



Article

Estimation of CO₂ Separation Performances through CHA-Type Zeolite Membranes Using Molecular Simulation

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Abstract: Chabazite (CHA)-type zeolite membranes are a potential material for CO₂ separations because of their small pore aperture, large pore volume, and low aluminum content. In this study, the permeation and separation properties were evaluated using a molecular simulation technique with a focus on improving the CO₂ separation performance. The adsorption isotherms of CO₂ and CH₄ on CHA-type zeolite with Si/Al = 18.2 were predicted by grand canonical Monte Carlo, and the diffusivities in zeolite micropores were simulated by molecular dynamics. The CO₂ separation performance of the CHA-type zeolite membrane was estimated by a Maxwell–Stefan equation, accounting for mass transfer through the support tube. The results indicated that the permeances of CO₂ and CH₄ were influenced mainly by the porosity of the support, with the CO₂ permeance reduced due to preferential adsorption with increasing pressure drop. In contrast, it was important for estimation of the CH₄ permeance to predict the amounts of adsorbed CH₄. Using molecular simulation and the Maxwell–Stefan equation is shown to be a useful technique for estimating the permeation properties of zeolite membranes, although some problems such as predicting accurate adsorption terms remain.

Keywords: CO₂ separation; zeolite membrane; chabazite; grand canonical Monte Carlo; molecular dynamics; Maxwell–Stefan equation



Citation: Hasegawa, Y.; Natsui, M.; Abe, C.; Ikeda, A.; Lundin, S.-T.B. Estimation of CO₂ Separation Performances through CHA-Type Zeolite Membranes Using Molecular Simulation. *Membranes* **2023**, *13*, 60. <https://doi.org/10.3390/membranes13010060>

Academic Editors: Norikazu Nishiyama, Shigeyuki Uemiyu, Nobuo Hara and Kueir-Rarn Lee

Received: 30 November 2022

Revised: 26 December 2022

Accepted: 30 December 2022

Published: 3 January 2023



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1. Introduction

Zeolite membranes separate via molecular sieving and selective adsorption, which makes them a promising candidate technology for energy-efficient separations. Geus et al. successfully formed polycrystalline MFI-type zeolite layer on a porous substrate and investigated the permeation properties of hydrocarbons [1–5]. In the 1990s, Kita and coworkers developed a commercially available LTA-type zeolite membrane and applied it to dehydration of ethanol [6–8].

Although it is well known that polymeric membranes are currently employed [9–12], zeolite membranes exhibit excellent dehydration performance. FAU, DDR, AEI, and CHA-type zeolite membranes show high CO₂ separation performance [13–28]. Kusakabe et al. developed the FAU-type zeolite membranes, and the influence of the membrane composition and cations species on the adsorption and diffusion properties of CO₂ in the zeolite were investigated to improve the CO₂ separation performance [13–16]. As a result, the CO₂ permeance and CO₂/N₂ permeance ratio were ca. 10^{−6} mol m^{−2} s^{−1} Pa^{−1} and 40–100, respectively. Noble and coworkers investigated a SAPO-34 membrane and applied it to CO₂ separation from CH₄ [17–19]. The CO₂ permeance and CO₂/CH₄ permeance ratio were ca. 10^{−6} mol m^{−2} s^{−1} Pa^{−1} and 80–170, respectively. DDR-type zeolite membranes [20,21] exhibited a higher CO₂/CH₄ permeance ratio of 200–2000, although the CO₂ permeance was lower than those of FAU and CHA-type zeolite membranes. Recently, we have developed a high-silica CHA-type zeolite membrane (Si/Al = 18) for CO₂ separation [26–28]. The CO₂ permeance and CO₂/CH₄ permeance ratio were ca. 5 × 10^{−7} mol m^{−2} s^{−1} Pa^{−1}

and 200, respectively. This is important for improving the CO₂ separation performance to understand the permeation mechanisms in zeolite membranes.

There are many reports about the permeation and separation mechanisms in zeolite membranes [3–5,14–16]. Since CO₂ and hydrocarbon molecules adsorb onto zeolite strongly, the adsorbed molecules move to a neighboring adsorption site according to the concentration gradient across the membrane. The permeation phenomenon due to the surface diffusion is quantitatively described by the Maxwell–Stefan equation [3–5]. Many studies have predicted the permeation and separation properties of zeolite membranes from the adsorption and diffusion properties of single gases. Bakker et al. checked that the equation is suitable for expression of the single gas permeation properties through a silicalite-1 membrane [4]. Additionally, van den Broeke et al. applied the equation to separation of binary hydrocarbon mixtures [5], and the gas permeation properties for binary mixtures could be described using the adsorption and diffusion parameters obtained by single component gases.

The permeation and separation properties of zeolite membranes are explained by adsorption of molecules on zeolite and diffusion in zeolite channels. Both the adsorption and diffusion properties can be predicted by molecular simulation such as grand canonical Monte Carlo and molecular dynamics, respectively [29–34]. Vujic et al. reported the potential parameters applicable to many zeolites [33].

In this study, the CO₂ separation performances of CHA-type zeolite membranes with Si/Al = 18 were predicted using the molecular simulation technique and Maxwell–Stefan equation to understand the permeation behavior in CHA-type zeolite membranes.

2. Theory

2.1. Molecular Simulation

The interaction between adsorbate and adsorbent atoms is described as the sum of interactions between bonded and nonbonded atoms as [33]:

$$\Phi_t = \Phi_{\text{bond}} + \Phi_{\text{non-bond}} \quad (1)$$

The interaction between bonded atoms is calculated as the sum of bond-stretching and angle-bending as:

$$\Phi_{\text{bond}} = \Phi_{\text{bond-stretch}} + \Phi_{\text{angle-bend}}, \quad (2)$$

$$\Phi_{\text{bond-stretch}} = \frac{1}{2}k_b(r - r_0)^2, \quad (3)$$

$$\Phi_{\text{angle-bend}} = \frac{1}{2}k_\theta(\theta - \theta_0)^2, \quad (4)$$

where k_b and k_θ are the force constants for bond-stretching and angle-bending, respectively. The interaction between nonbonded atom pair is calculated as the sum of van der Waals and coulomb interactions as:

$$\Phi_{\text{non-bond}} = \Phi_{\text{vdW}} + \Phi_{\text{coulomb}}, \quad (5)$$

$$\Phi_{\text{vdW}} = 4\phi_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (6)$$

$$\Phi_{\text{coulomb}} = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q_i Q_j}{r_{ij}}, \quad (7)$$

where the depth of interaction ϕ_{ij} and zero-interaction distance σ_{ij} for the pair of different atoms are calculated as:

$$\phi_{ij} = \sqrt{\phi_i \phi_j}, \quad (8)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j). \quad (9)$$

When two atoms are in the same structure and separated by three covalent bonds (known as a 1–4 interaction), the interaction is treated as a nonbonded interaction with scaling factor of 0.5. Nonbonded interactions are ignored for directly bonded atoms (1–2 interaction) and two atoms separated by two bonds (1–3 interaction) since they are included in the bond-stretching and angle-bending interactions.

2.2. Gas permeation through Zeolite Layer

Zeolite membranes are often prepared on porous supports, as shown in Figure 1. The molecules are transferred by the concentration gradient across the membrane.

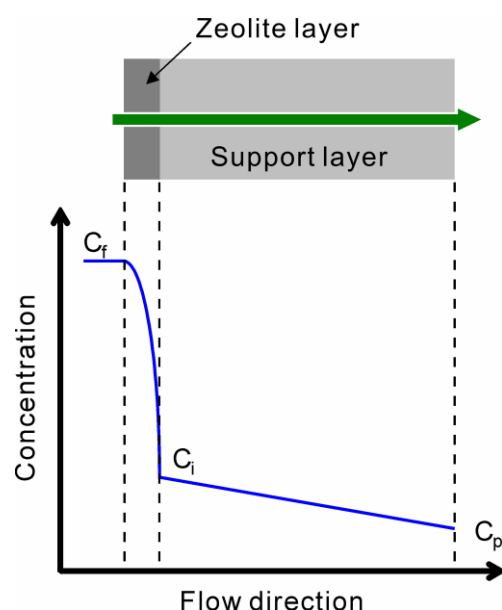


Figure 1. Schematic illustration of concentration gradient across the zeolite membrane supported by porous substrate. C_f is the concentration in the feed, C_p is the concentration in the permeate, and C_i is the concentration at the interface of the zeolite and support layers.

In the zeolite layer, molecules adsorbed on the adsorption sites within zeolite channels, and then move to a neighboring site according to the concentration gradient. The permeation flux is described as [3–5]:

$$\begin{pmatrix} J_1 \\ \vdots \\ J_n \end{pmatrix} = -\varepsilon\rho \begin{bmatrix} a_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & a_n \end{bmatrix} \begin{bmatrix} B_{11} & \cdots & B_{1n} \\ \vdots & \ddots & \vdots \\ B_{n1} & \cdots & B_{nn} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & \cdots & \Gamma_{1n} \\ \vdots & \ddots & \vdots \\ \Gamma_{n1} & \cdots & \Gamma_{nn} \end{bmatrix} \begin{pmatrix} \nabla\Theta_1 \\ \vdots \\ \nabla\Theta_n \end{pmatrix}. \quad (10)$$

The elements of matrix B are calculated by:

$$B_{ii} = \frac{1}{D_i} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{\Theta_j}{D_{ij}}, \quad B_{ij} = -\frac{\Theta_i}{D_{ij}}, \quad (11)$$

where the mutual diffusivity can be approximated as:

$$D_{ij} = D_i^{\Theta_i/(\Theta_i+\Theta_j)} D_j^{\Theta_j/(\Theta_i+\Theta_j)}. \quad (12)$$

When the adsorption isotherm is described by a Langmuir Equation (13), the elements of matrix Γ are described using Equation (14).

$$q_i = a_i \Theta_i = \frac{a_i b_i p_i}{1 + \sum b_i p_i}, \quad (13)$$

$$\Gamma_{ij} = \delta_{ij} + \frac{\Theta_i}{1 - \sum_i \Theta_i}, \quad (14)$$

where $\delta_{ij} = 1$ for $i = j$, and $\delta_{ij} = 0$ for $i \neq j$. The adsorption and diffusion parameters are summarized in Tables 2 and 3, respectively.

2.3. Mass Transfer in the Support Tube

In the porous support tube, the overall permeation flux is:

$$J_t = \sum_i^n J_i = D \frac{dC}{dL}, \quad (15)$$

where L is the thickness of the support, and C is the concentration shown by:

$$C = \frac{\varepsilon p}{RT}, \quad (16)$$

where ε is the porosity of the support. The diffusivity in the porous support is estimated by the Fuller equation [4,35]:

$$D = \frac{1.01 \times 10^{-5} T^{1.75} (M_i^{-1} + M_j^{-1})^{1/2}}{p (V_i^{1/3} + V_j^{1/3})^2}, \quad (17)$$

where M_i is the molecular mass of component i and V_i is the diffusion volume of component i . The diffusion volumes of CO_2 and CH_4 were taken as 26.9 cm^3 and 25.1 cm^3 , respectively [35].

3. Methods

3.1. Adsorption on Zeolites

The adsorption isotherms of CO_2 and CH_4 on the CHA-type zeolite were simulated by a grand canonical Monte Carlo (GCMC) technique using software (Biovia, Materials Studio 2021 Sorption). For the GCMC simulation, fugacity was applied to the canonical ensemble, and the number and location of molecules with the lowest potential energy were calculated probabilistically. The cutoff distance of the van der Waals interaction was 1.25 nm, and the Ewald summation method was used for the integration of the coulomb interaction. The total number of Monte Carlo cycles were 10^6 , and the average of the final 10^5 steps were used as the simulation result. The fugacity was assumed to be equal to the pressure in this study since the difference between fugacity and pressure is less than 5% below 1 MPa.

Figure 2 shows the atomistic models of CO_2 , CH_4 , and CHA-type zeolite. The model of the CO_2 molecule reported by Harris et al. [36] was used. This model can describe the gas–liquid coexistence curve including the critical point region. The carbon atom was connected to two oxygen atoms by chemical bonds 0.1149 nm long, and the bond-stretching was ignored ($k_b = 0$). The original angle of $\text{O}=\text{C}=\text{O}$ was 180° , and the force constant was $k_\theta = 1236 \text{ kJ mol}^{-1} \text{ rad}^{-2}$. For CH_4 , the model reported by Siepmann et al. [37] was used. The carbon atom was connected to four hydrogen atoms with bond lengths of 0.11 nm, and each $\text{H}-\text{C}-\text{H}$ angle was 109.5° . Although the bond-stretching and angle-bending are ignored in this model ($k_b = k_\theta = 0$), the gas–liquid coexistence curve can be expressed. The crystal structure of the CHA-type zeolite was imported from the IZA zeolite database [38]. The CHA-type zeolite model with a composition of $\text{Si}_{91}\text{Al}_5\text{Na}_5\text{O}_{192}$ was prepared by

substituting Si atoms with Al atoms followed by introduction of Na^+ cations by GCMC simulation. Table 1 lists the non-bonding interaction parameters for CO_2 , CH_4 , and zeolite. Vujic et al. reported that the adsorption of gases such as CO_2 on CHA-type zeolite can be predicted with high accuracy by using these parameters [33].

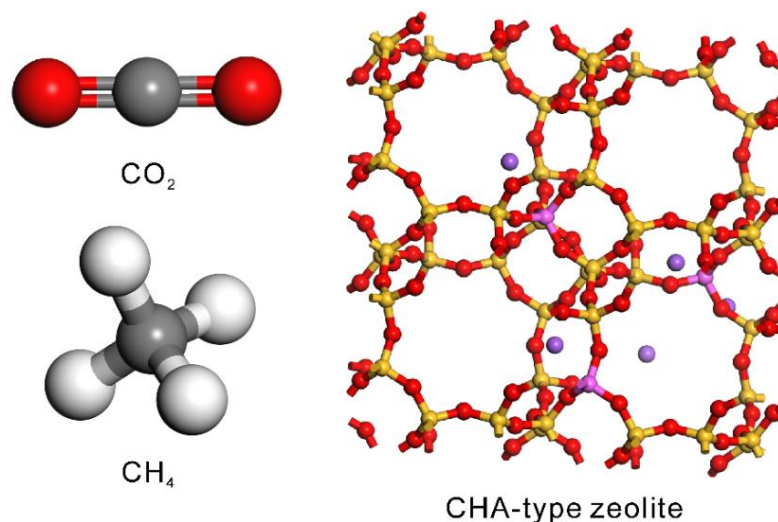


Figure 2. Atomistic models of CO_2 , CH_4 , and CHA-type zeolite used in this study.

Table 1. Nonbonding interaction parameters of CH_4 , CO_2 , and zeolite.

Molecule	Element	σ (nm)	ϵ/k (K)	q (e)	Ref.
CH_4	C	0.3730	148.0	0	[33]
	H	—	—	0	
CO_2	C	0.2757	28.1	0.6512	[32]
	O	0.3033	80.5	−0.3256	
Zeolite	Si	0.2970	32.0	1.413	[29]
	Al	0.3140	24.0	1.072	
	O(Si–O–Si)	0.3011	52.0	−0.7065	
	O(Si–O–Al)	0.3011	55.0	−0.8712	
	Na	0.3230	234.1	1.000	

3.2. Diffusion in Zeolite

The self-diffusivities of CH_4 and CO_2 in CHA-type zeolite channels were also simulated by a molecular dynamic technique (Biovia, Materials Studio 2021 Forcite Plus). CH_4 and CO_2 molecules were adsorbed at 1 MPa by GCMC, and the molecular dynamic simulation was conducted with a time step of 2 fs. The total simulation time was 1 ns, and the mean square displacement every 10 ps was plotted against the simulation time. The self-diffusivity was calculated using the slope by the Einstein equation. The procedure was repeated 5 times and the average value taken as the diffusivity.

4. Results and Discussion

4.1. Adsorption Isotherms

Figure 3 shows the adsorption isotherms of CO_2 and CH_4 on the CHA-type zeolite with Si/Al = 18.2 at 253–473 K. The amounts of adsorbed CO_2 at 253 K increased significantly at low pressures and was 6.0 mol kg^{-1} at 100 kPa. At higher pressures, in contrast, the increment became small, with 7.1 mol kg^{-1} adsorbed at 1000 kPa. This isotherm is typical for adsorption in micropores, and the relationship is described by the Langmuir equation (Equation (13)). The adsorption isotherms of CO_2 became linear as temperature increased. A similar trend was observed for CH_4 . The estimated isotherms were calculated for each temperature using the simulated points by Equation (13) and are shown as lines in

Figure 3. The agreement between simulated points and estimated isotherm suggests the Langmuir equation is applicable at 253–473 K. Furthermore, the adsorption isotherms of CO₂ and CH₄ on CHA-type zeolite have been reported by several groups [39,40] and our simulated isotherms agree well with their experimental data, which suggests that the potential parameters are reasonable for simulating the adsorption and diffusion behaviors of CO₂ and CH₄ for CHA-type zeolite.

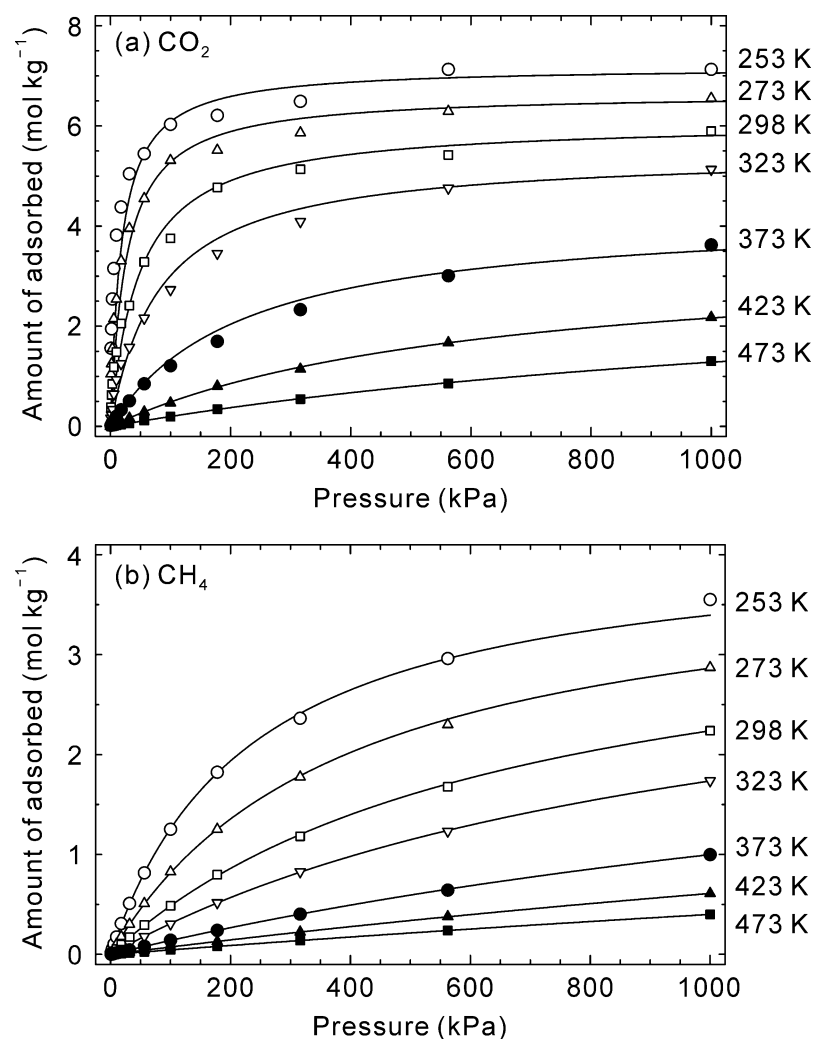


Figure 3. Simulated adsorption isotherms of (a) CO₂ and (b) CH₄ on CHA-type zeolite with Si/Al = 18.2 at 253–473 K. Symbols describe the simulated data, and lines are calculated values by Equation (13) and Table 2.

Table 2. Pre-exponential factors and activation energies of CO₂ and CH₄ for the adsorption on CHA-type zeolite with Si/Al = 18.2.

	Unit	CO ₂	CH ₄
a_i^*	mol kg ⁻¹	1.24	1.92
E_a	kJ mol ⁻¹	3.8	1.6
b_i^*	kPa ⁻¹	5.53×10^{-6}	3.57×10^{-6}
E_b	kJ mol ⁻¹	20.0	15.0

Figure 4 shows the effect of temperature on the adsorption amounts at saturation and Langmuir constants of CO₂ and CH₄. Both the saturated adsorption amounts, a , and Langmuir constants, b , decreased with increasing temperature. An Arrhenius dependence

was observed, as is typical for adsorption isotherms, with the temperature dependencies described by:

$$a_i = a_i^* \exp\left(-\frac{E_a}{RT}\right), \quad (18)$$

$$b_i = b_i^* \exp\left(-\frac{E_b}{RT}\right). \quad (19)$$

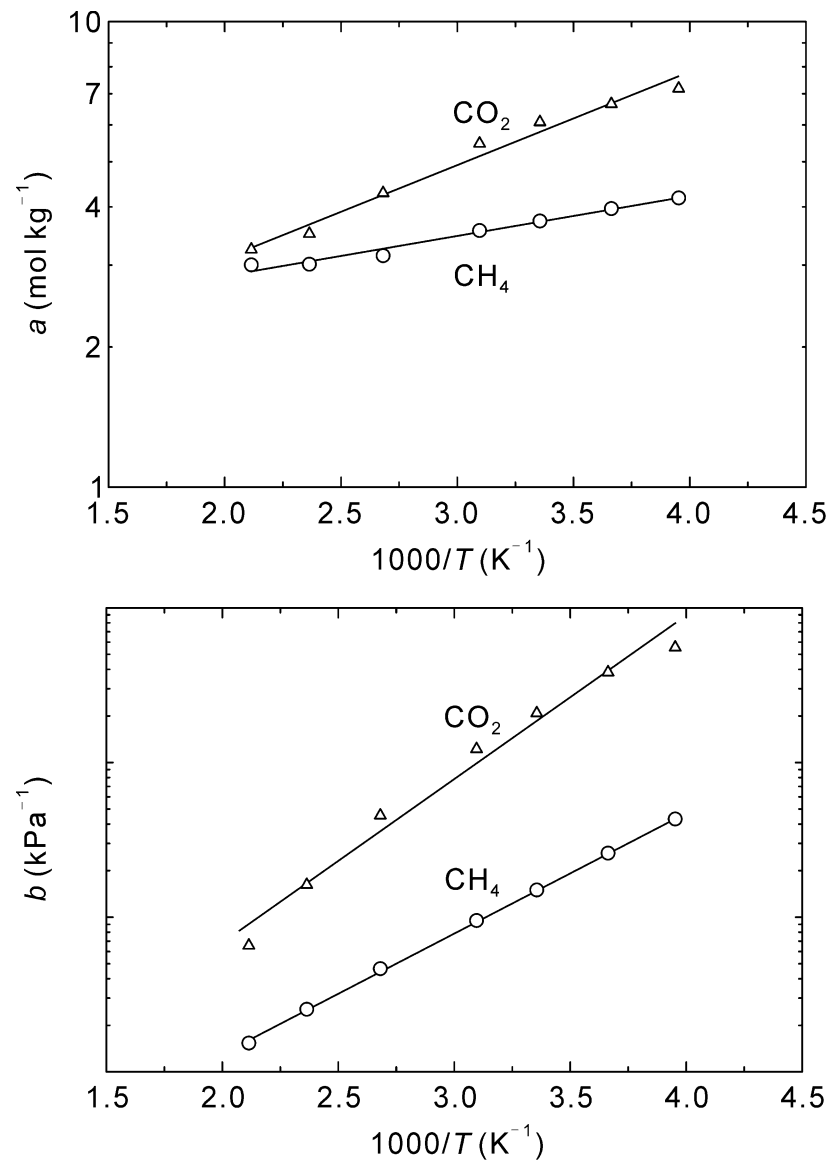


Figure 4. Arrhenius plots of amount of adsorbed at saturation a and Langmuir constant b for CO_2 and CH_4 for the adsorption on CHA-type zeolite with $\text{Si}/\text{Al} = 18.2$.

The pre-exponential factors and activation energies are listed in Table 2. Assuming the heat of adsorption is equal to $-(E_a + E_b)$, the heats of adsorption for CO_2 and CH_4 are 23.8 kJ mol^{-1} and 16.6 kJ mol^{-1} , respectively. Maghsoudi et al. experimentally measured the heats of adsorption of CO_2 and CH_4 to be 21.0 kJ mol^{-1} and 17.1 kJ mol^{-1} , respectively [40], which shows good agreement with the current work and further justifies the proposed methods for simulating the adsorption and diffusion behaviors of CO_2 and CH_4 in CHA-type zeolite.

4.2. Diffusivities

Figure 5 shows the time courses in the mean square displacement of CO₂ and CH₄ at 298–473 K. Because the mean square displacements were linearly proportional to simulation time before 1 ns, longer diffusional times were not required. The diffusivities of CO₂ and CH₄ in the CHA-type zeolite were calculated as 1/6 of the slope [33], which resulted in temperature dependencies as reported in Figure 6. The diffusivities of CO₂ and CH₄ at 298 K were $3.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, respectively. The pore diameter of the CHA-type zeolite is 0.38 nm [38], which is identical to the molecular diameter of CH₄ (0.38 nm [41]). In contrast, the molecular diameter of CO₂ (0.33 nm [41]) is smaller than the pore diameter, which results in molecular sieving behavior with a CO₂ diffusivity nearly an order of magnitude higher than CH₄.

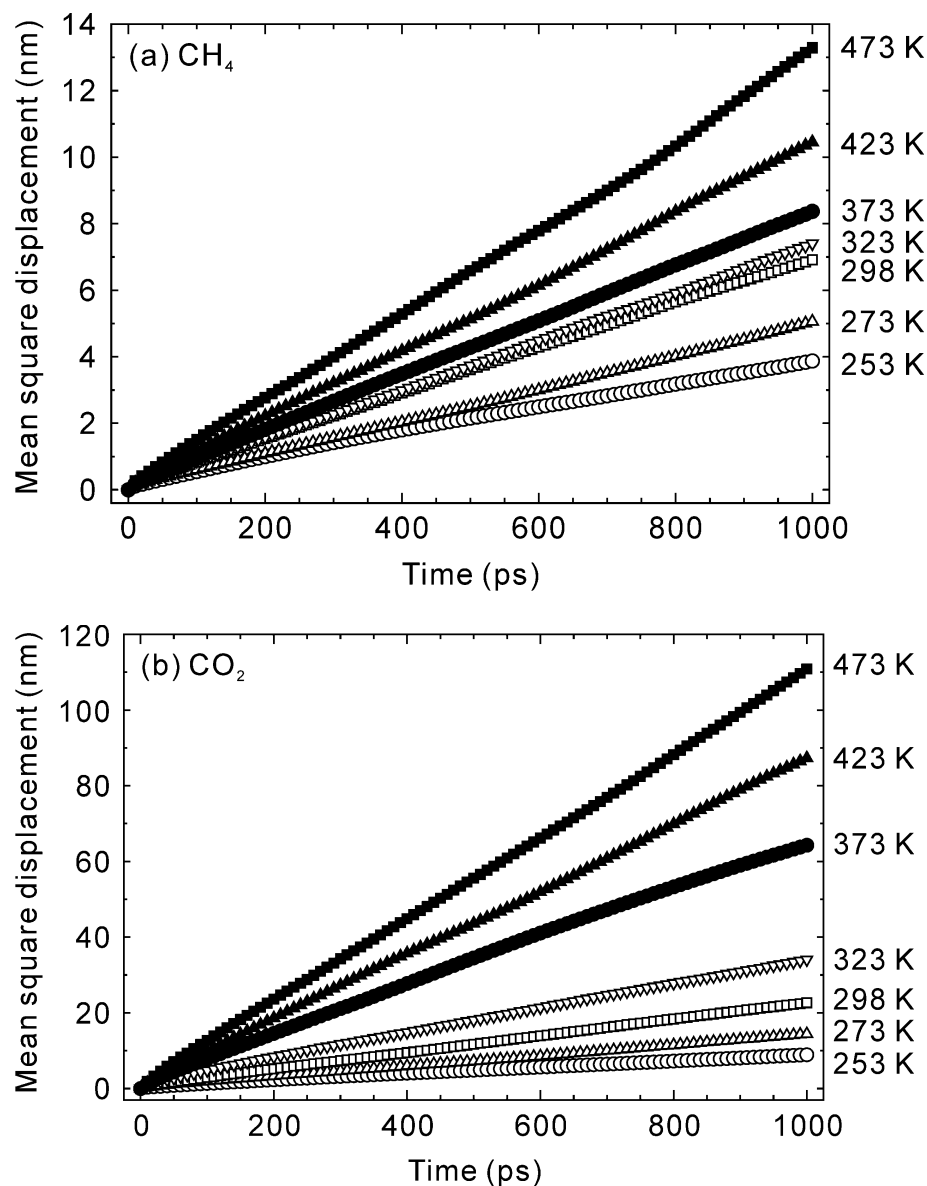


Figure 5. Time courses in the mean square displacements of (a) CH₄ and (b) CO₂ at 253–473 K.

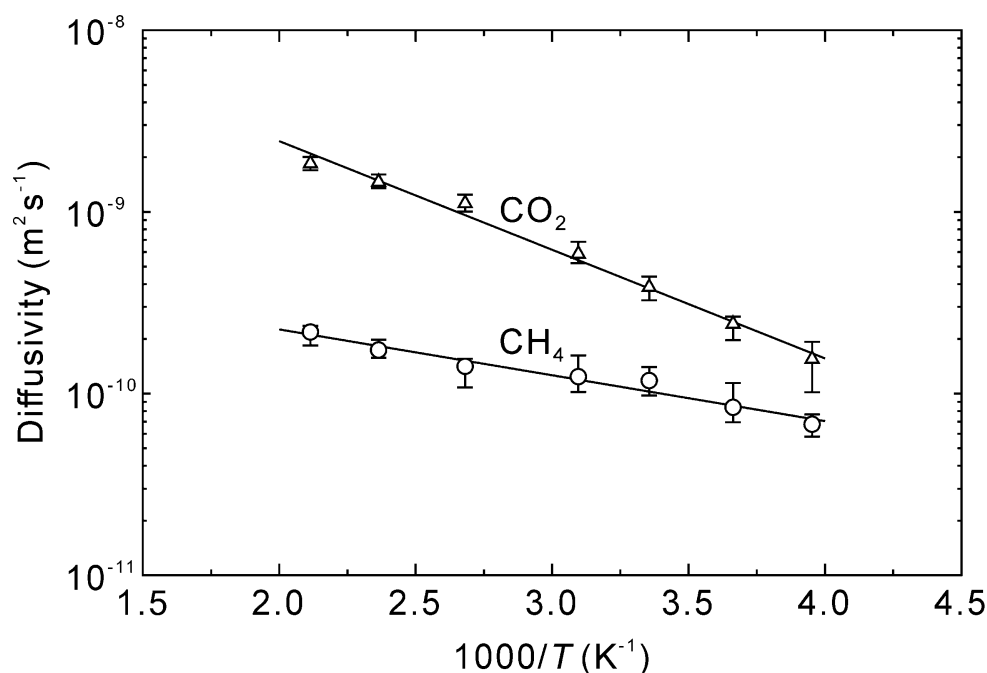


Figure 6. Arrhenius plots of CO₂ and CH₄ diffusivities within the CHA-type zeolite channels.

Vujic et al. compared to the simulated CO₂ diffusivities with those obtained by experiments [33], and the simulated diffusivities were twice higher than the experimental values for high silica zeolites. Krishna et al. [42] also simulated the diffusivities of CO₂ and CH₄ in all-silica CHA-type zeolite at 300 K. When the fugacities of CO₂ and CH₄ were 1 MPa, their diffusivities were ca. $4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for CO₂ and $8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for CH₄. The similarity in diffusivity measurements with the current work suggests aluminum and sodium do not have a significant effect on gas diffusivity. This is considered reasonable because only one aluminum and sodium atom are incorporated per cavity for a Si/Al ratio of 18.2, as shown in Figure 2.

The effect of temperature on the diffusivity is also described by the Arrhenius equation as follows:

$$D_i = D_i^* \exp\left(-\frac{E_d}{RT}\right). \quad (20)$$

The diffusivities at infinite temperature and activation energies of CO₂ and CH₄ are listed in Table 3. Sladek et al. [43] investigated the relationship between the diffusivity and heat of adsorption for physical and chemical adsorption species and concluded that the activation energy for diffusion was 0.45 times the heat of adsorption. This compares well with the current work wherein the activation energy of CO₂ diffusivity is 0.48 times the heat of adsorption.

Table 3. Diffusivities at infinite temperature and activation energies of CO₂ and CH₄ within CHA-type zeolite with Si/Al = 18.2.

	Unit	CO ₂	CH ₄
D_i^*	$\text{m}^2 \text{ s}^{-1}$	3.8×10^{-8}	7.2×10^{-9}
E_d	kJ mol^{-1}	11.4	4.8

4.3. CO₂ Separation Performance

Figure 7 shows the influence of accounting the material transfer in porous support on the calculated permeation properties of CO₂ and CH₄ for the equimolar mixture at 323 K. When the polycrystalline zeolite layer was not supported by a substrate (self-standing membrane), the permeances of CO₂ and CH₄ were predicted to

be 2.3×10^{-6} and 1.7×10^{-8} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, respectively. The permeances were reduced to 6.3×10^{-7} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ for CO_2 and 5.0×10^{-9} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ for CH_4 by supporting with the porous support (porosity = 35% and thickness = 0.3 mm). The reduction of CO_2 permeance could be explained by the porosity of the support tube and pressure drop across the support (3.9 kPa). The calculated permeance of CO_2 was almost identical to the experimental data [28]. However, the calculated CH_4 permeance was higher than the experimental value. Since the amounts of adsorbed CO_2 and CH_4 were calculated using the extended Langmuir Equation (13) in this study, it is considered that the concentration gradient of CH_4 across the polycrystalline zeolite layer was estimated to be high. As a result, the higher CH_4 permeance was obtained compared to the experiment.

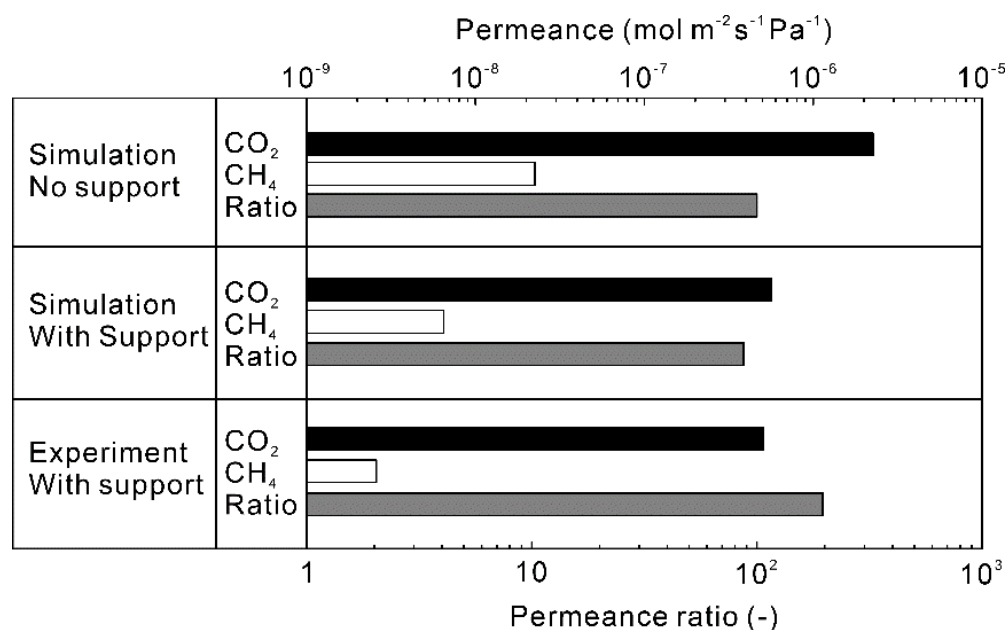


Figure 7. Comparison of simulated permeation properties of the CHA-type zeolite membrane with $\text{Si}/\text{Al} = 18.2$ to experimental results [28]. The permeation properties were calculated at CO_2 concentration = 50 vol%, total pressure = 300 kPa, and temperature = 323 K. The thickness of zeolite layer was 5 μm , and the pore size, porosity and thickness of the support tube were 150 nm, 35% and 0.3 mm [24].

Figure 8 shows the effect of temperature on the estimated permeation properties of CO_2 and CH_4 for an equimolar mixture. The permeances of CO_2 and CH_4 at 253 K were 3.3×10^{-7} and 1.8×10^{-9} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, respectively, with a resultant CO_2/CH_4 permeance ratio of 190. The CO_2 permeance increased with increasing temperature until reaching a maximum at 323 K and then decreasing with further rising temperatures. As a result, the CO_2 permeance decreased to 1.5×10^{-7} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ at 473 K, with the permeance ratio also decreasing to 38. Notably, the simulated permeances followed similar trends as the experimental data and the permeances at 473 K were nearly identical. This convergence is because the effect of preferential adsorption was marginal at 473 K compared to lower temperatures, which suggests accurate prediction of permeation properties requires accurate estimates of adsorption amounts.

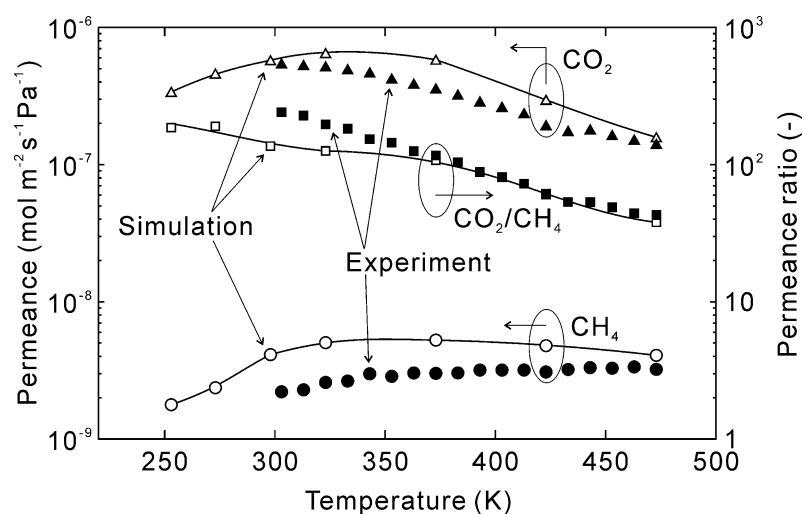


Figure 8. Effect of temperature on the permeation properties of the CHA-type zeolite membrane with Si/Al = 18.2. The permeation properties were calculated at CO₂ concentration = 50 vol% and total pressure = 300 kPa, experimental data were taken from [28].

Figure 9 shows the influence of the CO₂ concentration on the permeation properties of CO₂ and CH₄ at 303 K. The pure gas CO₂ permeance was estimated to be $3.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and slightly increased with decreasing CO₂ concentration until around 40%. However, below 40% CO₂ the CO₂ permeance increased significantly. This was due to a relative change in the permeance versus partial pressure difference between feed and permeate streams. At 40% CO₂, the partial pressures of CO₂ on the feed and permeate sides were 120 kPa and 96 kPa, respectively, with a permeate flux of $1.5 \times 10^{-2} \text{ mol m}^{-2} \text{ s}^{-1}$. At 30% CO₂ concentration, the partial pressures and permeate flux were 90 kPa, 84 kPa, and $6.0 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively. This means the relative permeate flux at 30% CO₂ compared to 40% CO₂ was 1/2.5, whereas the partial pressure difference was 1/4. As a result, the CO₂ permeance increased below 40% CO₂. For all conditions, the estimated CH₄ permeance was higher than the experimental data, as discussed in Figures 7 and 8, which is the cause of the lower CO₂/CH₄ permeance ratio.

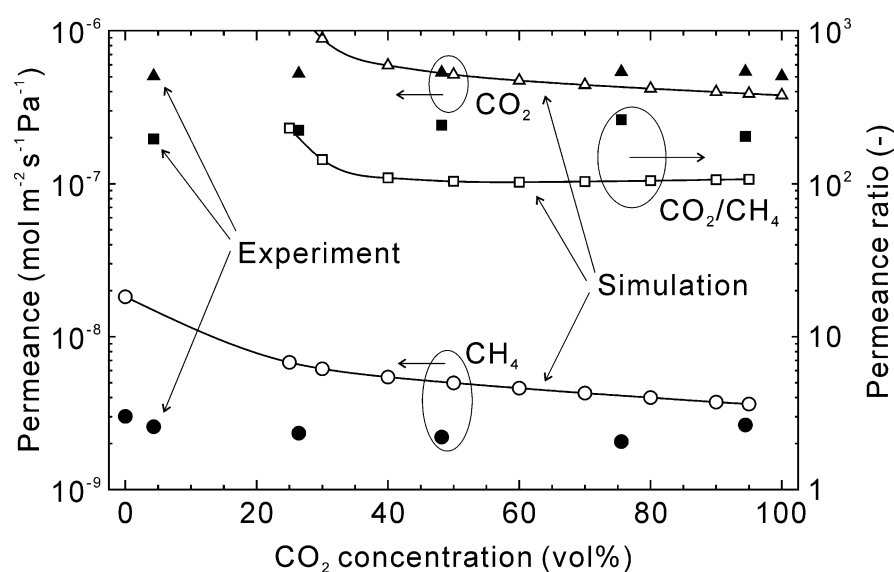


Figure 9. Influence of the CO₂ concentration on the permeation properties of the CHA-type zeolite membrane with Si/Al = 18.2 at 303 K. The permeation properties were calculated at the total pressure of 300 kPa, and experimental data were taken from [28].

Figure 10 shows the influence of the total pressure on the permeation properties of CO₂ and CH₄ at 303 K. When the total pressure was 200 kPa, the estimated permeances of CO₂ and CH₄ were 6.8×10^{-7} and 5.8×10^{-9} mol m⁻² s⁻¹ Pa⁻¹, respectively, with a CO₂/CH₄ permeance ratio of 120. The permeances decreased with increasing total pressure and at 1000 kPa were 2.9×10^{-7} for CO₂ and 2.4×10^{-9} mol m⁻² s⁻¹ Pa⁻¹ for CH₄. The decrease was calculated to be similar for both gases so the permeance ratio was nearly independent of total pressure.

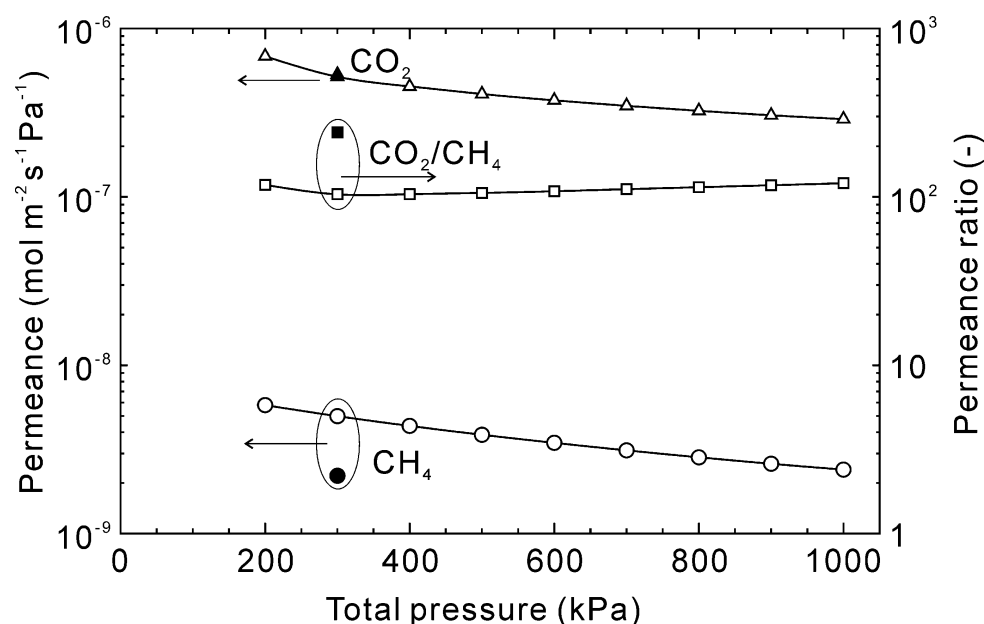


Figure 10. Influence of total pressure on the permeation properties through the CHA-type zeolite membrane with Si/Al = 18.2 at 303 K. The permeation properties were calculated at a CO₂ concentration of 50 vol%, and experimental data were taken from [28].

5. Conclusions

In this study, the permeation and separation properties of a CHA-type zeolite membrane were evaluated for improving the CO₂ separation performance. The adsorption isotherms of CO₂ and CH₄ on CHA-type zeolite with Si/Al = 18.2 were predicted by grand canonical Monte Carlo, and the diffusivities in zeolite micropores were simulated by molecular dynamics. The CO₂ separation performance of the CHA-type zeolite membrane was estimated by a Maxwell–Stefan equation, accounting for mass transfer through the support tube. In this study, the influences of the support tube, temperature, CO₂ concentration, and total pressure on the permeation properties were calculated, and the estimated permeation properties were compared with experimental data [24]. The estimated CO₂ permeance agreed well with the experimental results due to the inclusion of the effect of the support tube. However, the estimated CH₄ permeance was slightly overestimated, suggesting that better predictions of the amount of adsorbed CH₄ on both the sides of the membrane must be made to obtain more accurate results.

Author Contributions: Conceptualization, Y.H.; methodology, Y.H.; software, Y.H.; validation, Y.H.; formal analysis, Y.H.; investigation, M.N. and C.A.; resources, Y.H.; data curation, Y.H.; writing—original draft preparation, Y.H.; writing—review and editing, A.I. and S.-T.B.L.; visualization, Y.H.; supervision, Y.H.; project administration, Y.H.; funding acquisition, Y.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

a	Amount adsorbed at saturation (mol kg^{-1})
b	Langmuir constant (Pa^{-1})
B	Mobility as defined by Equation (11)
C	Concentration (mol m^{-3})
D	Diffusivity ($\text{m}^2 \text{s}^{-1}$)
E	Activation energy (kJ mol^{-1})
J	Permeation flux ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$)
k_b	Force constant for bond-stretching ($\text{kJ mol}^{-1} \text{m}^{-2}$)
k_θ	Force constant for angle-bending ($\text{kJ mol}^{-1} \text{rad}^{-2}$)
L	Thickness (m)
M	Molecular mass (g mol^{-1})
p	Partial pressure (Pa)
Q	Partial atomic charge (e)
q	Amount of adsorbed (mol kg^{-1})
r	Distance (m)
R	Gas constant ($=8.314 \text{ J K}^{-1} \text{mol}^{-1}$)
T	Temperature (K)
V	Diffusion volume (cm^3)

Symbols

Γ	Thermodynamic factor defined by Equation (14)
δ	Kronecker delta (dimensionless)
ε	Porosity (dimensionless)
ε_0	Vacuum permittivity ($=8.85 \times 10^{-12} \text{ F m}^{-1}$)
Φ	Interaction potential energy (kJ mol^{-1})
ϕ	Depth of potential (kJ mol^{-1})
θ	Binding angle (rad)
Θ	Surface coverage (dimensionless)
ρ	Density of zeolite (kg m^{-3})
σ	Distance at zero-potential energy (m)

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