

The formation and growth model of a CO₂ hydrate layer based on molecular dynamics

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Abstract (Within 150 Words)

In this work, a model was developed to predict CO₂ hydrate layer thickness. To achieve this, the mass transfer coefficients at the interface between the water phase and CO₂ hydrate layer, as well as the diffusion coefficients in the CO₂ hydrate were determined. Firstly, the dissolution behavior of the CO₂ hydrate layer was investigated to obtain its mass transfer coefficient. The experimental results show good agreement with the existing empirical equation. Secondly, molecular dynamics simulations of the CO₂ hydrate were conducted to determine the self-diffusion coefficients of CO₂ and H₂O molecules. In these calculations inter-cage hopping and intra-cage movement of molecules were identified based on the distance traveled by the molecules. Finally, the results indicate that the kinetic model proposed in this study can be used to well reproduce the layer thickness.

Topical Heading and Keywords

Clathrate hydrate, Mass transfer, Molecular dynamics simulation, Visualization

1. Introduction

In 2015 at COP21, the Paris agreement was adopted, which details a set of goals that must be achieved to keep the average global temperature rise to below 2 K above pre-industrial levels, and after to further limit the increase in temperature by another 1.5 K¹. To this aim, carbon capture and storage technology (CCS) is expected to present an effective way of reducing CO₂ emissions. The International Energy Agency have reported that CCS is necessary worldwide to achieve a 13% reduction in CO₂ emissions by 2050². Also, the International Panel on Climate Change has suggested that without CCS, it will be difficult to maintain the increase in global temperature to within 2°C by 2100³. Therefore, the use of CCS worldwide is essential for mitigating global warming.

CCS technology can be divided into two categories of processes: separation and recovery, and injection and sequestration. In separation and recovery, CO₂ is separated from the exhaust of large emission sources (e.g., thermal power stations, liquefied natural gas (LNG) plants, etc.). In injection and sequestration, the separated CO₂ is then injected into a reservoir located beneath the ground (e.g., in aquifers or depleted oil fields), where the main type of reservoir used for CO₂ storage in CCS projects is the aquifer⁴.

However, some articles have suggested that it is possible for CO₂ leakage from reservoirs to occur^{5,6}, where the CO₂ that escapes is then dissolved in surrounding water. This process is believed to result in acidification of the oceans and groundwater, damage to ecosystems, and the CO₂ is eventually released into the atmosphere, where it is thought to contribute to global warming. Therefore, CO₂ leakage into the environment needs to be prevented.

Under some conditions, a CO₂ hydrate layer may be formed between CO₂ and the surrounding water. Some studies have reported the effect that the CO₂ hydrate has on suppressing the rate that CO₂ dissolves into water^{7,8}. Therefore, the formation of a CO₂ hydrate layer is thought to be invaluable in contributing toward the prevention of CO₂ leakage.

CO₂ hydrate is a crystalline compound that consists of H₂O and CO₂ in which H₂O molecules are connected to one another via hydrogen bonding into a cage-like structure (commonly just referred to as a cage), and with CO₂ molecules trapped within it. The unit cell of CO₂ hydrate is a cube of 1.203 nm on one side ideally containing 46 H₂O molecules and 8 CO₂ molecules⁹. However, the actual number of molecules is known to be smaller, and specific numbers have been measured and reported¹⁰.

As one of the mechanisms to suppress the dissolution rate of CO₂, some molecular dynamics study reported the distinctive mechanism of diffusion of CO₂ molecules in the CO₂ hydrate^{11,12}. As mentioned above, CO₂ is trapped inside cages made up of H₂O molecules. Thus, it is considered that there are two types of ways in which CO₂ molecules can move. One is intra-cage movement, in which CO₂ molecules do not escape the cage.

The other is inter-cage movement, in which CO₂ molecules moves between two cages in the form of “hopping”¹¹. Hopping is thought to enable CO₂ molecules to diffusion into a CO₂ hydrate¹¹. Therefore, this hopping process needs to be investigated to quantify the self-diffusion coefficient of the CO₂ molecules.

However, to the best of our knowledge, there are no studies in the literature that report the diffusion coefficients of H₂O molecules, although, Liang et al.¹³ have reported the presence of H₂O molecules also trapped within the cage. These H₂O molecules are able to travel between cages in the same way as the CO₂ molecules.

Therefore, to evaluate the suppression effect of the CO₂ hydrate, the mass transfer around the CO₂ hydrate layer needs to be elucidated. Thus, the transition of the hydrate layer thickness as a result of mass transfer needs to be focused on. To date, growth models for CO₂ hydrate have been proposed and reviewed by Yin et al.¹⁴ However, there are only a few examples that have been reported that are similar to the real-life process. Therefore, in previous work, we measured the time transition of the layer thickness of a CO₂ hydrate layer¹⁵. Additionally, we developed a kinetic model of the growth rate of a flat-plate CO₂ hydrate layer, and found that there was good agreement with the experimental results at the laboratory scale¹⁵. There are two types of key parameters in the developed model, the mass transfer coefficient at the interface, and the mass diffusion coefficient of the hydrate. Since these parameters are not clear, some assumptions needed to be made about the growth rate of the hydrate layers. However, these assumptions need to be clarified to extend the scope of this model.

Figure 1 shows the reported mass transfer coefficient of CO₂ at the interface of the CO₂ hydrate and water has been reported. In previous studies, the shape of the interface has been described as being mainly spherical, sometimes as a water phase that allows flow. Gabitto et al.¹⁶, Zhang et al.¹⁷, and Aya et al.¹⁸ conducted experiments on the CO₂ droplets. Since the surrounding water phase flows, there are some differences between the values reported by, with those of Gabitto et al. and Zhang et al. being higher than those of Aya et al. The same is true for some of the reports on the mass transfer coefficients of CO₂, as the coefficient depends on the shape of the interface and flow conditions of the surrounding water. Therefore, the mass transfer coefficient of CO₂ needs to be determined in water without flow on a flat surface.

To this aim, the molecular diffusion coefficients of CO₂ in CO₂ hydrate were measured both experimentally and via MD simulations, the results of which are shown in Figure 2.

Experimental molecular diffusion coefficients of CO₂ in CO₂ hydrate have been reported by Takeya et al.¹⁹ and Falenty et al.²⁰ Due to the experimental apparatus used in the experiments, values above the melting point of ice are hard to obtain. Hence, in this study an approximation curve for each result was drawn using the aforementioned developed model. In Figure 2, the black dotted lines indicate an approximation curve to the values

obtained from neutron diffraction and pressure–volume–temperature (PVT) cell measurements. The approximation shows a range of an order of magnitude of around 280 K.

However, there are values reported in the literature that have also been obtained using a MD approach. The values reported by Demurov et al.²¹ are considerably greater than the experimental values. And, even in cases where the calculated values reported are similar to the experimental values, as in work by Liang et al., the values have a wide margin of error¹³. To date, the closest match between calculated and experimental values was reported by Lo et al.¹², as their calculated values are in good agreement with the results of PVT measurements conducted by Falenty et al.. Lo et al. calculated the diffusion coefficient of CO₂ molecules by counting the number of hops that occur between cages. Hence, their calculation method is consistent with what is experimentally observed. However, the system they used in the simulation lacked only a CO₂ molecule, despite this number being greater in real observations. Therefore, the movement of molecules in the CO₂ hydrate needs to be simulated for a more realistic situation.

To this end, to extend the scope of the kinetic growth model of the CO₂ hydrate layer, the assumptions need to be clarified, which first requires the model to be modified. Then, the mass transfer and molecular diffusion coefficients need to be ascertained. After that, the mass transfer coefficient needs to be calculated according to the growth behavior of the CO₂ hydrate layer. In terms of the diffusion coefficients, MD simulations of the CO₂ hydrate were conducted to calculate the diffusion coefficients of both the CO₂ and H₂O molecules. Finally, the mass transfer coefficients of the CO₂ hydrate and the self-diffusion coefficient of the CO₂ hydrate were applied to the kinetic model of the hydrate layer growth, and the estimations were compared with the experimental values.

2. Theory of the macroscale kinetic model for clathrate hydrate layer growth

The developed kinetic model used to investigate the clathrate hydrate layer growth was reported previously in the literature. In this section, a new model is developed that approaches the phenomena in question more rigorously.

Figure 3 shows the distribution of the CO₂ and H₂O around the CO₂ hydrate layer. This system consists of 3 phases; liquid CO₂ in the upper half, water in the lower half, and a CO₂ hydrate layer in the middle. The concentrations of both chemical species are represented by the curved lines in the middle of the figure, where the dotted line represents H₂O and the solid line represents CO₂.

Before developing this model, some assumptions were made. First, it is thought that large vacancies such as capillaries do not exist in the hydrate, as CO₂ hydrate is immediately formed at the interface if liquid CO₂ comes directly into contact with water. Second, both the CO₂ and H₂O molecules are able to penetrate the CO₂ hydrate. Someya

et al.²² reported the shrinkage of CO₂ droplets in H₂O, however, conversely, Kuang et al.²³ reported the shrinkage of a H₂O phase in liquid CO₂. These results indicate that both CO₂ and H₂O are able to penetrate the CO₂ hydrate layer. Additionally, the results also indicate that the formation and dissociation of the CO₂ hydrate occur at both interfaces of the CO₂ hydrate. Thus, a third assumption was made in which formation and dissociation occur at both interfaces.

With this assumption, the mass flux can be calculated according to the analogy between the mass and heat transfer. The system can be defined by heat transfer between two liquids separated by a wall. Heat is transported in two ways in such a system. Convection transport of the heat occurs between the liquid phase and the surface of the wall and diffusion transport of the heat occurs in the wall.

The heat flux J_j^H by convection can be described using:

$$J_j^H = h_j^H \Delta T \quad (1)$$

where, h_j^H represents the heat transfer coefficient at the j phase, and ΔT represents the temperature difference between the surface of the wall and at infinity.

The heat flux J_w^H by diffusion can be expressed as follows:

$$J_w^H = \frac{k}{\delta_w} \Delta T \quad (2)$$

where, k represents the thermal conductivity, δ_w represents the thickness of the wall, and ΔT represents the temperature difference between the surfaces of the wall.

From these equations, the heat flux through the wall can be expressed as:

$$J^H = \alpha^H \Delta T \quad (3)$$

$$\text{where } \alpha^H = \frac{1}{\frac{1}{h_1^H} + \frac{1}{h_2^H} + \frac{\delta_w}{k}} \quad (4)$$

where α is the overall heat transfer coefficient and ΔT represents the temperature difference between two liquids. The values of h_1 , h_2 , and k need to be known in order to determine α^H . The thermal diffusivity h is easy to determine because it is dependent on the material of the wall. However, the thermal conductivity k is quite difficult to ascertain because it depends on the condition of both of the flow and the geometry of the surface. However, there are empirical equations that can be used to calculate these coefficients. If convective heat transfer occurs upward from a heated plate or downward from a cooled plate, the heat transfer coefficients can be calculated using the equation below.

$$Nu = \frac{h_j L}{k_j} \quad (5)$$

In this equation, k_j represents the thermal conductivity of the liquid, L represents the characteristic length, and Nu represents the Nusselt number.

Nu can be calculated using the following empirical equations depending on the

conditions,

$$Nu = 0.15 (GrPr)^{\frac{1}{3}} \quad (10^7 < GrPr < 10^{12}) \quad (6)$$

$$Nu = 0.54 (GrPr)^{\frac{1}{4}} \quad (10^4 < GrPr < 10^7) \quad (7)$$

where Gr represents the Grashoff number and Pr represents the Prandtl number. These non-dimensional numbers are defined by the following equations:

$$Gr = \frac{g \zeta_j^H L^3 \Delta T}{\nu_j} \quad (8)$$

$$Pr = \frac{\nu_j}{k_j} \quad (9)$$

In these equations, g represents the acceleration of gravity, ζ_j^H represents the volume expansion rate, ΔT represents the temperature difference between the wall and the liquid, and ν_j represents the kinematic viscosity.

Based on the discussion on heat transfer, a model of the mass transfer at the system with a CO₂ hydrate layer was considered, in which the mass flux $J_{i,j}$ at the interface between the hydrate and liquid phase can be expressed as follows:

$$J_{i,j} = K_{i,j} \Delta C_i \quad (10)$$

and the mass flux $J_{i,hyd}$ in the hydrate phase as:

$$J_{i,hyd} = \frac{D_{i,hyd}}{\delta} \Delta C_i \quad (11)$$

where subscript i indicates either CO₂ or H₂O molecules; subscript j is the solvent, liquid CO₂, or water; K is the mass transfer coefficient; C is the concentration; D is the diffusion coefficient in the hydrate; and δ is the thickness of the hydrate layer.

From these measurements, the hydrate layer can be calculated to maintain its layer thickness for around 10 h. Therefore, it is considered that the mass flux at the interface and inside the hydrate are equal. Thus, the macroscopic mass flux $J_{i,t}$ can be defined as follows:

$$J_{i,t} = J_{i,j} = J_{i,hyd} \quad (12)$$

From these equations, the mass permeation rate α can be defined as:

$$J_{i,j} = \alpha_i \Delta C_i \quad (13)$$

$$\text{where } \alpha_i = \frac{1}{\frac{1}{K_{i,C}} + \frac{1}{K_{i,W}} + \frac{\delta}{D_{i,hyd}}} \quad (14)$$

The hydrate layer thickness can be calculated based on the mass flux. The hydrate layer formation rate V_i^f can thus be expressed as follows:

$$V_i^f = \frac{J_{i,j}}{C_{i,hyd}} = \frac{\alpha_i}{C_{i,hyd}} \Delta C_{i,j} \quad (15)$$

where $C_{i,hyd}$ represents the concentration of chemical species i in the hydrate.

Likewise, the hydrate layer dissolution rate V_i^d can be expressed as follows:

$$V_i^d = \frac{J_{i,j}}{C_{i,hyd}} = \frac{K_{i,j}}{C_{i,hyd}} \Delta C_i \quad (16)$$

From these equations, the velocities of the interface can be calculated as shown below:

$$V_C = V_{H_2O}^f - V_{H_2O}^d \quad (17)$$

$$V_W = -V_{CO_2}^f + V_{CO_2}^d \quad (18)$$

where subscript C and W represent the interface between the hydrate and liquid CO_2 or water, respectively.

Therefore, the time variation of the hydrate layer thickness can be expressed as follows:

$$\frac{d\delta}{dt} = \sum_i (V_i^f - V_i^d) \quad (19)$$

From above, the hydrate layer thickness can be expressed according to the mass transport coefficient as follows:

$$\delta(t + \Delta t) = \delta(t) + \sum_i \left(\frac{\alpha_i}{C_{i,hyd}} \Delta C_{i,j} - \frac{K_{i,j}}{C_{i,hyd}} \Delta C_i \right) \cdot \Delta t \quad (20)$$

3. Imaging of the macroscopic mass transfer

3.1 Experimental apparatus

To estimate the mass transfer coefficient, it is necessary to assess the mass flux. To this aim, an experiment was conducted to determine the amount of CO_2 that dissolves in water. Figure 5 shows the experimental apparatus used for this purpose, consisting of a visualization vessel, two plunger pumps, a compressor, a water tank, and a CO_2 tank. The vessel is in a thermostatic chamber to maintain its temperature during the experiment, in which the inner diameter of the vessel is 40 mm and the height is 150 mm. Two thermocouples are fixed at the top and the bottom of the vessel, and a pressure gage is fixed at the top to measure the temperature and pressure in the section.

First, the vessel is half filled with water. After that, CO_2 is injected from the top of the vessel and the valve is closed. The volumetric transition of the water phase is then recorded using a digital video camera. In the water, a pH indicator is dissolved to visualize the changes in pH associated with the dissolution of CO_2 . Two types of indicator were used, methyl red (MR) and bromophenol blue (BPB). MR is red at pH values under 4.4 and yellow at pH values over 6.2. BPB is yellow at pH values below 3.0 and blue at pH values over 4.6.

The experimental temperature and pressure conditions are shown in Figure 6, in which it can be seen that experiments A and C were initially under hydrate formation conditions

and then transitioned to near the coexistence line of the three phases (CO₂ hydrate, liquid, and gaseous CO₂) as the time passed. Experiment B was carried out under three phase coexistence conditions.

3.2 Visualization results

Figure 7 shows the time variation of the state of the water phase in experiment A, in which BTB was used as the pH indicator. The color of the water phase changed from blue-violet to yellowish-brown indicating the lowering of the pH during the experiment due to CO₂ dissolution.

To clarify the time variation of the height of the interface, binarization was applied to the image. After that, to quantify the volume, the volume of the solution was calculated in the accordance with the equations below:

$$Z(t) = \sum_{n=1}^{\text{number of pixel}} \pi r_n^2(t) H \quad (21)$$

where $Z(t)$ represents the volume of the solution, H represents the height per pixel and r_n represents the radius of the solution at the n pixel from the bottom of the image. r_n was calculated from the binarized images from the bottom to the top by each pixel. Using r_n , the volume as a cylinder at each pixel was calculated, and summarized in the height direction.

The mass of the dissolved CO₂ can be calculated from the volume using the equation below:

$$X(t) = \rho_{CO_2} (Z(t) - Z_0) \quad (22)$$

where $X(t)$ represents the mass of the dissolved CO₂, ρ_{CO_2} represents the density of the liquid CO₂, and Z_0 represents the initial volume of the solution.

Figure 8 shows the time versus the transition of masses of both the solution and dissolved CO₂, in which it can be seen that the mass of the dissolved CO₂ increased over time and converged. This indicates that the CO₂ concentration is saturated at the end of the experiment.

3.3 Mass transfer coefficient of the solution

The objective in this section is to calculate the mass transfer coefficient from the time variation of the CO₂ in solution. For this purpose, the relationship between the mass transfer coefficient and CO₂ concentration needs to be ascertained.

First, the distribution of the concentration in the solution was considered as being close to negligible. Furthermore, the area of the interface and the volume of the solution are considered to be constant. Finally, the concentration of the CO₂ in water can be regarded as being saturated in the vicinity of the surface of the hydrate.

Based on these assumptions, the relationship between the mass flux and the concentration can be expressed as follows:

$$J_{CO_2, W} = -S K_{CO_2, W} (C_{CO_2, sat} - C_{CO_2, W}(t)) \quad (23)$$

where S represents the area of the interface, $K_{CO_2, W}$ represents the mass transfer coefficient of CO_2 in the water, and C_{CO_2} represents the concentration of CO_2 . The subscript W represented the water phase and sat indicates saturation. In addition, the relationship between the mass flux and concentration of the water can be described as:

$$J_{CO_2, W} = Z \frac{dC_{CO_2, W}(t)}{dt} \quad (24)$$

where Z represents the volume of the solution.

From these equations, the relationship between the time variation of the concentration and the mass transfer can be represented as:

$$Z \frac{dC_{CO_2, W}(t)}{dt} = -S K_{CO_2, W} (C_{CO_2, sat} - C_{CO_2, W}(t)) \quad (25)$$

Integrating the equation shown above, with the consideration that $C_{CO_2, W}(0)=0$, the following equation can be obtained:

$$\frac{C_{CO_2, sat} - C_{CO_2, W}(t)}{C_{CO_2, sat}} = \exp\left(\frac{-S K_{CO_2, W}}{Z} t\right) \quad (26)$$

where the left side of the equation is referred to as the dimensionless concentration, $\theta(t)$.

Figure 9 shows the time variation of $\theta(t)$ in terms of the data to $C_{CO_2, sat}$, taken from the Chemical Engineer's Handbook²⁴. The plots represent the experimental data and the dashed lines represent the exponential approximation.

From the approximations, $K_{CO_2, W}$ was calculated using the empirical equation shown below:

$$K_{CO_2, W} = Sh \frac{D_{CO_2, W}}{L} \quad (27)$$

where $D_{CO_2, W}$ represents the diffusion coefficient of CO_2 in the water phase and the length L represents the diameter of the vessel. $D_{CO_2, W}$ can be calculated using the following equation proposed by Wilke and Chang²⁵:

$$D_{CO_2, W} = \frac{7.4 \times 10^{-8} (\phi_{H_2O} M_{H_2O})^{\frac{1}{2}} T}{\eta_{H_2O} V_{CO_2}^{0.6}} \quad (28)$$

where, ϕ_{H_2O} is an association parameter, T is the temperature, η_{H_2O} is the viscosity coefficient for water, and $V_{CO_2}^{0.6}$ is the molar volume of CO_2 . The value of ϕ_{H_2O} is proposed to be 2.26 for hydrates²⁵.

It is known that the Sherwood number, Sh , is a function of the Glashoff number, Gr , and the Schmitt number, Sc :

$$Gr = \frac{g\zeta L^3 (C_{CO_2,o} - C_{CO_2,\infty})}{\nu_{H_2O}} \quad (29)$$

$$Sc = \frac{\nu_{H_2O}}{D_{CO_2,W}} \quad (30)$$

In these equations, g represents the gravitational acceleration, ζ represents the volume expansion rate, and ν_{H_2O} represents the kinematic viscosity coefficient of H_2O . Additionally, the subscript O means near to the interface and ∞ indicates infinity. $C_{CO_2,O}$ is considered to be equal to $C_{CO_2,sat}$. Also, $C_{CO_2}(t)$ was applied as $C_{CO_2,\infty}$.

Sh can be calculated using the empirical formula shown below:

$$Sh = 0.54 Ra^{\frac{1}{4}} \quad (10^4 < Ra < 10^7) \quad (31)$$

$$Sh = 0.15 Ra^{\frac{1}{3}} \quad (10^7 < Ra < 10^{12}) \quad (32)$$

where $Ra = Gr \cdot Sc$.

Figure 10 shows a comparison of the experimental and calculated mass transfer coefficients, in which the y-axis represents the mass transfer coefficient and the x-axis represents the temperature. All of the experimental results are in good agreement with $Sh = 0.54 Ra^{\frac{1}{4}}$, even though Ra is not in the range of application. This result suggests that

the mass transfer coefficient of CO_2 in aqueous solution can be represented using the empirical equations above. Therefore, the above equations were used to estimate the mass transfer coefficient.

4. MD simulation of micro-scale mass transfer

4.1 Systems

CO_2 hydrate adopts an sI structure, with 46 H_2O and 8 CO_2 molecules per unit cell. The unit cell contains 8 H_2O cages (6 tetradecahedra $5^{12}6^2$ and 2 dodecahedra 5^{12} cages), with 1 CO_2 molecule in each cage. For this study, a system of $6 \times 6 \times 6$ unit cells was used. The total numbers of molecules are 432 CO_2 molecules in 5^{12} cages, 1296 molecules in $5^{12}6^2$ cages, and 9936 H_2O molecules in the entire system. The molecular occupancy rate of CO_2 reported by Salamatian et al.¹⁰ was adapted in this work. To fulfill the rate, randomly selected molecules were deleted. Figure 11 shows the system, in which the cyan spheres represent the carbon atoms, the red spheres represent the oxygen atoms, and the white spheres represent hydrogen atoms. Periodic boundary conditions were applied in the x, y, and z directions. The numbers of both molecules and atoms, as well as molecular

occupancy rate, are shown in Table 4.1.

4.2 Simulation details

Miguez et al.²⁸ have reported that TIP4P/ice reproduces the three phase coexistence line of the CO₂ hydrate well and that the choice of CO₂ forcefields does not affect the reproducibility of the line, in the simulations conducted in this work, the TIP4P/ice model²⁶ was used for the H₂O potential and OPLS-AA²⁷ for the CO₂ forcefield. The cut off distances of both the van der Waals potential and the Coulomb potential were set to 1.2 nm. All of the simulations were performed using the GROMACS 5.1.4 and GROMACS 2016 software packages.

The energy of the system was minimized through a 100 ps simulation using the steepest descent method. After that, a 10 ps NVT simulation was carried out at 200 K, followed by a 210 ps NpT annealing simulation. In the NVT simulation, the temperature is controlled according to the velocity rescaling method. Additionally, in the annealing simulation, the temperature was controlled using a Nosé–Hoover thermostat^{29, 30} and the pressure was controlled using a Berendsen barostat³¹. The temperature was increased linearly from 200 K to the required setting. Then, a 10 ps NpT simulation was carried out at settings of 200, 240, and 280 K, under 6 MPa to equilibrate the pressure. After that, a 50 ns NpT simulation was carried out. In both the 10 ps and 50 ns NpT runs, the temperature is controlled using a Nosé–Hoover thermostat and the pressure was controlled using a Parrinello–Rahman barostat³².

4.3 Simulation results

The relationship between the self-diffusion coefficient and the movement of particles is represented by the Einstein equation:

$$D^i = \frac{a^2}{6\tau} \quad (33)$$

where D^i represents the self-diffusion coefficient and a^2 represents the mean square of the deviation in time τ .

Liang et al. reported that the diffusion of CO₂ molecules in the hydrate occurs as a result of inter-cage hopping¹³. Therefore, the inter-cage hopping needs to be investigated. However, it is hard to distinguish it from all of the movements associated with the system. Thus, the inter-cage hopping based on the distances that the molecules traveled was considered by referring to the study by Lo et al.¹² Based on this consideration, we calculated the self-diffusion coefficient using the following equation:

$$D_i^i = \frac{d^2}{6 \left(t \frac{m_i}{n} \right)} \quad (34)$$

where D_i^t represents the self-diffusion coefficient, d represents the baseline of the traveled distance, m_i represents the number of molecules, n represents the number of movements that have a distance greater than the baseline, and t represents the duration of the simulations.

In a previous study by Liang et al., movements of CO₂ molecules of over 5 nm that occur within 10 ns were defined as hopping¹³, whereas in work by Lo et al., movements of over 6 nm that occur with 5 ps were defined as hopping¹². In this study, the distance CO₂ molecules traveled every 6 ps was calculated. To determine the baseline of the distance considered as hopping, the relationship between the distance and number of movements was investigated.

Figure 12 shows the relationship between the distance molecules traveled and the number of molecular movements, where the distance traveled was calculated in 6 ps intervals. From the plot it can be seen that the movements follow a lognormal distribution. As the temperature rises, the distribution becomes more gradual as the distance to the peak of the migration frequency increases. This result indicates that the movement of CO₂ is activated due to a rise in the temperature. The peaks of each graph lie between 0.06 and 0.1 nm. Therefore, it can be assumed that these peaks are due to the movement inside the cage.

Figure 13 shows the relationship between the distance that the molecules travel and the integrated number of movements, $F(x_i)$.

$F(x_i)$ can be obtained by integrating the number of movements that are longer than the specified distance, x_i , as follows:

$$F(x_i) = \sum_{x_{max}}^{x_i} f(x) \quad (35)$$

where x_i is the specified distance, x_{max} is the maximum value of the traveled distance, and $f(x)$ is the number of molecules traveled at each distance.

It is clear from Figure 13 that the number of molecular movements that are greater than 0.6 nm is extremely small.

The results of the calculations of the self-diffusion coefficients of both the CO₂ and H₂O molecules are shown in Figure 14, in which the self-diffusion coefficients are 0 if the distance traveled is greater than 0.6 nm. This measurement of 0.6 nm is close to the distance between the center of the cages. However, the molecules can still migrate between the cages even if the molecular travel distance is less than 0.6 nm. This phenomenon can be explained by considering that the inter-cage migration of molecules is a combination of both intra-cage movement and movement across the walls of the cage

¹³.

Figure 15 shows the self-diffusion coefficients of both the CO₂ and H₂O molecules when the baseline of the travel distance is set to 0.3 nm, which is half the length between the center of adjacent cages. The dashed line in the plot shows the approximation derived

using the Arrhenius equation.

Figure 16 shows a comparison between the self-diffusion coefficient of CO₂ derived in this and previous reported values. As can be seen from the figure, the results of this study are in good agreement with the neutron diffraction results reported by Falenty et al.²⁰ Therefore, the calculation method developed in this work is shown to be valid.

4.4 Calculation of the intrinsic diffusion coefficient

In the previous section, self-diffusion coefficients were determined from MD simulations. In this section, the intrinsic diffusion coefficients are calculated based on the self-diffusion coefficients.

The relationship between the self and the intrinsic diffusion coefficient is:

$$D_i = D_i^s \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \quad (36)$$

where D_i represents the intrinsic diffusion coefficient, D_i^s represents the self-diffusion coefficient, C_i represents the molar fraction of the chemical species i in the hydrate.

The activity constant γ_i is

$$\gamma_i = \frac{e^{\frac{\Delta \mu_i}{RT}}}{C_i} \quad (37)$$

where $\Delta \mu_i$ represents the chemical potential difference, R represents the gas constant, and T is the characteristic temperature.

For H₂O, $\Delta \mu_{H_2O}$ is calculated using the van der Waals and Plattew model³³:

$$\Delta \mu_{H_2O} = k_B T \left[x_L \ln(1 - y_L) + x_S \ln(1 - y_S) \right] \quad (38)$$

$$\text{where } x_n = \frac{N_n}{46 y_{H_2O}}$$

In this equation, k_B represents the Boltzmann constant, y_n represents the molecular occupancy of CO₂ in cage type n , N_n represents the number of n cages per unit cell, and y_{H_2O} represents the molecular occupancies of H₂O. In the equation, all of the parameters are calculated based on MD simulation settings.

For CO₂, $\Delta \mu_{CO_2}$ is calculated using the following equation⁹:

$$\Delta \mu_{CO_2,n} = k_B T \ln \left(\frac{1}{C_n} \frac{y_n}{1 - y_n} \right) \quad (39)$$

where y_n represents the molecular occupancy rate of CO₂ in cage type n .

The Langmuir constant C_n is calculated using the following equation:

$$C_n = \frac{q_n \lambda_n}{P} \quad (40)$$

where P represents the pressure and q_n represents the number of CO₂ molecules in cage

type n .

The absolute activity λ is calculated using the following equation:

$$\lambda_n = \frac{P}{k_B T \left(\frac{2\pi m_{CO_2} k_B T}{h^2} \right)^{\frac{3}{2}} q_{n,f}^{\ddagger}} \quad (41)$$

where m_{CO_2} represents the mass of CO_2 , h represents Planck's constant, and $q_{n,f}^{\ddagger}$ represents the number of CO_2 molecules in the cage.

Therefore, $\Delta\mu_{CO_2,n}$ can be expressed as follows:

$$\Delta\mu_{CO_2,n} = k_B T \ln \left(\frac{k_B T \left(\frac{2\pi m_{CO_2} k_B T}{h^2} \right)^{\frac{3}{2}}}{1 - y_n} \right) \quad (42)$$

Hence, the intrinsic diffusion coefficient of the CO_2 molecules can be calculated as:

$$D_{CO_2} = \frac{D_i^{\ddagger}}{M_{Large} + M_{Small}} \left\{ \left(1 + \frac{d \ln y_{Large}}{d \ln C_{Large}} \right) M_{Large} + \left(1 + \frac{d \ln y_{Small}}{d \ln C_{Small}} \right) M_{Small} \right\} \quad (43)$$

5. A kinetic model for calculating clathrate hydrate layer growth

The mass permeation coefficient was calculated using Equation (4), with the mass transfer coefficients estimated from the experiments and the intrinsic diffusion coefficient estimated using MD simulations. The time variation of the CO_2 hydrate layer thickness was calculated using Equation (9). Additionally, the initial thickness of the CO_2 hydrate layer was experimentally determined. The mass transfer coefficients of both CO_2 and H_2O at each interface can be derived using Equation (7).

Figure 17 shows a comparison of the hydrate layer thicknesses. The square symbols represent the experimental results obtained in our work¹⁵ and the circles represent the calculated values. The experimental conditions used were a temperature of 279.45 K, a pressure of 6 MPa, and an initial layer thickness of 22.89 nm¹⁵. Both the predicted and experimental results are in the order of 10^{-6} . The results indicate that the kinetic model proposed herein can be used to reproduce the layer thickness, with good agreement.

6. Conclusions

In this work, the time variation of the CO_2 hydrate layer thickness was determined using a kinetic model. To enable this estimation, the mass transfer and diffusion coefficients of the layer needed to be ascertained.

Thus, the melting behavior of the CO_2 hydrate layer was determined to calculate the mass transfer coefficient. As a result, it was found that the mass transfer coefficient of CO_2 could be well calculated using empirical equations.

In terms of the diffusion coefficients, MD simulations of CO_2 hydrate were conducted to

calculate the self-diffusion coefficients. To calculate the self-diffusion coefficients, inter-cage hopping and the intra-cage movement of molecules were determined based on the distances traveled by each molecule. When half the length between the center of adjacent cages is used, the self-diffusion coefficient of the CO₂ molecules shows good agreement with the experimental results.

Finally, the mass transfer coefficients and the self-diffusion coefficients of the CO₂ hydrate were applied to a kinetic model of the hydrate layer growth. The results indicate that the kinetic model proposed can be used to well reproduce the layer thickness.

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