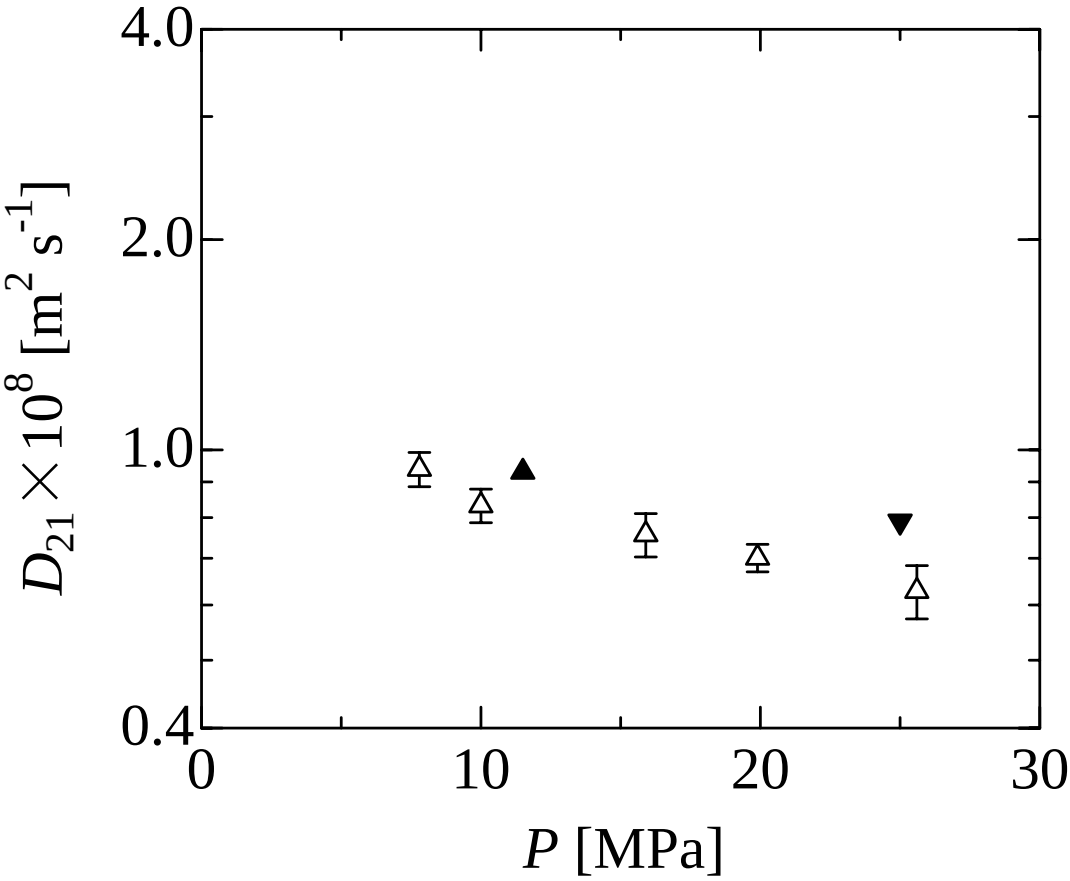
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