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Diffusivity of CO₂ in H₂O: A Review of Experimental Studies and Molecular Simulations in the Bulk and in Confinement

H. Mert Polat,^{||} Felipe M. Coelho,^{||} Thijs J. H. Vlugt, Luís Fernando Mercier Franco,^{*} Ioannis N. Tsimpanogiannis,^{*} and Othonas A. Moultos^{*}



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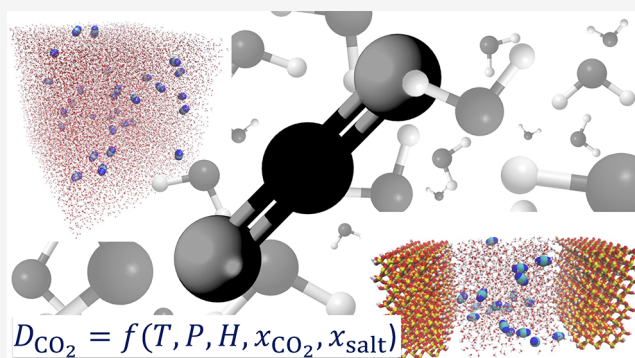


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ABSTRACT: An in-depth review of the available experimental and molecular simulation studies of CO₂ diffusion in H₂O, which is a central property in important industrial and environmental processes, such as carbon capture and storage, enhanced oil recovery, and in the food industry is presented. The cases of both bulk and confined systems are covered. The experimental and molecular simulation data gathered are analyzed, and simple and computationally efficient correlations are devised. These correlations are applicable to conditions from 273 K and 0.1 MPa up to 473 K and 45 MPa. The available experimental data for diffusion coefficients of CO₂ in brines are also collected, and their dependency on temperature, pressure, and salinity is examined in detail. Other engineering models and correlations reported in literature are also presented. The review of the simulation studies focuses on the force field combinations, the data for diffusivities at low and high pressures, finite-size effects, and the correlations developed based on the Molecular Dynamics data. Regarding the confined systems, we review the main methods to measure and compute the diffusivity of confined CO₂ and discuss the main natural and artificial confining media (i.e., smectites, calcites, silica, MOFs, and carbon materials). Detailed discussion is provided regarding the driving force for diffusion of CO₂ and H₂O under confinement, and on the role of effects such as H₂O adsorption on hydrophilic confining media on the diffusivity of CO₂. Finally, an outlook of future research paths for advancing the field of CO₂ diffusivity in H₂O at the bulk phase and in confinement is laid out.



1. INTRODUCTION

The accurate knowledge of the intradiffusivity of CO₂ in liquid H₂O over a wide range of temperatures and pressures is crucial for the design and optimization of numerous industrial and environmental processes and applications. The most prominent applications are the following:

- (i) *Carbon Capture & Sequestration (CCS)*. CO₂ is a greenhouse gas, produced from virtually every industrial process, and emitted into the atmosphere.^{1–3} In an effort to reduce the emissions of “man-made” CO₂, and thus, partially mitigate the effects on the global climate change, CCS has been explored as a promising technology.⁴ CCS involves three major steps. At first, CO₂ is captured from stationary CO₂-intensive sources (i.e., fossil-fuel-burning power plants, cement, steel, hydrogen, ammonia, and other chemical industries).⁵ During the second step, the captured gas is transported through a network of pipelines to a permanent gas-storage site.^{6,7} During the third step, the captured gas is stored into subsurface, geological formations,^{8–10} such as active or depleted gas/oil reservoirs,^{11–14} saline aquifers,^{15–22} and methane-gas-producing coal deposits or unminable coal seams.^{23–26}

The diffusivity of CO₂ in aqueous solutions is an important transport property mainly encountered in steps one and three.

- (ii) *CO₂-based Enhanced Geothermal Systems (EGS)*. Conventional geothermal systems that use H₂O for the transmission of heat suffer from the drawback of fluid loss that has a significant negative economic effect. Dense-phase CO₂ has thermal characteristics that allow it to transfer large quantities of heat, while at the same time having better physical characteristics (e.g., lower viscosity, higher compressibility, and expansibility).^{27,28} Therefore, CO₂ has been considered for utilization in the process of geothermal energy by extracting heat from the ground.^{29–31} Such a process combines heat recovery from the subsurface, while the working fluid (e.g., CO₂)

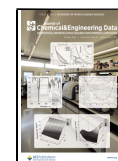
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losses can be considered as a part of CCS. In this way, value is added to the heat recovery process instead of considering it a financial loss, as occurs when using H₂O as the working fluid. Depending on the depth from which heat is extracted, CO₂ may encounter aqueous solutions, therefore CO₂ dissolution, and subsequent diffusion in the aqueous phase, need to be studied to accurately describe the evolution of the CO₂ plume. The flow of CO₂ over aqueous brines is accompanied by a series of phenomena such as H₂O evaporation^{32,33} and salt precipitation,^{34,35} thus affecting the porosity and permeability of the geologic formation.

- (iii) *Enhanced Oil Recovery (EOR)*. The injection of CO₂ into an oil-producing reservoir has been considered as an alternative approach to increase oil production during tertiary oil recovery³⁶ and is known as an EOR process. Usually EOR follows the secondary (i.e., waterflooding) oil recovery. Therefore, during the design of such a process, it is essential to account for the dissolution and diffusion of CO₂ in the aqueous phase (e.g., either the formation water or the residual water after the waterflooding process).
- (iv) *CO₂ ocean uptake*. Oceanic waters have absorbed approximately 40% of CO₂ emissions since the beginning of the industrial era^{37,38} making the oceans the largest sink for anthropogenic CO₂.³⁹ Therefore, it is essential to accurately know the dissolution and diffusion mechanisms/parameters to delineate the amount of CO₂ stored in the oceanic waters and its fate.
- (v) *CO₂ in the food industry*. The diffusivity of CO₂ in carbonated hydroalcoholic drinks, particularly in champagne, plays a pivotal role in influencing bubble dynamics and gas discharge kinetics, ultimately shaping the taste and mouthfeel of these beverages.⁴⁰ Thus, the accurate knowledge of various thermophysical properties (with transport mechanisms being central) of CO₂ in aqueous solutions relevant to this industry is essential for the production and quality control phases.

Therefore, it becomes apparent that during the preliminary study, and the design and optimization of the processes described above, the accurate knowledge of the diffusivity of CO₂ in liquid H₂O under bulk conditions (applications (iv) and (v)) and in confined media (applications (i), (ii), and (iii)) is crucial. As shown in the schematic of Figure 1, the three major routes that are usually followed for the measurement/estimation of diffusion coefficients are experimental measurements, theoretical/semiempirical models, and molecular simulations, with the most common method used being molecular dynamics (MD).

At relatively low pressures (e.g., below 1 MPa), the solubilities of CO₂ in H₂O are rather low.⁴¹ For example, the solubility of CO₂ in H₂O at atmospheric pressure and temperatures in the range 303.15–363.15 K ranges from 5.03×10^{-3} to 6.50×10^{-5} (in mole fractions).⁴¹ At pressures up to 10 MPa and temperatures up to 423 K, the solubilities can increase by 2 orders of magnitude. For high pressures (i.e., 100 MPa), the solubilities can increase to a maximum of approximately 4.3×10^{-2} . An extensive discussion on the effect of pressure on the solubility of CO₂ in H₂O can be found in a number of studies.^{41–44} Therefore, the intradiffusivity of CO₂ in H₂O essentially corresponds to the infinite dilution limit,⁴⁵ since for

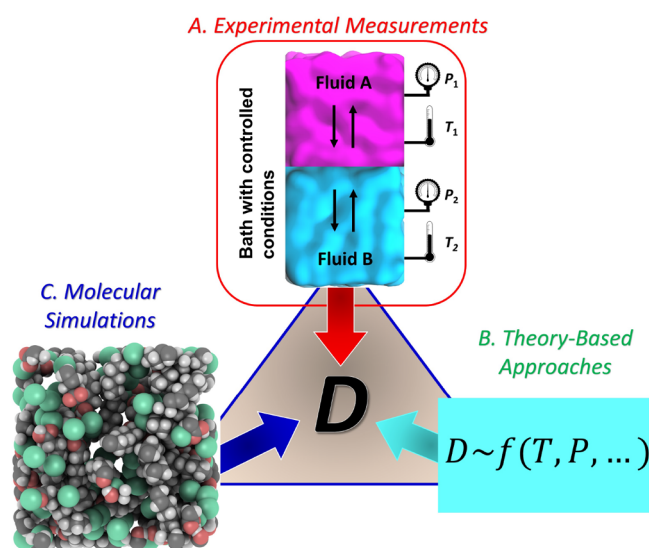


Figure 1. Schematic showing the common approaches considered for the estimation of diffusivities. A. Experiments, B. Theory-Based modeling, and C. Molecular Simulation.

most applications relatively low pressures and temperatures are concerned.

At higher pressures, at which the solubilities of CO₂ in H₂O are significantly higher than in the infinite dilution limit, it is of practical interest to measure/compute the mutual diffusivities (Fick and Maxwell-Stefan^{46–49}) since the mass transport occurs due to gradients in chemical potentials.^{46,50,51} To this end, one can either use models that are based on the Darken equation^{46,52,53} or can follow the well-established methodology of computing the Maxwell-Stefan diffusivities (D_{MS}) from the Onsager coefficients in MD simulations,^{47,49,54} and the thermodynamic factor (Γ), e.g., from Kirkwood-Buff integrals^{55–58} or with Continuous Fractional Component Monte Carlo (CFCMC) simulations.⁵⁹ In binary systems, Fick diffusivities follow from $D_{Fick} = \Gamma D_{MS}$.^{46–49} In this review paper, we limit our attention to the diffusivity of infinite diluted CO₂ in H₂O. In this case, the intra-, Maxwell-Stefan, and Fick diffusivities are all equal $D_{self} = D_{MS} = D_{Fick}$.⁴⁶

Experimentally measured diffusivities are often scarcely available, and in most cases at/or close to the atmospheric pressure.^{60,61} A detailed discussion on how to overcome this lack of data through the use of semiempirical approaches is provided elsewhere.^{50,53} Namely, semiempirical correlations have been extensively used for obtaining the self- and intradiffusivity values at conditions outside the range of experimental measurements.^{46,50,53,62,63} The accuracy of such semiempirical methods depends on the extent and quality of the experimental measurements that have been used for their development and calibration. Although these methods are relatively easy to use and computationally fast, almost no insight into the physical mechanisms controlling the mass transport in the real system can be obtained.

Alternatively, approaches such as MD simulations can provide detailed physical insight;^{64,65} the downside being that they are significantly more computationally demanding compared to engineering models. During the past three decades years, MD has become a reliable and widely used approach for obtaining diffusivities of pure components and mixtures.^{21,49,66–82} This development is the direct result of a number of factors including: (i) the increase of available computational power, (ii) the

availability and wide use of optimized open-source software,^{83,84} and (iii) the development of accurate force fields.^{85–88} The data obtained from MD simulations can be further used to devise engineering models and validate the semiempirical approaches.^{72,89,90} Macro-scale modeling approaches involving an equation-of-state such as PC-SAFT coupled with Stokes–Einstein equation or entropy scaling to compute self-diffusivities have been reported in literature, although, to the best of our knowledge, such methods have not been used to compute diffusivity of CO₂ in H₂O.^{91–96}

This review paper focuses on: (a) reporting diffusivity data (experimental or from MD) of CO₂ in pure H₂O or brines, in bulk or under confinement, (b) providing engineering-type correlations of the collected data when possible, (c) critically discussing the insights from the literature, and (d) providing a few opinions to guide future developments. The remainder of this review paper is organized as follows: in Section 2, we examine the CO₂ diffusion in bulk H₂O, considering both experimental and MD studies. In Section 3 the corresponding cases under confinement are discussed. Finally, in Section 4 the future outlook and the conclusions are presented, respectively.

2. AQUEOUS CO₂ DIFFUSION IN THE BULK

2.1. Experimental Studies. **2.1.1. Experimental Measurement Techniques.** Many different methods have been reported in the literature for the experimental measurement of the diffusion coefficients of gases in liquids, and have been extensively reviewed in a number of studies.^{50,60,97–99} Providing a detailed description of all these methods is beyond the scope of the current study. Instead, we provide a brief description of the experimental methods that have been used for the measurement of gas diffusivity in liquids, focusing primarily on those used for CO₂ diffusing in H₂O or brines. Such experimental methodologies include the following: (1) diaphragm cells,^{100–102} (2) wetted surface absorbers,^{103,104} (3) laminar jets,^{105–108} (4) capillary cells,^{109,110} (5) Taylor dispersion,^{111–113} (6) laser-induced fluorescence,¹¹⁴ (7) dynamic light scattering (DLS),¹¹⁵ (8) in situ Raman spectroscopy,^{116,117} (9) nuclear magnetic resonance (NMR) spectroscopy using pulsed field gradients (PFG),^{118–120} (10) pH-based methods,¹²¹ (11) pressure decay methods,^{122–124} and (12) dynamic interfacial tension method.¹²⁵ Additional methodologies used for measuring gas diffusion in other liquids (e.g., CO₂ in heavy oil or bitumen) include, but are not limited to, the following: (1) the dynamic pendant drop volume analysis (DPDVA),¹²⁶ (2) the dynamic pendant drop surface analysis (DPDSA),¹²⁷ (3) X-ray computer-assisted tomography (CAT) scanning,^{128,129} and (4) magnetic resonance imaging (MRI).¹³⁰

The experimental methods mentioned above can be divided into conventional (direct) and nonconventional (indirect),⁹⁹ as shown in Figure 2. For the direct methods (e.g., diaphragm cells, wetted surface absorbers, laminar jets, capillary cells), it is essential to perform compositional measurements of fluid mixtures collected during the diffusion experiment to determine the gas diffusion coefficients. Therefore, direct methods are intrusive, can disturb the experiment if the removed samples are not minimal, can be time-consuming and labor intensive, are often expensive, and complex. These drawbacks are more pronounced when diffusion coefficients at higher temperatures/pressures are required.¹²² On the contrary, the indirect methods (e.g., laser-induced fluorescence, dynamic light scattering, Raman spectroscopy, nuclear magnetic resonance, pH-based methods, pressure decay methods) require less time compared

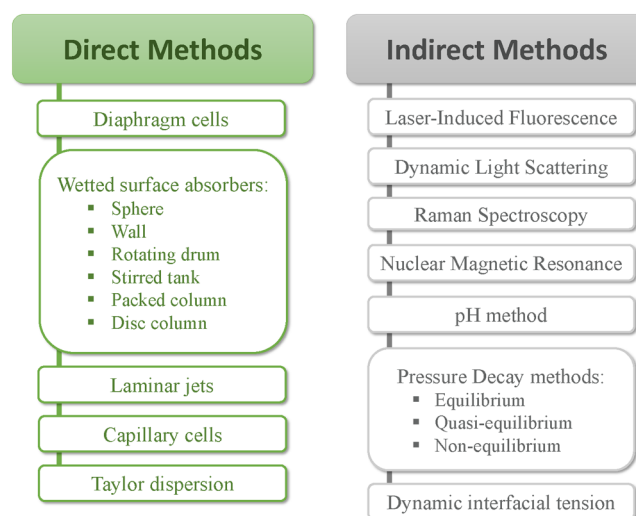


Figure 2. Direct and indirect experimental methods that have been used for the measurement of gas diffusivity in liquids.

to the conventional methods, and thus, are preferable in engineering applications.¹²³ In these methods, the diffusion coefficients are indirectly determined by measuring a different property (e.g., interfacial tension, pH, gas pressure, gas volume, gas/liquid interface position) of the gas/liquid system that is known to be directly affected by the diffusion process. Diffusivity measurement methods, such as DLS, Raman spectroscopy, and NMR, that were mentioned earlier, or similar ones such as magnetic resonance imaging (MRI) and X-ray computer-assisted tomography (CAT) scanning (reported for the study of gas diffusion in hydrocarbon systems), require very expensive and highly sophisticated equipment, whose operation is limited to highly specialized technicians.¹²⁶

In a diaphragm cell, two solutions of different composition are brought into contact by a diaphragm. The cell usually has to be calibrated with a mixture of known diffusion coefficient. The method has a significant drawback, since it requires a large amount of time (i.e., 2–3 days) for each measurement.

In the wetted surface absorber technique, absorption takes place in a thin laminar film flowing over a surface of defined geometry, such as a sphere¹⁰⁴ or a wall/plate.^{131,132} This method has the following two limitations that are important only at high degrees of liquid saturation: (i) the finite thickness of the liquid film, which absorbs finite amount of gas, and (ii) nonuniform velocity profile. Olbrich and Wild¹³³ extended the earlier mathematical analysis of Davidson¹³⁴ for absorption on a sphere to any flow geometry exhibiting a certain degree of symmetry. In a similar manner, the laminar jet method is based on the gas absorption taking place in a free-flowing laminar jet. Both these methods require knowledge of the fluid dynamics for the analysis and calculation of the diffusion coefficients. Tang and Himmelblau¹³¹ reviewed other gas–liquid contacting devices that have been used in fundamental studies including the rotating drum,¹³⁵ the stirred tank,¹³⁶ the packed column, and the disk column,¹³⁷ and concluded that in such devices it is difficult to measure the hydrodynamic characteristics of the liquid phase, therefore making it difficult to interpret the obtained diffusivity results.

Single¹¹⁰ or multiple¹⁰⁹ capillary cells (with the capillaries having size of approximately 1 mm) are used to restrict liquid convection within the capillaries. The liquid component is placed in the capillary and then brought into contact with the

second diffusing component. If diffusion is allowed to proceed until the steady-state is reached, then the rate of diffusion can be described by relatively simple mathematics. This method has, however, two disadvantages: (i) solubility data are required; therefore, the accuracy of diffusivity depends on the accuracy of the solubility data, and (ii) as a result of the gas absorption rate being measured volumetrically, accurate diffusivities are limited only to systems for which gas solubilities are at least moderate.

The measurement of the diffusion coefficient of a gas in a solvent with the Taylor dispersion technique requires the simultaneous injection of a sample of a solution containing the gas and the solvent into a stream of the pure solvent while the dispersion of the gas during the laminar flow through a capillary is monitored. In this approach, the parabolic flow profile results in spreading the solute pulse out longitudinally, while simultaneously radial diffusion acts to keep the pulse confined. Extracting the diffusion coefficient from the mathematical analysis of this problem is based on the seminal work of Taylor¹¹¹ and Aris.¹¹² An extensive discussion on the accuracy of this methodology has been presented by Alizadeh et al.¹³⁸ For experimental studies using the Taylor dispersion method for the diffusivity of CO₂ in H₂O, the reader is referred to refs 113, 139–141.

By performing an analysis of the intensity of the quasielastically scattered light, a number of thermophysical properties (i.e., viscosity, surface tension, speed of sound, thermal diffusivity) can be determined in an absolute way by using dynamic light scattering (DLS).¹¹⁵ Klein et al.¹⁴² provided a comprehensive description of the techniques used, including the optical and electronic arrangement of the setup used for performing those measurements. Therefore, when applying DLS to the bulk of fluids which are at macroscopic thermodynamic equilibrium, the mean lifetimes of fluctuations in concentration, temperature or entropy, and pressure are analyzed by calculating the correlation function (CF) of the scattered light intensity. By such an analysis the thermophysical properties of interest can be extracted. Contrary, inelastically scattered light analyzed by Raman spectroscopy can provide insight into the molecular structure. In situ Raman spectroscopy in horizontal fused silica capillary has become a powerful technique utilized to determine CO₂ diffusion coefficients at high pressures and temperatures.^{116,117} In an alternative approach, Hirai et al.¹¹⁴ used laser-induced fluorescence (LIF) to measure CO₂ dissolution in water under high pressures.

The PFG-NMR methodology is a noninvasive means for measuring translational motion and is based on the use of magnetic gradient fields which imprint phase shifts on the nuclear spins of the diffusing species.¹²⁰ For cases in which an increase in gradient strength or the Brownian motion is present, a decrease in NMR signals is observed. As a result, the molecular motion can be quantified and the self-diffusion coefficient can be obtained. The PFG-NMR method does not require any calibration or additional information on the investigated systems, which constitutes an advantage of this method when compared to others discussed earlier. A detailed description of the theory behind this method, as well as the experimental aspects associated with the method, can be found in the review articles of Price.^{143,144}

Sell et al.¹²¹ utilized a microfluidic-based approach to measure the mutual diffusion coefficient of carbon dioxide in water and brine. With their approach the diffusion is quantified by imaging fluorescence quenching of a pH-dependent dye, and subsequent mathematical analysis. An important advantage of the method is

the efficacy and speed of the diffusivity measurements. The authors reported measurements completed in less than 90 s, which should be compared to hours or days required by other methods.

The pressure decay method is considered the most widely applied indirect method for the measurement of gas diffusivities in the liquid phase.^{99,123} The method was established by Riazi¹⁴⁵ for the measurement of diffusion coefficients of gas in hydrocarbon systems. The method is based on the measurement of the decrease in the pressure of gas in direct contact with a liquid at a constant temperature PVT setup or diffusion cell. To obtain the gas diffusion coefficient, the pressure decay data as a function of time are matched with a mathematical model. Therefore, such an approach makes the calculation of the diffusion coefficient dependent on how detailed the mathematical model used for the analysis is.¹⁴⁶ This issue becomes more evident when the pressure decay method is used to measure the diffusivity of CO₂ in H₂O where the density-driven convection needs to be considered.^{147,148} A number of studies^{124,147,149–154} used the pressure decay method for the measurement of the diffusivity of CO₂ in H₂O.

Based on the boundary condition of the gas/liquid interface used in the modeling of the pressure decay method, Tharanivasan et al.¹⁵⁵ recommended the classification of the mathematical models under three categories as follows: (i) equilibrium, (ii) quasi-equilibrium, and (iii) nonequilibrium. The first category considers that the concentration on gas/liquid interface is constant and always equal to the equilibrium concentration. An important limitation of the models belonging to the first category is that the decay in pressure of the gas phase should be very small; otherwise, higher errors (originating from the assumption of constant equilibrium concentration at the interface) will occur when the model is used to analyze pressure-decay data. Models of the second category consider a nonconstant concentration, corresponding to the existing cell pressure at the gas/liquid interface, resolving thus, the deficiency of the equilibrium model. However, for quasi-equilibrium models an exact analytical solution has not been reported to date. Finally, the nonequilibrium models^{156,157} assume that a mass transfer resistance is considered at the gas/liquid interface. Such an assumption, however, is still under scientific debate.¹²³

The dynamic interfacial tension method¹²⁵ is capable of simultaneously determining the gas diffusion coefficient and the interface mass transfer coefficient in a liquid. Initially, the dynamic and equilibrium interfacial tensions of the gas–liquid system are measured by using the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case. Next, a mathematical model is developed to study the mass transfer in the gas–liquid system. The gas diffusion coefficient in the liquid is used as an adjustable parameter and is the result of an optimization process to match the numerically calculated and experimentally measured dynamic interfacial tensions.

2.1.2. Correlation of Experimental Data. Mutoru et al.⁶¹ presented a comprehensive collection of experimental data of CO₂ diffusion in bulk pure H₂O that are available in the open literature. This database covers studies up to 2010, and includes 150 experimental data points (also incorporating the experimental data from the earlier review by Himmelblau⁶⁰), the majority of which are at pressure equal to 0.1 MPa. Mutoru et al.⁶¹ presented a detailed discussion of mean-field-theory models that consider the diffusion coefficient of CO₂ in H₂O. They also reported a novel methodology for the calculation of the diffusion coefficient at infinite dilution of either of the two components.

Table 1. Percentage Average Absolute Deviation (% AAD) between Experimental Data and Correlations for the Diffusion Coefficient of CO₂ in H₂O^a

case	parameter fitting	data base used for %AAD calculations	ARR (%AAD)	VTF (%AAD)	SA (%AAD)	Mutoru et al. (%AAD)
1	original	original	4.9	5.0	5.7	4.9
2	original	new data	24.6	30.8	16.4	11.5
3	extended	extended	11.2	5.7	6.9	na
4	extended	new data	10.8	7.7	7.5	na
5	limited	limited	3.7	3.7	4.3	3.7
6	limited	original	5.1	5.2	5.2	na
7	limited	extended	7.4	7.4	5.9	na
8	limited	new data	17.2	17.2	8.7	na

^aNotation for the experimental data: Original: database reported by Mutoru et al.;⁶¹ New data: Lu et al.,¹¹⁶ Cadogan et al.;¹¹³ Extended: Original + New data; Limited: database reported by Versteeg et al.;¹⁶¹ na: not applicable. ARR stands for the Arrhenius equation (eq 1), VTF stands for the Vogel–Tamann–Fulcher equation (eq 2), and SA stands for the Speedy–Angell power-law equation (eq 3).

Magalhães et al.¹⁵⁸ examined the performance of a number of empirical correlations for the diffusion coefficients of CO₂ in H₂O. The experimental data were correlated as a function of temperature and the viscosity or density of the solvent. For the particular system they limited their study to 111 experimental data points that are mainly at 0.1 MPa (all data were included in the database of Mutoru et al.⁶¹).

Since the methodology of Mutoru et al.⁶¹ seems to be in principle accurate, and general in nature, it can be used for computing the diffusion coefficient of other gases in H₂O as well, but requires significant computational effort to be applied. This section is motivated by the need to develop an equally accurate method for the calculation of the diffusion coefficient of CO₂ in H₂O, yet simple enough to be used in reservoir simulators, where the repeated use of the diffusivity correlation is required. In reservoir simulators,¹⁵⁹ the domain of interest is discretized in a (usually) large number of grid-blocks, and the balance equations of momentum, mass, and energy need to be numerically solved in each one of them, while the solution process is repeated for all the time-steps considered.¹⁶⁰ To this purpose, two different groups of correlations are examined. The first considers two Arrhenius-type correlations,^{116,161} while the second group considers the Speedy–Angel power-law type of correlation.¹⁶²

Two are the major advantages of the correlations that were examined in the current study: (i) they are equally accurate at low pressures (0.1 MPa) and provide higher accuracy at pressures that are higher than atmospheric, and (ii) they are simple to use, and therefore, they are computationally efficient, and thus can be used during the process design and optimization. However, they are component-specific, therefore they are not general in nature. To examine different diffusion systems, the parameters of the equations need to be refitted to the corresponding, component-specific experimental diffusivity data.

Initially, we briefly present three correlations that have been reported in literature. Next, the three correlations are fitted to the experimental data used for the development of the Mutoru et al.⁶¹ methodology to obtain the correlation parameters. Then, the three correlations, and the methodology of Mutoru et al.⁶¹ are extrapolated to pressure and temperature conditions that are outside the range of development, and are compared to the experimental data of Lu et al.¹¹⁶ and Cadogan et al.¹¹³ Finally, an extended experimental database that includes the database of Mutoru et al.⁶¹ and the experimental studies of Lu et al. and Cadogan et al. is used to re-evaluate the parameters for the three correlations. The new correlations are further tested against

experimental data at higher pressures that have not been included in the correlation development.

2.1.3. Model Development for Diffusion in Pure H₂O. Here, we consider three literature-reported correlations presented in eqs 1–3 below to describe the experimental data of the diffusion coefficient of CO₂ in pure H₂O collected by Mutoru et al.⁶¹ This database is termed “original” in Table 1. The term “limited” in the same table corresponds to the experimental data used by Versteeg et al.,¹⁶¹ which is a subset of the “original” database that contains only 30 experimental data points. “new data” correspond to the experimental values reported by Lu et al.,¹¹⁶ and Cadogan et al.¹¹³ that are at higher pressures. The three correlations examined have been previously reported in the literature, and have been used in a number of studies to correlate experimental data^{116,161} or molecular simulation results.^{45,163}

Versteeg et al.¹⁶¹ used a limited number of experiments (i.e., 30 data points of diffusion coefficients of CO₂ in H₂O at 0.1 MPa and for temperatures up to 348 K) and fitted the experimental data to an Arrhenius-type equation (denoted with superscript “ARR”) given as follows:

$$D_{\text{CO}_2}^{\text{ARR}} = D_0 \exp\left(\frac{\alpha}{T}\right) \quad (1)$$

where D_0 and α are fitting parameters, and T is the temperature. The correlation has high accuracy within the range of development (i.e., for temperatures up to 348 K). Moulton et al.⁴⁵ showed that the extrapolation of the correlation by Versteeg et al.¹⁶¹ to temperatures higher than 348 K deviates significantly from recent experimental data that were not included in the original development of the Arrhenius-type correlation.

This is clearly shown in Table 1 where the percentage average absolute deviation (%AAD), defined as

$$\% \text{AAD} = 100 \times \left| \frac{D_{\text{CO}_2}^{\text{calc}} - D_{\text{CO}_2}^{\text{exp}}}{D_{\text{CO}_2}^{\text{exp}}} \right|$$

is given for a number of different cases. The superscripts “calc” and “exp” denote the computed and experimental values respectively of the diffusion coefficients, D_{CO_2} , of CO₂ in H₂O. When the correlation by Versteeg et al.¹⁶¹ is used to compute the D_{CO_2} at the temperatures in the “limited” database, it produces a value for %AAD equal to 3.7% (i.e., case 5). Alternatively, %AAD rises to 17.2% when the experimental data of Lu et al.¹¹⁶ and Cadogan et al.¹¹³ are considered (i.e., case 8).

Lu and co-workers¹¹⁶ used a modified Arrhenius-type of equation, known as the Vogel–Tamann–Fulcher (denoted with superscript “VTF”) to correlate the experimental data from a new set of experimental measurements that they performed in

Table 2. Parameters for the Diffusion Coefficient of CO₂ in H₂O Calculated Using Different Correlations^a

correlation	D_0 (m ² s ⁻¹)	m	α	β	γ
ARR-type	3.657×10^{-6}	na	2.2546×10^3	na	na
VTF-type	na	na	4.3152×10^3	-123.2149	9.84018
SA-type	19.798×10^{-9}	2.01489	na	na	na

^aThe case of using the "Original" database.

the pressure range 10–45 MPa and temperature range 268–473 K. The VTF equation is given as

$$D_{\text{CO}_2}^{\text{VTF}} = \exp \left[\frac{-\alpha}{(T - \beta)} - \gamma \right] \quad (2)$$

where α , β , and γ are fitting parameters. Lu et al.¹¹⁶ found better agreement, however, with their experimental data when they used a power-law-type of equation expressed as follows:

$$D_{\text{CO}_2}^{\text{SA}} = D_0 \left(\frac{T}{T_s} - 1 \right)^m \quad (3)$$

where D_0 , T_s , and m are fitting parameters. In most cases, $T_s = 227$ K. This type of correlation is known as the Speedy-Angell power-law equation¹⁶² and is denoted with the superscript "SA".

2.1.4. Results for Experimental Data at Low Pressures. Initially, we used the experimental data collected by Mutoru et al.⁶¹ to perform comparisons between the methodology of Mutoru et al.⁶¹ and the three correlations examined here. The computed values for the parameters of the three correlations are reported in Table 2.

The values for the %AAD in calculating the diffusion coefficients of CO₂ in H₂O for the three correlations are given in Table 1. All correlations are in very good agreement with the methodology of Mutoru et al.⁶¹ with the Arrhenius-type (ARR-type) correlation having the lowest %AAD. When the pressure is equal to 0.1 MPa, the temperature range of applicability of the three correlations, as well as the methodology of Mutoru et al.,⁶¹ is limited to temperatures up to 373 K.

The good agreement between the experimental data and the methods considered is also demonstrated in Figure 3, where D_{CO_2} is shown as a function of temperature. In Figure 3, we show

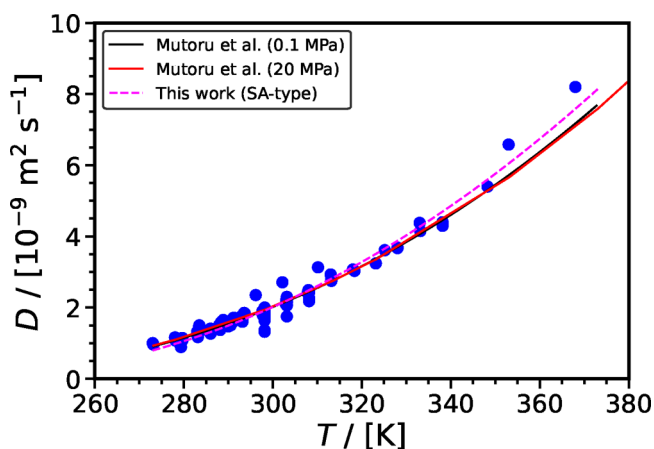


Figure 3. Diffusion coefficient of CO₂ in H₂O as a function of temperature. Circles denote the experimental data collected by Mutoru et al.⁶¹ The solid lines denote the calculations using the methodology by Mutoru et al. [calculations at: 0.1 MPa (black line), and 20 MPa (red line)]. The magenta dashed line denotes the correlation (SA-type) developed in this work.

only the SA-type correlation, which performs the least satisfactory among the three correlations considered. Yet we can observe that this correlation follows very closely the calculations using the methodology of Mutoru et al.⁶¹

The calculations discussed so far correspond to pressures that are equal to 0.1 MPa. Figure 3 also shows the calculations of D_{CO_2} using the methodology of Mutoru et al.,⁶¹ however at pressure equal to 20 MPa. The resulting curve for the diffusion coefficient of CO₂ in H₂O as a function of temperature is practically indistinguishable from the case of 0.1 MPa. Pressure effects on the diffusion coefficient of CO₂ in H₂O is addressed further in the following section.

2.1.5. Results for Experimental Data at High Pressures. The extensive experimental studies by Lu et al.¹¹⁶ and Cadogan et al.¹¹³ have shown that pressure has a very limited effect on the diffusion coefficient of CO₂ in H₂O, up to 45 MPa and temperatures up to 473 K. This is expected due to the low compressibility of liquid H₂O at these conditions. For this pressure and temperature range, a similar conclusion was reached from the MD simulations reported by Moulton et al.⁴⁵ Interestingly, MD simulations show that pressure effects could become significant at higher temperatures and pressures.

Therefore, for all practical engineering applications at the conditions where pressure has a negligible effect on the diffusion coefficient of CO₂ in H₂O, one could use the correlation that gives the diffusion coefficient of CO₂ in H₂O only as a function of temperature (which is independent of pressure). Essentially, one could use the correlations developed in section 2.1.2 (i.e., for pressures equal to 0.1 MPa and temperatures up to 373 K) or the methodology developed by Mutoru et al.⁶¹ In Figure 4(a), the diffusion coefficient of CO₂ in H₂O is shown as a function of temperature for temperatures up to 473 K. Namely, we extrapolate the use of the methodology of Mutoru et al.⁶¹ or the three correlations by 100 K. These calculations are compared with the experimental data by Lu et al.,¹¹⁶ and Cadogan et al.,¹¹³ which are at higher pressures. While very good agreement is observed for temperatures lower than 373 K, deviations increase significantly for higher temperatures as can be seen by the values of %AAD listed in Table 1. Among all cases considered in this section, the methodology of Mutoru et al.⁶¹ performs better in predicting the diffusion coefficient of CO₂ in H₂O under extrapolated conditions.

2.1.6. Results for Combined Experimental Data. Motivated by the observations in the previous section, we re-evaluate the parameters of the three correlations using the "extended" database that includes also the experimental data of Lu et al.¹¹⁶ and Cadogan et al.¹¹³ at higher pressures and temperatures in addition to the experimental data collected by Mutoru et al.⁶¹ The new parameters that resulted from the fitting are reported in Table 3. %AAD in calculating D_{CO_2} for the three correlations are also given in Table 1. Significant improvements can be observed in the calculations of the diffusion coefficients of the experimental data of Lu et al.¹¹⁶ and Cadogan et al.¹¹³ In particular, for the case of the SA-type correlation, the %AAD

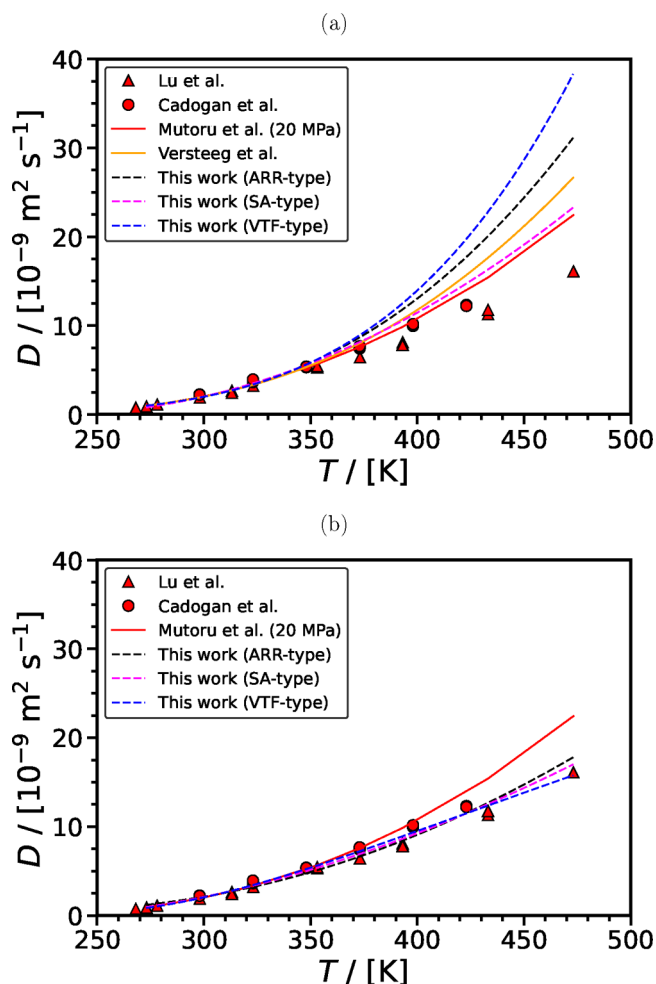


Figure 4. Diffusion coefficient of CO_2 in H_2O as a function of temperature. Triangles denote the experimental data by Lu et al.¹¹⁶ and circles the experimental data by Cadogan et al.¹¹³ The red solid line denotes the calculations of the diffusion coefficient of CO_2 in H_2O at various temperatures and 20 MPa using the correlation of Mutoru et al.,⁶¹ and the orange solid line denotes the calculation using the correlation of Versteeg et al.¹⁶¹ The dashed lines denote the correlations examined in this work (SA-type: magenta; VTF-type: blue; ARR-type: black): (a) Extrapolation and comparison with recent experimental data at higher pressures. (b) The parameters for the three correlations are re-evaluated to include recent experimental data (Lu et al.,¹¹⁶ Cadogan et al.¹¹³).

drops from 16.4% to 7.5% when the new parameters are used. The improvement is more pronounced for the case of the VTF-type correlation. The %AAD drops from 30.8% to 7.7% when the new parameters are used. An intermediate behavior is observed for the case of the ARR-type correlation (the %AAD drops from 24.6% to 10.8%).

Figure 4(b) shows the diffusion coefficient of CO_2 in H_2O as a function of temperature. As can be seen, the reparameterized

correlations are in very good agreement with the experimental values at higher temperatures and pressures. All three correlations examined here perform better than the methodology of Mutoru et al.⁶¹

The proposed correlations are further tested with some additional experimental data at higher pressures which are indicated in Figure 5. These experimental studies have not been

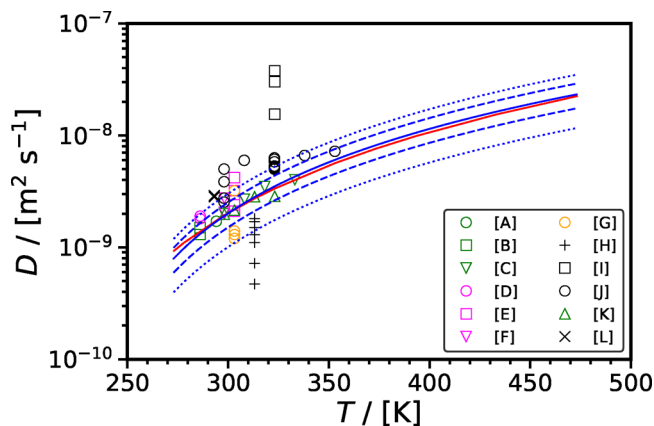


Figure 5. Diffusion coefficient of CO_2 in H_2O as a function of temperature. The solid red line denotes the calculations using the methodology by Mutoru et al. at 20 MPa. The solid blue line denotes the correlation (SA-type) developed in this work, while the dashed and dotted blue lines indicate the boundaries of $\pm 25\%$ and $\pm 50\%$ of the diffusion coefficient computed with the SA correlation, respectively. Symbols denote the experimental data. Legend: [A] Belgodere et al.;¹¹⁷ [B] Hirai et al.;¹¹⁴ [C] Bellaire et al.;¹²⁰ [D] Shimizu et al.;¹⁶⁴ [E] Tomita et al.;¹⁶⁵ [F] Farajzadeh et al.;¹⁴⁷ [G] Chiquet;¹⁶⁶ [H] Tewes and Boury;¹⁶⁷ [I] Li et al.;¹⁶⁸ [J] Ahmadi et al.;¹⁶⁹ [K] Lee et al.;¹³² and [L] Basilio et al.¹²⁴

included in any of the databases^{61,158,161} discussed in the previous sections. The figure shows the comparison of the experimental diffusion coefficient of CO_2 in H_2O as a function of temperature against calculations using (i) the Mutoru et al. methodology (at 20 MPa) and (ii) the SA correlation developed in the current study. The dotted lines indicate the boundaries of $\pm 25\%$ and $\pm 50\%$ of the diffusion coefficient calculated with the SA correlation. There are four different groups of experimental data which are indicated by a different color in the figure. The experimental data (green symbols) of Belgodere et al.,¹¹⁷ Hirai et al.,¹¹⁴ Bellaire et al.,¹²⁰ and Lee et al.¹³² are in good agreement with the SA correlation. Most of the experimental data (magenta symbols) of Shimizu et al.,¹⁶⁴ Tomita et al.¹⁶⁵ and Farajzadeh et al.¹⁴⁷ fall in the zone of $\pm 25\%$ from the SA correlation (with a limited number of experimental data falling outside). The experimental data (orange symbols) of Chiquet¹⁶⁶ fall in the range $\pm (25-50)\%$ from the SA correlation. Finally, the experimental data (black symbols) of Tewes and Boury,¹⁶⁷ Li et al.,¹⁶⁸ Basilio et al.,¹²⁴ and Ahmadi et

Table 3. Parameters for the Diffusion Coefficient of CO_2 in H_2O Calculated Using Different Correlations^a

correlation	D_0 ($\text{m}^2 \text{s}^{-1}$)	m	α	β	γ
ARR-type	0.7056×10^{-6}	na	1.7407×10^3	na	na
VTF-type	na	na	0.52369×10^3	159.003	16.2975
SA-type	14.802×10^{-9}	1.72362	na	na	na

^aThe case of using the “extended” database.

Table 4. List of Experimental Studies for the Diffusion Coefficient of CO₂ in Aqueous Brines

year	authors	T range (K)	P range (MPa)	D range (10 ⁻⁹ m ² s ⁻¹)	salinity	variable	brine solution
1959	Nijssing et al. ¹⁷³	298.15	0.1	1.06–1.95	0–1.28 mol L ⁻¹	S	Na ₂ SO ₄ ; MgSO ₄
1963	Ratcliff & Holdcroft ¹⁷⁰	298.15	0.1	1.28–1.84	0.32–3.78 mol L ⁻¹	S	NaCl; NaNO ₃ ; Na ₂ SO ₄ ; MgCl ₂ ; Mg(NO ₃) ₂ ; MgSO ₄
1996	Wang et al. ¹⁷⁴	311.15	1.524–5.178	2.925–4.827	0.25 N	P	NaCl
2006	Yang & Gu ¹⁴⁹	300.15, 331.15	2.6–7.54	170.7–269.8	4310 mg L ⁻¹	P	reservoir (Instow) brine
2006	Yang et al. ¹²⁵	300.15	0.1–6	0.31–1.34	64 160 mg L ⁻¹	P	reservoir (Weyburn) brine
2008	Bahar & Liu ¹⁷⁵	356.15	na	na	2 wt %	na	NaCl
2013	Azin et al. ¹⁵¹	305.15–323.15	5.9–6.9	3.52–6.16	182 513 mg L ⁻¹	T, P	Aquifer brine
2013	Wang et al. ¹⁷⁶	318.15	3.43–8.02	233.6–251.34	6778 mg L ⁻¹	P	reservoir brine
2015	Cadogan et al. ¹¹⁹	298.15	0.1	1.25–2.13	0–5 mol kg ⁻¹	S	NaCl; CaCl ₂ ; Na ₂ SO ₄
2015	Belgodere et al. ¹¹⁷	294.15	4	0.93–1.71	0–6 mol kg ⁻¹	S	NaCl
2015	Zhang et al. ¹⁵³	298.15	1.17	1.5–1.91	0–100 000 ppm	T, P, S	NaCl; Na ₂ SO ₄ ; NaHCO ₃ ; MgCl ₂ ; CaCl ₂
2015	Jafari et al. ¹⁵²	303.15, 313.15	5.459–6.10	0.678–23.3	0–200 000 mg L ⁻¹	P, S	NaCl; KCl; CaCl ₂ ; MgCl ₂ ; reservoir brine
2017	Zarghami et al. ¹⁷⁷	341.15	1.745	6.5–8.2	0–80 ppt	T, S	NaCl
2017	Shu et al. ¹⁷⁸	293.15	1.7–2.2	18.08–22.42	3 wt %	P	NaCl
2017	Shu et al. ¹⁷⁹	293.15, 303.15	1.77–2.22	1.0–3.5	3 wt %	P	NaCl
2018	Shi et al. ¹⁵⁴	323.15	4.25–5.786	1.25–293	248 991 mg L ⁻¹	na	reservoir (Mt. Simon) brine
2018	Perera et al. ¹⁷²	323.15	9	1.72–3.08	0–4 M	S	NaCl
2018	Li et al. ¹⁸⁰	313	2–8	1.92–2.1	1 M	P	NaCl + KI
2019	Tang et al. ¹⁸¹	355.65	14–24	4.98–9.04	243 143 mg L ⁻¹	P	reservoir brine
2019	Tang et al. ¹⁸¹	293–393	20.2	3.09–8.46	243 143 mg L ⁻¹	T	reservoir brine
2023	Zhang et al. ¹⁸²	286.15–303.15	0.1–5	0.126–0.73	3 wt %	T, P	NaCl
2024	Basilio et al. ¹²⁴	293.15	1.5	1.28–2.91	0–5 mol L ⁻¹	S	NaCl

al.¹⁶⁹ exhibit deviations which can be significantly higher than 50%.

2.1.7. Diffusion in Brines. Only a limited number of experimental measurements has been reported for the case of CO₂ diffusing in brines of various compositions. Table 4 shows a number of experimental studies that were identified in this review. The table also shows the range of parameters examined and the different brines considered.

Figure 6 shows the effect of salinity [in units of mol NaCl/(kg H₂O)] on the diffusion coefficient of CO₂ in various aqueous solutions of NaCl. Each set of experiments is performed at constant temperature and pressure. We observe that for a constant temperature and pressure the diffusivity of CO₂ in the brine decreases as the salinity increases. This observation is

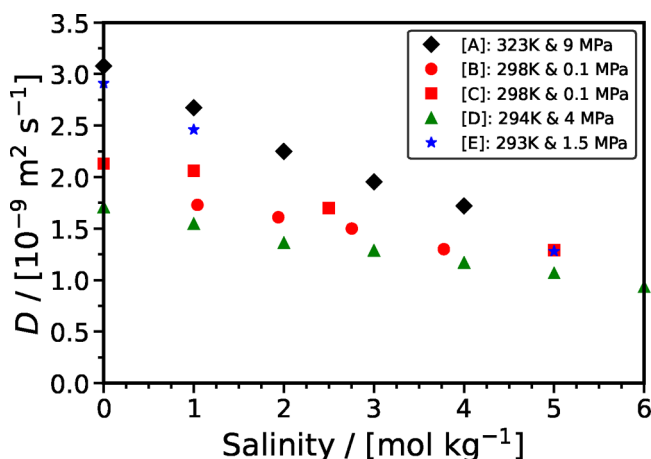


Figure 6. Effect of temperature and salinity [mol NaCl/(kg H₂O)] on the diffusion coefficient of CO₂ in brines. Symbols denote the experimental data. Legend: [A] Perera et al.;¹⁷² [B] Ratcliff and Holdcroft;¹⁷⁰ [C] Cadogan et al.;¹¹⁹ [D] Belgodere et al.;¹¹⁷ and [E] Basilio et al.¹²⁴

confirmed by all five experimental studies considered in Figure 6. As expected, higher temperatures result in higher diffusivities.

The experimental data of Ratcliff and Holdcroft¹⁷⁰ and Cadogan et al.¹¹⁹ exhibit an increasing deviation at lower salinity values, even though both studies are performed at the same *P* and *T* conditions. In particular, for the case of salinity equal to 1 mol L⁻¹, the CO₂ diffusivity reported by Cadogan et al. (using the Taylor dispersion method) is higher than the value reported by Ratcliff and Holdcroft (using the wetted sphere absorber technique) by approximately 16%. For the limiting case of pure H₂O, Cadogan et al. reported a diffusivity equal to $(2.130 \pm 0.028) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while the calculation with the method of Mutorou et al.¹⁷¹ resulted in a value equal to $(1.927 \pm 0.001) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while the calculation with the SA-type correlation of this study resulted in a value equal to $(1.917 \pm 0.001) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Both calculations indicate that the experimental measurements of Cadogan et al. seem to be overestimated.

Finally, the experimental data of Basilio et al.¹²⁴ performed at 293 K and 1.5 MPa have higher values than the data from Belgodere et al.¹¹⁷ performed at 294 K and 4 MPa. A similar analysis indicates that the data of Basilio et al. are higher than expected when compared to calculations with the method of Mutorou et al. and the SA-type correlation. For example, the SA-type correlation estimates the diffusivity to be $(1.664 \pm 0.001) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $(1.715 \pm 0.001) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 293 and 294 K, respectively. However, Basilio et al. (at 293 K) reported an experimental value equal to $2.91 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while Belgodere et al. (at 294 K) reported an experimental value equal to $1.71 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Figure 7 shows the effect of pressure on the diffusion coefficient of CO₂ in various brines. A mixed picture is obtained regarding the effect of pressure. While the data of Tang et al.¹⁸¹ indicate that the CO₂ diffusivity decreases as the pressure increases (at constant temperature and salinity), the opposite conclusion is reached when examining the data of Yang et al.,¹²⁵ Shu et al.,^{178,179} Zhang et al.,¹⁸² and Wang et al.¹⁷⁴ This

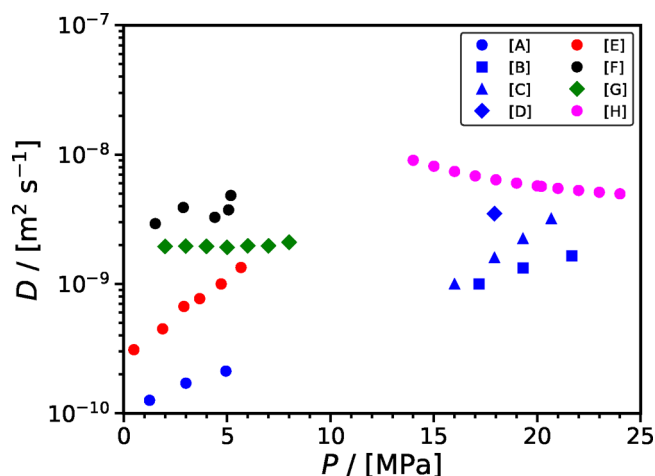


Figure 7. Effect of pressure and salinity on the diffusion coefficient of CO₂ in aqueous brines as a function of pressure. Symbols denote the experimental data. Legend: [A] Zhang et al.¹⁸² (288.15 K & 3 wt % salinity); [B] Shu et al.¹⁷⁸ (293.15 K & 3 wt % salinity); [C] Shu et al.¹⁷⁹ (293.15 K & 3 wt % salinity); [D] Shu et al.¹⁷⁹ (313.15 K & 3 wt % salinity); [E] Yang et al.¹²⁵ (300.15 K & 64,160 mg L⁻¹ Reservoir (Weyburn) brine); [F] Wang et al.¹⁷⁴ (311.15 and 0.25N NaCl); [G] Li et al.¹⁸⁰ (313 K & 1 M NaCl + KI); and [H] Tang et al.¹⁸¹ (355.65 K & 243,143 mg L⁻¹ Reservoir brine).

discrepancy could be resolved by (i) either performing a new series of experiments or (ii) performing an extensive series of molecular dynamics simulations. From Figure 7, the majority of the experimental measurements for the CO₂ diffusivity fall in the range 10⁻⁹–10⁻⁸ m² s⁻¹, there are also measurements in the range 10⁻¹⁰–10⁻⁹ m² s⁻¹ (e.g., Yang et al.¹²⁵ using the dynamic interfacial tension method; Zhang et al.¹⁸² using the pressure decay method). A systematic study at the molecular level could shed additional light into this discussion.

Figures 6 and 7 clearly show that the diffusion coefficient of CO₂ in brines depends on temperature, pressure, and salinity. Nonetheless, as a result of a lack of systematic experimental measurements (completely covering the three parameter space), a scarcely populated parameter space is currently available.

Motivated by the emerging application of CO₂ oceanic storage, Zhang et al.¹⁸² performed a systematic study of CO₂ diffusion in brines (3 wt %) under various offshore conditions covering a temperature range of 286.15–303.15 K and a pressure range 0.1–5 MPa. The *P*, *T* conditions examined cover different oceanic depths. For a scenario of oceanic sequestration, the pressure and temperature profile will change as the oceanic depth changes (i.e., the pressure increases while the temperature decreases as the depth of the water column increases). Figure 8 shows the combined effect of pressure and temperature on the CO₂ diffusion coefficient. The authors concluded that the influence of the pressure on the CO₂ diffusivity was stronger at the higher temperatures considered.

2.1.8. Convection-Enhanced Effective Diffusion Coefficients. While the molecular diffusion of CO₂ in pure H₂O or brines (in bulk or under confinement) is the primary focus of this review, natural convection-induced enhanced diffusion is briefly discussed in this section.

For constant temperature and salt concentration, as the pressure increases, the CO₂ solubility in H₂O increases as well.^{41,44} Yang and Gu¹⁴⁹ reported that the density of CO₂-saturated brine increased linearly with CO₂ concentration. Consequently, as CO₂ initially gets transferred through the gas–

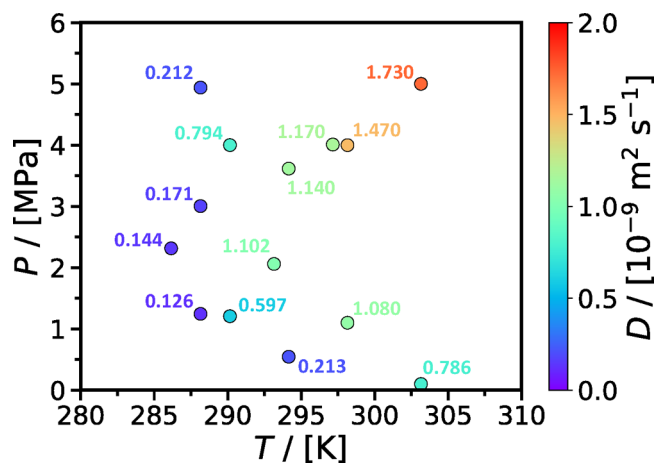


Figure 8. Combined effect of temperature and pressure on the diffusion coefficient of CO₂ in oceanic brine (3 wt %). Symbols denote the experimental data of Zhang et al.¹⁸²

liquid interface, and subsequently dissolves into the brine, a density gradient evolves in the brine phase, as a result of the concentration gradient. Namely, the brine near the interface becomes heavier than the brine further away from the interface. Instability is created in the brine which results in a natural convection flow in the brine phase. This mechanism of forced mixing results in an accelerated mass transfer of CO₂ in the brine under reservoir conditions (i.e., higher pressures). Often in the literature, this behavior has been interpreted using Fick's second law:

$$\frac{\partial C(z, t)}{\partial t} = D^* \frac{\partial^2 C(z, t)}{\partial z^2} \quad (t > 0, 0 \leq z \leq H) \quad (4)$$

where $C(z, t)$ is the CO₂ concentration in the fluid, H is the height of the fluid, and D^* is a characteristic diffusion coefficient to be further discussed below. Equation 4 is subject to the following initial (eq 5) and boundary conditions (eqs 6 and 7). The initial condition is

$$C(z, t)|_{t=0} = 0 \quad (0 \leq z \leq H) \quad (5)$$

The boundary condition (B.C. 1) at the CO₂-liquid interface is

$$C(z, t)|_{z=H} = C_{eq} \quad (t > 0) \quad (6)$$

where C_{eq} is the equilibrium CO₂ concentration at the interface.

The boundary condition (B.C. 2) at the bottom of the cell is

$$\left. \frac{\partial C(z, t)}{\partial z} \right|_{z=0} = C_{eq} \quad (t > 0) \quad (7)$$

By combining the solution of the diffusion equations shown above with a mass balance, an expression can be developed which connects the pressure evolution of the diffusion process with time. If pressure decay experiments are available, then by plotting the curve:

$$\ln[P(t) - P_{eq}] = \text{intercept} + \text{slope} \cdot t \quad (8)$$

we can obtain the diffusivity D^* from the slope of eq 8 (slope = $\pi^2 D^* / (4H^2)$), where also intercept is a function of various parameters associated with the diffusing system.

Figure 9 shows a number of different experimental studies that followed such an approach. The CO₂ diffusivity values, D^* , are

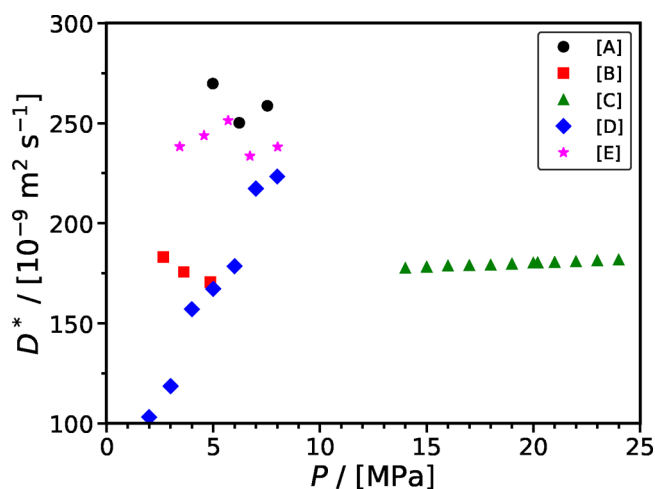


Figure 9. Effective diffusion coefficient, D^* , of CO_2 in different brines. Legend: [A] Yang and Gu¹⁴⁹ (331.15 K & 4310 mg L^{-1} reservoir brine), [B] Yang and Gu¹⁴⁹ (300.15 K & 4310 mg L^{-1} reservoir brine), [C] Tang et al.¹⁸¹ (355.65 K & 243 143 mg L^{-1} reservoir brine), [D] Li et al.¹⁸⁰ (313 K & 1 M NaCl + KI), and [E] Wang et al.¹⁷⁶ (318.15 K & 6,778 mg L^{-1} reservoir brine).

more than ca. 2 orders of magnitude higher than the rest of the experimental data that have been discussed earlier in Figure 7. This is due to the fact that D^* is an effective diffusivity which accounts for the combined effect of both molecular diffusion and natural convection on the mass transfer of CO_2 in the liquid phase. To apply the methodology explained earlier, Wang et al.¹⁷⁶ limited their analysis to the early time values from their pressure-decay experiments instead of the late-time. Even though their pressure decay measurements extended to more than 100 min, the analysis was limited to the first 40 min. At approximate that time, CO_2 arrived at the closed end of the cell, and therefore the assumption that the liquid medium is infinite (i.e., an assumption required for the analytical solution of the diffusion problem) is not valid any more. Consequently, at the initial stages of the process, the calculated effective diffusivity includes both molecular diffusion and natural convection effects.

To accurately model the complex mass-transfer process (i.e., accounting for both the molecular diffusion and the natural convection), the diffusion equation with molecular diffusivity has to be solved simultaneously with the Navier–Stokes equation, which is essential for the description of fluid flow due to natural convection. Nevertheless, this approach requires the solution of a complex numerical problem.

2.2. Molecular Simulations. The versatility of MD simulations has been proven in literature for computing the self-diffusivity of CO_2 in various solvents, such as aqueous alkanolamine solutions,^{77,78,183} ionic liquids,^{184,185} and deep eutectic solvents.^{186,187} MD simulation is a powerful method for the computation of diffusion coefficients of CO_2 in H_2O that can complement experimental measurements and provide useful insight into the physical mechanisms governing diffusion at the nanoscale. MD often take less time and are less expensive than experiments, providing researchers with quicker means of studying diffusion phenomena.^{45,188} MD simulations eliminate safety concerns associated with high-pressure and high-temperature experimental setups.^{45,78} Furthermore, MD simulations provide the flexibility to ignore reactions between CO_2 and H_2O , enabling the focus on the diffusion without considering reaction products.^{77,189,190} Nevertheless, MD simulation results

should always be validated against experimental data to ensure accuracy and reliability in predicting diffusion coefficients under different conditions. To validate computed diffusivities, comparisons with available experimental data are performed. In the absence of experimental diffusivities, researchers often resort to assessing agreement between the computed and readily accessible experimentally obtained thermodynamic and transport properties, such as densities and viscosities.^{77,78,183}

2.2.1. Simulation Methods. The computation of diffusivities can be achieved through either nonequilibrium MD (NEMD) or equilibrium MD (EMD) simulations.^{64,65,191} NEMD involves simulating the response of molecular systems to external perturbations. The results in NEMD simulations are heavily dependent on the specific applied external perturbation.^{64,192} Because of this reason, EMD simulations are commonly preferred for computing the diffusivity of CO_2 in H_2O .^{45,73,191,193} Two different methods can be used within EMD simulations to compute diffusivities: (i) The Green–Kubo method which involves integrating the velocity autocorrelation function over time, with this function slowly converging to zero.^{64,65,194} (ii) The Einstein relation which establishes a linear relationship between time and the mean-square displacement (MSD) of molecules to determine diffusivity.^{64,65} This linear relation is valid when the slope of mean-square displacement as a function of time equals 1 in a $\log(t)$ - $\log(\text{MSD})$ plot. Open-source MD software for computing transport properties is available. The most widely used codes are GROMACS¹⁹⁵ and LAMMPS.⁸³ Recently, Jamali et al.⁴⁷ developed the OCTP plugin for LAMMPS which allows the on-the-fly computation of diffusivities in MD simulations. Additionally, postprocessing tools such as PyLAT¹⁹⁶ can be used to compute diffusivities using the molecular trajectories generated by MD simulations.

2.2.2. Force Fields. In MD simulations, the so-called force fields play a crucial role since they provide the necessary description of the interactions between atoms and molecules within a system.^{64,65} Essentially, force fields describe the functional forms of the nonbonded potentials (e.g., van der Waals and electrostatic interactions) and bonded potential (i.e., bond stretching, angle bending, and dihedral rotations), allowing researchers to model the behavior of a molecular system. The accuracy and reliability of an MD simulation heavily depends on the accuracy of the chosen force field. Consequently, a well-parametrized force field is essential for obtaining meaningful insights into the structural and dynamic properties of molecular systems in silico.^{64,65}

Although numerous force fields have been developed for CO_2 , the EPM2 force field by Harris and Jung¹⁹⁷ and the TraPPE force field by Potoff and Siepmann¹⁹⁸ are the most used for computing the diffusivity of CO_2 in H_2O . Both of these force fields include Lennard–Jones (LJ) interaction sites and point charges on the mass-centers of carbon and oxygen atoms of CO_2 . The point charges represent the quadrupole moment of CO_2 (experimentally¹⁹⁹ -4.3×10^{-26} esu) and the computed quadrupole moment of both of these force fields agree with the experimental value within the statistical uncertainty (for EPM2¹⁹⁷ -4.1×10^{-26} esu and for TraPPE -4.52×10^{-26} esu).

In both EPM2 and TraPPE force fields, the C–O bonds are rigid. The C–O–C angle in the TraPPE force field is rigid, while in the EPM2 model, it is flexible (although the differences in the vapor liquid equilibria (VLE) and critical properties computed using a rigid angle and a flexible one are small).¹⁹⁷ TraPPE uses the Lorentz–Berthelot combining rules (arithmetic mean for σ

and geometric mean for ϵ), while in the EPM2 force field, a geometric mean is also used for the σ parameter of unlike atoms. The EPM2 force field was fitted to the VLE and critical properties of pure CO₂. The change in the combining rule of the σ parameter between unlike atoms has a subtle impact on the σ parameter in interactions involving CO₂ and H₂O. For example, using arithmetic and geometric means, the computed σ parameters for carbon (EPM2 CO₂)¹⁹⁷ and oxygen (TIP4P/2005 H₂O)⁸⁵ are 2.957 95 Å and 2.951 11 Å, respectively. Although the EPM2 force field consistently underestimates the liquid phase densities by 1–2% between 221–289 K, the predicted VLE, critical temperature (within 3% of experimental value), critical density (within 4% of the experimental value), and critical pressure (within 1% of the experimental value) are in good agreement with experiments.^{197,200} The TraPPE force field was parametrized to reproduce the VLE of binary *n*-alkane/CO₂ mixtures, specifically the propane/CO₂ mixture.¹⁹⁸ The VLE of pure CO₂ is accurately captured by the TraPPE force field,¹⁹⁸ demonstrating a good agreement between predicted and experimental densities. Notably, there is a slight overestimation in liquid densities and a minor underestimation in gas phase densities according to the force field predictions. The TraPPE force field exhibits excellent accuracy in predicting the critical properties of CO₂, with agreement within 1% for critical temperature and density, and within 4% for critical pressure when compared to the experimental values.²⁰⁰ This shows the reliability of the TraPPE force field in capturing central thermodynamic properties.

Het Panhuis et al.²⁰¹ developed a new force field which adopts the LJ parameters for carbon and oxygen atoms from GROMOS,²⁰² while partial charges were fitted to reproduce the quadrupole moment of CO₂, similar to the approach used for the point charges in the EPM2 force field,¹⁹⁷ resulting in comparable point charges for these two force fields. Other force fields such as CHARMM27,²⁰³ COMPASS,²⁰⁴ and the force field from Merker et al.²⁰⁵ have also been used to model pure CO₂ and mixtures.

An alternative method of designing a force field for accurately capturing the LJ interactions between CO₂ and H₂O involves using a specific set of LJ cross-interaction parameters rather than conventional mixing rules such as the Lorentz–Berthelot rules.⁶⁵ Given the low solubility of CO₂ in H₂O, this approach proves particularly advantageous, ensuring that the calculated properties of pure CO₂ and pure H₂O remain unaffected. The study by Orozco et al.²⁰⁶ exemplifies this strategy by tailoring the LJ cross-interaction parameters between CO₂ and H₂O to achieve excellent agreement between the computed vapor–liquid equilibrium curve of CO₂/H₂O mixtures and experimental data. Vlcek et al.²⁰⁷ used a similar approach to optimize the cross-interaction parameters between CO₂ and H₂O to reproduce the mutual solubility of CO₂ and H₂O. Vlcek et al.²⁰⁷ showed that the optimized parameters were able to accurately reproduce the self-diffusivities of CO₂ in H₂O in a temperature range of 298–353 K and 0.1 MPa. In a different, yet related context, Costandy et al.²⁰⁸ used a modification factor (i.e., $\chi = 1.08$ for TIP4P/Ice water model,²⁰⁹ and $\chi = 1.13$ for TIP4P/2005 water model)⁸⁵ to correct the Lorentz–Berthelot cross interaction energy parameter for the oxygen atom in the CO₂ molecule and the oxygen atom in H₂O. This approach has been used successfully for hydrate-related calculations in both MD^{208,210} and MC simulations.²¹¹

As one of the most important solvents in industrial and environmental processes, many different force fields have been

developed for H₂O. A few examples are SPC by Berendsen et al.,²¹² SPC/E by Berendsen et al.,²¹³ TIP4P/2005 by Abascal and Vega,⁸⁵ OPC by Izadi et al.,²¹⁴ and TIPSP by Mahoney and Jorgensen.²¹⁵ Polarizable force fields have also been developed for H₂O^{216–218} and CO₂.^{87,219} Such models can be more accurate in predicting phase equilibria and transport properties of pure components and mixtures, however, as they have not been used to compute the intradiffusivity of CO₂ in H₂O, further discussion is not provided in this review. A detailed discussion on polarizable and nonpolarizable H₂O force fields falls outside the scope of this review. For more information about H₂O force fields the reader is referred elsewhere.^{85,212–215,220–223} Nevertheless, it is crucial to exercise caution when selecting a force field for H₂O to compute the self-diffusion coefficient of CO₂ in H₂O. Given the low solubility of CO₂ under ambient conditions,⁴² the force field for H₂O determines the density and viscosity of the solution. The self-diffusion coefficients of solutes and the solvent largely depend on these properties.

2.2.3. Self-Diffusivity of CO₂ in H₂O at Ambient Pressure. Figure 10 shows the self-diffusivity of CO₂ in H₂O computed

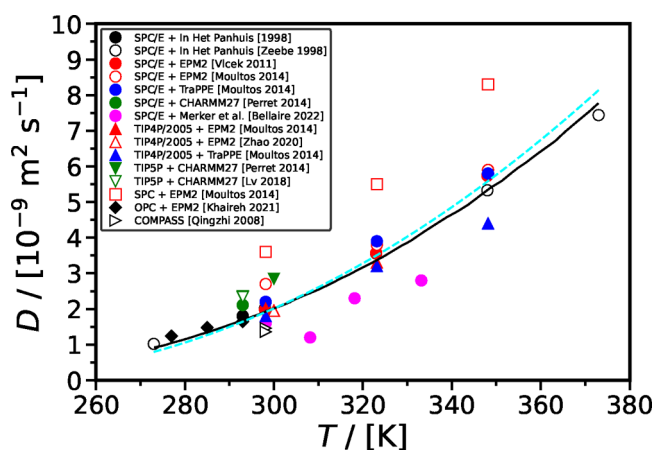


Figure 10. Intradiffusion coefficients of CO₂ in H₂O computed using different force fields^{40,45,120,163,193,201,207,224–226} as a function of temperature at 0.1 MPa. The black solid line and cyan dashed line represent the correlation developed by Mutoru et al.⁶¹ and the correlation developed in this work (SA-type), respectively.

using different force fields^{40,45,120,163,193,201,207,224–226} along with the correlations from Mutoru et al.⁶¹ and from this work (SA-type) as a function of temperature at 0.1 MPa. The self-diffusivities of CO₂ computed in SPC H₂O is the highest when compared with other force fields for H₂O and do not agree with the experimental correlations. As shown in Figure 11, SPC force field significantly underestimates densities (up to 5% deviation from experiments) and viscosities (up to 32% deviation from experiments) of H₂O. This implies that the SPC force field overestimates the free volume in the solution, leading to a significant overestimation of the self-diffusivities of the gas solute (i.e., CO₂). The self-diffusivities of CO₂ computed in TIPSP H₂O are slightly higher than those computed in SPC/E H₂O, and those in SPC/E H₂O are higher than in TIP4P/2005 H₂O. This pattern can be attributed to the fact that TIPSP underestimates the density and viscosity of the solution to the greatest extent, followed by the SPC/E force field and then TIP4P/2005 (Figure 11). The self-diffusion coefficients of CO₂ computed with the EPM2 and TraPPE force fields are very similar, with TraPPE yielding slightly higher values than EPM2.

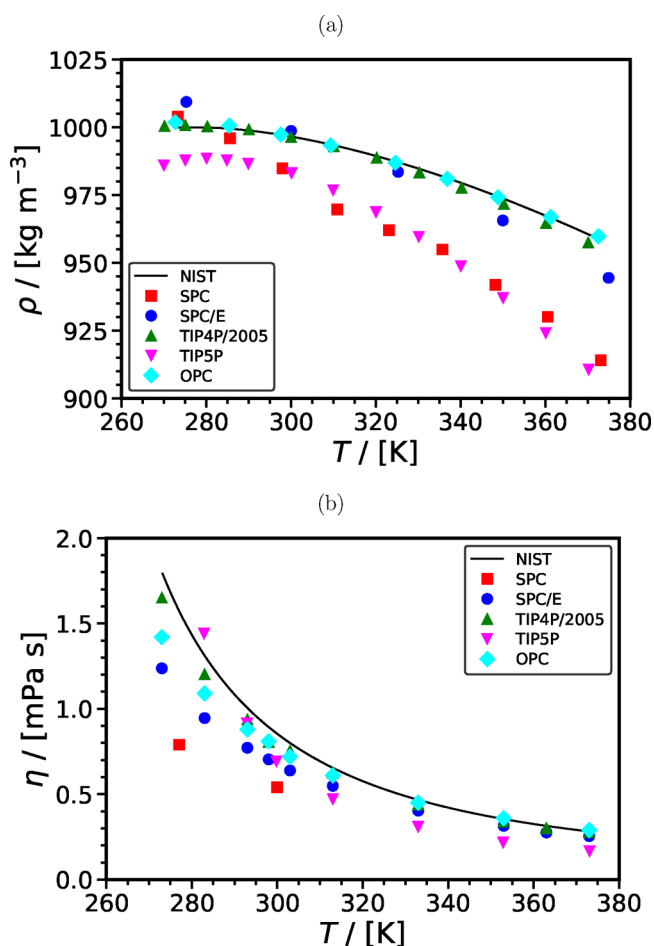


Figure 11. (a) Densities and (b) viscosities computed using SPC,^{227,228} SPC/E,^{229–232} TIP4P/2005,^{230,233} TIP5P,^{233,234} and OPC^{214,235} force fields for H₂O and their comparison with the values from NIST database²³⁶ as a function of temperature at 0.1 MPa.

The self-diffusivities of CO₂ in H₂O computed with the same force field are generally consistent throughout literature, except in the studies by Vlcek et al.²⁰⁷ and Moulτος et al.⁴⁵ In both these studies, SPC/E and EPM2 force fields were used for H₂O and CO₂, respectively. Vlcek et al.,²⁰⁷ however, computed the self-diffusivity of CO₂ as $1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K and 0.1 MPa, while at the same conditions, the self-diffusivity of CO₂ was computed as $2.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ by Moulτος et al.⁴⁵ The differences between the computed self-diffusivities by Vlcek et al.²⁰⁷ and Moulτος et al.⁴⁵ decrease with increasing temperature. This difference may be originating from the fact that Vlcek et al.²⁰⁷ used 512 molecules in total in their simulations and did not apply finite-size corrections. Finite-size effects were investigated by Moulτος et al.⁴⁵ and found to be negligible for the system size used, i.e., 2000 molecules. Later in this review, a detailed discussion on the finite-size effects on the diffusivities of CO₂ in H₂O is provided.

Overall, the data from literature suggest that the force field selection for H₂O has a predominant influence on the self-diffusion of CO₂ in H₂O, particularly given the low concentration of CO₂ in the solution due to its limited solubility in H₂O. This is in line with MD studies of other gases diffusing into H₂O, e.g., see Tsimpanogiannis et al.⁷² for the cases of H₂ and O₂. At ambient pressure, compared to the experimental correlations shown in Figure 10, the best performing

combination of force fields are TIP4P/2005-EPM2 for $T < 323 \text{ K}$ and SPC/E-TraPPE for $T > 323 \text{ K}$.

2.2.4. Self-Diffusivity of CO₂ in H₂O at High Pressure. At temperatures well below the critical point, the effect of pressure on the density and viscosity of the solution—and consequently on the self-diffusivity of CO₂—is relatively minimal, given the low compressibility of the liquid phase. For example, at a temperature of 373.15 K, the viscosity of TIP4P/2005 H₂O model demonstrates a slight 8% increase from 0.1 to 100 MPa.²³⁷ Similarly, the density of the TIP4P/2005 H₂O model shows a 4% increase from 0.1 to 48 MPa at the same temperature.⁴⁵ At elevated temperatures, however, the effect of pressure on the self-diffusivity of CO₂ becomes more noticeable, as the solution exhibits higher compressibility under these conditions. For instance, at 1023.15 K, the density of TIP4P/2005 H₂O increases by 69% from 250 to 1000 MPa.⁷³

Figure 12 shows the available self-diffusivities of CO₂ from

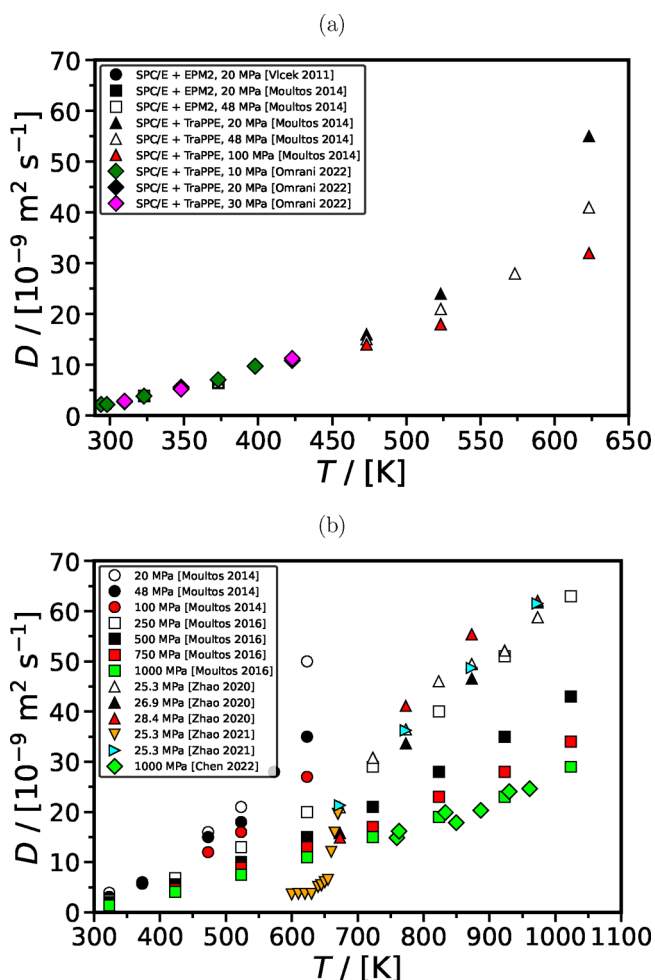


Figure 12. Self-diffusivities of CO₂ computed using the (a) SPC/E force field for H₂O and different force fields for CO₂,^{45,207,240} and (b) TIP4P/2005 force field for H₂O and EPM2 force field for CO₂^{45,73,193,241–243} as a function of temperature and pressure.

literature computed using MD simulations under high pressure. The data show that an increase in pressure causes a decrease in the self-diffusivities of CO₂ in H₂O. This becomes significant at $T > 500 \text{ K}$. At 623.15 K, the self-diffusivity of CO₂ in SPC/E H₂O and TraPPE CO₂ experiences a significant decrease (42%) over the pressure range from 20 to 100 MPa.⁴⁵ This reduction in

self-diffusivity closely aligns with a corresponding 40% increase in the density of the solution over the same pressure range at the given temperature.⁴⁵

As shown in Figure 12, toward the critical temperature of H₂O (experimentally 647 K²³⁶ while for TIP4P/2005 and SPC/E force fields, the critical temperatures are 623.3 K²³⁸ and 640 K,²³⁹ respectively), at ca. 22 MPa, the self-diffusivities of CO₂ in H₂O computed using all combinations of force fields for H₂O and CO₂ show a rapid increase. This is because the density of H₂O changes rapidly toward the critical point.²³⁹ For higher pressures ($P > 500$ K), the computed self-diffusivities of CO₂ in H₂O show a linear increase with increasing temperature. Comparing the computed self-diffusivities of CO₂ with experimental values is challenging given the scarcity of experimental data in the literature for high pressures and temperatures (relevant to CCS processes). As discussed earlier, the available experimental data by Lu et al.¹¹⁶ and Cadogan et al.¹¹³ is limited to temperatures up to 473 K and pressures up to 45 MPa. Moulτος et al.⁴⁵ computed the self-diffusivity of CO₂ in H₂O using the TIP4P/2005 force field for H₂O and EPM2 for CO₂ as $1.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at 473.15 K and 20 MPa. In comparison, Lu et al.¹¹⁶ experimentally measured the self-diffusivity of CO₂ under the same conditions as $1.61 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The excellent agreement between the computed and experimental values, coupled with TIP4P/2005's accurate predictions of H₂O density at higher temperatures and pressures,⁴⁵ suggests that the TIP4P/2005 and EPM2 force fields can be used for accurately predicting the intradiffusion coefficients of CO₂ in H₂O at elevated temperatures and pressures.

2.2.5. Finite-Size Effects. MD simulations with periodic boundary conditions for the computation of self- and collective diffusion coefficients (as well as other properties such as activity coefficients²⁴⁴ and thermal conductivities)^{245–247} are susceptible to finite-size effects due to the long-range nature of hydrodynamic and electrostatic interactions.^{248,249} To obtain the diffusivities at the thermodynamic limit, it is necessary to extrapolate the computed diffusivities which scale with $1/L$ ($1/L \rightarrow 0$, where L is the simulation box length).²⁵⁰ Commonly, the computed self-diffusivities are corrected with an analytical correction for finite-size effects derived by Yeh and Hummer:²⁵¹

$$D_i = D_i^{\text{MD}} + \frac{\xi k_B T}{6\pi\eta L} \quad (9)$$

where D_i is the self-diffusivity of species i at the thermodynamic limit, D_i^{MD} is the self-diffusivity (or intradiffusivity) of species i computed from the MD simulation, ξ is a dimensionless constant equal to 2.837297 obtained by an Ewald-like summation of a periodic lattice, k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity computed from MD simulation, and L is the length of the simulation box. An extension of this correction was developed by Jamali et al.^{54,252,253} for mutual diffusivities. For an in-depth understanding of the finite-size effects, readers are encouraged to refer to the review paper by Celebi et al.²⁴⁹ and the work by Jamali et al.⁵⁴

In MD literature reporting computations of CO₂ in H₂O intradiffusivities, the system sizes used in the simulations vary from a total of 216 molecules to 4124 molecules. Many of these studies do not correct the computed diffusivities for finite-size effects.^{45,73,120,163,201,207,243,254} In some of these studies, the diffusivities were computed using relatively big system sizes, and

finite-size effects found to be negligible.^{45,73,243,254} However, in some studies, small system sizes were used, and thus, it is expected that the diffusivity computations are relatively inaccurate. For example, In Het Panhuis et al.²⁰¹ computed the self-diffusivity of CO₂ in H₂O at 293 K and 0.1 MPa as $1.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ using 216 molecules in total and without correcting for finite-size effects. Considering eq 9 and the densities and viscosities shown in Figure 11, the finite-size corrected self-diffusivity of CO₂ in H₂O from this study is estimated to be $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This corrected value is 26% higher than the originally computed value by In Het Panhuis et al.²⁰¹ Another example showcasing the importance of correcting for finite-size effects is found in the study by Vlcek et al.²⁰⁷ In their work, Vlcek et al. (using 512 molecules) computed the self-diffusivity of CO₂ in H₂O as $1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K and 0.1 MPa. Interestingly, under identical conditions and using the same force field, Moulτος et al. (using 2000 molecules) computed the self-diffusivity of CO₂ as $2.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.⁴⁵ The inconsistency between these two studies can be attributed to the fact that Vlcek et al.²⁰⁷ did not account for finite-size effects, while using a relatively small system size. Considering eq 9, the finite-size corrected self-diffusivity of CO₂ from Vlcek et al.²⁰⁷ is 2.33×10^{-9} (17.7% change due to finite-size effects) $\text{m}^2 \text{ s}^{-1}$, aligning better with the value computed by Moulτος et al.⁴⁵ given the statistical uncertainty. From this discussion it becomes apparent that accounting for finite-size effects is crucial in MD simulations for accurately computing diffusivities, especially when rather small system sizes (<1000 molecules) are used.

2.2.6. Transport Diffusivities of Aqueous CO₂ Solutions. In most of the studies investigating the diffusivities of CO₂ in H₂O, the concentration of CO₂ in the solvent is very low (1–5 molecules of CO₂ in 216–4124 water molecules), as the solubility of CO₂ in H₂O under ambient conditions is quite low. At infinite dilution, the intradiffusivity of CO₂ is practically equal to transport diffusion coefficients.^{46,77,255} A comprehensive study of transport diffusivities in aqueous solutions of CO₂ was performed by Zhao et al.²⁴² These authors²⁴² computed the MS and Fick diffusivities (along with intradiffusivities) of aqueous solutions containing various gases, including CO₂, for a temperature range of 673–973 K and a CO₂ mole fraction range of 0.01–0.30. While the authors concluded that temperature and the concentration of CO₂ in the solution significantly influence the MS and intradiffusivities, the interpretation of MS diffusivity trends with changing CO₂ concentration remains challenging due to considerable scatter and uncertainties in the presented data (except for the data set at 673 K where a clear trend of increasing MS diffusivities with increasing CO₂ concentration can be seen). Zhao et al.²⁴² reported uncertainties up to 9% for MS diffusivities while the uncertainties for intradiffusivities were below 1%. For Fick diffusivities, Zhao et al.²⁴² noted an increase with temperature and also suggested that the concentration of CO₂ in the solution had no discernible effect on Fick diffusivities. The substantial scatter and uncertainties (up to 8%) in their Fick diffusivity data, potentially due to short simulation times (i.e., 1 ns), call for a careful interpretation.

Chen et al.²⁴³ also computed MS diffusivities of aqueous solutions of CO₂ at 923 K and 25 MPa for a mole fraction range of CO₂ between 0.005 and 0.900. Similar to the results from Zhao et al.,²⁴² the MS diffusivities computed by Chen et al.²⁴³ show substantial scatter and large uncertainties (up to 16%, potentially due to low simulation times of 3 ns). The results from these authors, however, are shown to agree well with Darken and

Vignes equations. Chen et al.²⁴³ argue that the composition effect of MS diffusivities comes with a trade-off between the number of hydrogen bonds per water and CO₂ diffusivity, both hindering collective diffusivity in the solution. Increasing the mole fraction of CO₂ in the solution decreases the average number of hydrogen bonds per water molecule, which increases the collective diffusivity. As the self-diffusivity of CO₂ is lower than H₂O, increasing the mole fraction of CO₂ in the solution, decreases the collective diffusivity. In summary, while the studies by Zhao et al.²⁴² and Chen et al.²⁴³ offered insights into MS and Fick diffusivities of aqueous CO₂ solutions, further investigation including the solution structure with extended run times are essential for acquiring more robust and meaningful data.

2.2.7. Correlations for the Diffusivity of CO₂ in H₂O from MD Simulations. During the design and optimization of industrial processes (e.g., CCS, EGS, EOR), calculations rely on the assessment of thermodynamic properties, such as the diffusivity of CO₂ in H₂O, at different conditions. Despite the numerous advantages of MD simulations, their application to compute diffusivities across a very wide range of conditions is often impractical due to the long simulation times and supercomputers required. As a solution, various simpler correlations for the diffusivity of CO₂ in H₂O have been established in the literature.^{45,73,163,193,241,242} These correlations are derived from data obtained from MD simulations at different conditions, providing a more accessible and efficient means for estimating diffusivities at different conditions. As discussed earlier, the influence of pressure on the intradiffusivity of CO₂ in H₂O is negligible at low temperatures ($T < 500$ K). In literature, three pressure-independent correlations have been proposed for computing the self-diffusivities of CO₂ in water at $T < 500$ K and 0.1 MPa.^{45,163} All these correlations have the functional form of eq 3. The comparison between the correlations developed using MD simulation data^{45,163} and the correlations developed using experimental results^{113,116} is shown in Figure 13. The first correlation, developed by Zeebe et al.¹⁶³ for a temperature range of 273–373 K, used MD simulation results obtained with the SPC/E force field for water and the force field from In Het Panhuis et al.²⁰¹ for CO₂. Zeebe et al.¹⁶³ demonstrated good agreement between their correlation, experimental values, and those calculated using the Stokes–Einstein equation. Moulτος et

al.⁴⁵ developed two correlations based on MD data from the force field combinations of SPC/E + TraPPE and TIP4P/2005 + EPM2. While the results from these force field combinations were similar, Moulτος et al.⁴⁵ found that the correlation using data from SPC/E + TraPPE better aligns with the correlation from Zeebe et al.¹⁶³ and the experimental correlation by Cadogan et al.¹¹³ The correlation derived from TIP4P/2005 + EPM2 agrees well with the experimental correlation by Lu et al.¹¹⁶ In Figure 13, the correlation from Zeebe et al.¹⁶³ agrees well with the experimental correlation from Cadogan et al.¹¹³ within the temperature range of 273–373 K, however, when extrapolated to 473 K, it diverges from the experimental correlations. Both correlations by Moulτος et al.⁴⁵ exhibit strong agreement with experimental correlations in the temperature range of 273–473 K. The application of the correlations from Moulτος et al.⁴⁵ within this temperature range at 0.1 MPa is expected to result in more accurate self-diffusivities of CO₂ in H₂O.

In a subsequent study Moulτος et al.⁷³ used the TIP4P/2005 + EPM2 force field combination for the calculation of the diffusivity of CO₂ in H₂O at temperatures in the range 323.15–1,023.15 K and pressures equal to 250, 500, 750, and 1,000 MPa. The computed data were correlated with a Speedy-Angel type of equation (eq 3). In order to account for the effect of high pressures, the parameters D_0 and m were given as functions of pressure (in MPa). Namely,

$$D_0 = a_1 \ln(P/\text{MPa}) + a_2 \quad (10)$$

and

$$m = b_1 \ln(P/\text{MPa}) + b_2 \quad (11)$$

where $a_1 = -2.3097 \times 10^{-9}$, $a_2 = 2.1064 \times 10^{-8}$, $b_1 = -0.17812$, and $b_2 = 2.59406$. This correlation, as clearly shown in Figure 14(a), describes the MD data very accurately at high pressures and temperatures. Furthermore, this correlation has been extrapolated to lower pressures, and compared against the MD data of an earlier study by Moulτος et al.,⁴⁵ at temperatures up to 623 K and pressures equal to 20, 48, and 100 MPa. Very good agreement was observed with these MD data, as well. Some deviations were observed for low temperatures, where the correlation reported by Moulτος et al.⁴⁵ should be used.

Two different correlations were developed for predicting the self-diffusivity of CO₂ in H₂O at higher temperatures (water at near- and supercritical conditions). Zhao et al.¹⁹³ developed a temperature, density, and viscosity-dependent correlation developed at 673–973 K and 25.33 MPa for the self-diffusivities of H₂, CH₄, CO, O₂, and CO₂ in supercritical H₂O expressed as

$$D_i = A_{0,i} \frac{T^c}{\rho^a \eta^b} \quad (12)$$

where $A_{0,i}$ is a gas specific constant (2.0078×10^{-8} for CO₂), ρ is the density, η is the viscosity, and a , b , c are the respective exponents characterizing the effect of density, viscosity, and temperature on the self-diffusivity of these gases in supercritical H₂O ($a = 0.44$, $b = 1.42$, and $c = 2.76$). The higher exponent on temperature suggests that temperature has the strongest effect on self-diffusivities, with the trend following $T > \eta > \rho$. To validate this correlation, Zhao et al.¹⁹³ computed the self-diffusivities of CO₂ under various conditions (673 to 973 K and 26.85 MPa, and 673 to 973 K and 28.37 MPa) using MD simulations and compared the results with those predicted by the correlation. Another correlation by the same group,²⁴¹

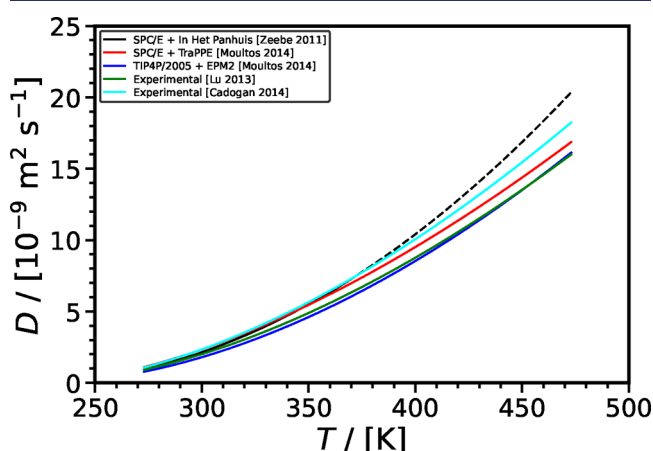


Figure 13. Correlations for the self-diffusivity of CO₂ in H₂O developed using the results from MD simulations^{45,73,163} and experimental data^{113,116} as a function temperature at 0.1 MPa. The solid lines represent the development temperature ranges of the correlations while the dashed lines show extrapolations to higher temperatures.

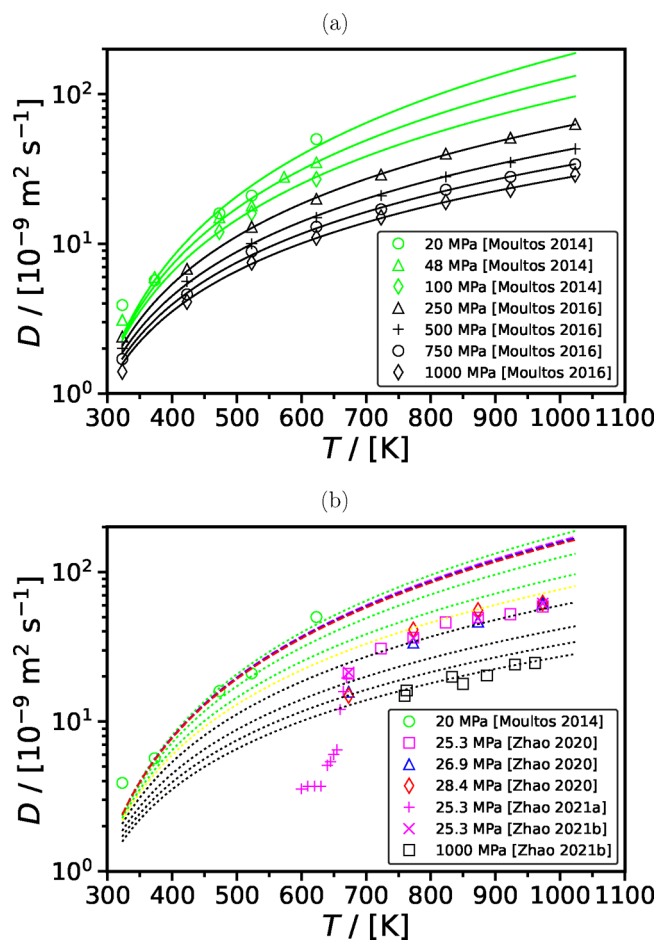


Figure 14. (a) Comparison of the MD data (denoted with symbols) and calculations (denoted with solid lines) using the pressure-dependent correlation of Moulτος et al.⁷³ Red symbols denote the data of Moulτος et al.,⁴⁵ while black symbols denote the data of Moulτος et al.⁷³ (b) Comparison of various MD data (denoted with symbols) and calculations (denoted with dotted/dashed lines) using the pressure-dependent correlation of Moulτος et al.⁷³ Notation for lines (from bottom to top): black dotted lines: 1000, 750, 500, and 250 MPa; yellow dotted line: 150 MPa; green dotted lines: 100, 48, and 20 MPa; and dashed lines: 28.4 MPa (red), 26.9 MPa (blue), 25.3 MPa (magenta).

applicable to near-critical H_2O , was developed for the self-diffusivities of H_2 , CH_4 , CO , O_2 , and CO_2 at a temperature range of 600–670 K and 25.33 MPa. While utilizing the same functional form (eq 12), different parameters were fitted to the data obtained using MD simulations ($A_{0,i} = 4.7155 \times 10^{-3}$ for CO_2 , $a = 0.47$, $b = 1.2$, and $c = 1.01$). The fitted values showed that viscosity has the most significant impact on intradiffusivities in near-critical H_2O , distinguishing it from the supercritical conditions. Although the authors²⁴¹ compared their results for H_2 and O_2 with other correlations from literature, they did not provide specific validation for the intradiffusivities of CO_2 , except for limited data from MD simulations at higher pressures. Validation for both of these correlations relies on data obtained through MD simulations. Direct comparison with experimental results is essential for assessing the reliability and predictive power of the correlations in capturing the real-world behavior of the self-diffusivity of CO_2 in near-critical and supercritical water.

In 2021, Zhao et al.²⁴² refined their correlation for the intradiffusivity of several gases, including CO_2 , in supercritical H_2O . This enhanced correlation incorporated the effect of CO_2 concentration in the solution, ranging from a mole fraction of 0.01 to 0.30. The functional form remains consistent with their prior studies (eq 12), but with additional factors accounting for solution composition and the thermodynamic factor. While these self-diffusivity correlations exhibit strong agreement with MD simulation data, direct comparisons with experimental data are challenging due to the limited availability of experimental results. Additionally, Zhao et al. extended their model to include MS and Fick diffusivities. For Fick diffusivities, the model relies solely on temperature and two gas-specific fitting parameters, while MS diffusivities are computed by dividing Fick diffusivities by the thermodynamic factor (which is a function of solution composition and temperature). As discussed earlier, the data presented by Zhao et al.²⁴² for the MS and Fick diffusivities show substantial scatter and uncertainties, emphasizing the need for cautious interpretation regarding the model's representation of reality.

Figure 14(b) shows the comparison between the calculations using the pressure-dependent correlation of Moulτος et al.⁷³ and the MD simulations reported by Zhao and Jin,¹⁹³ Zhao et al.,^{241,242} and Chen et al.²⁴³ as a function of temperature and pressure. As can be clearly seen, the data of Chen et al. follow closely the correlation of Moulτος et al. In sharp contrast, a large

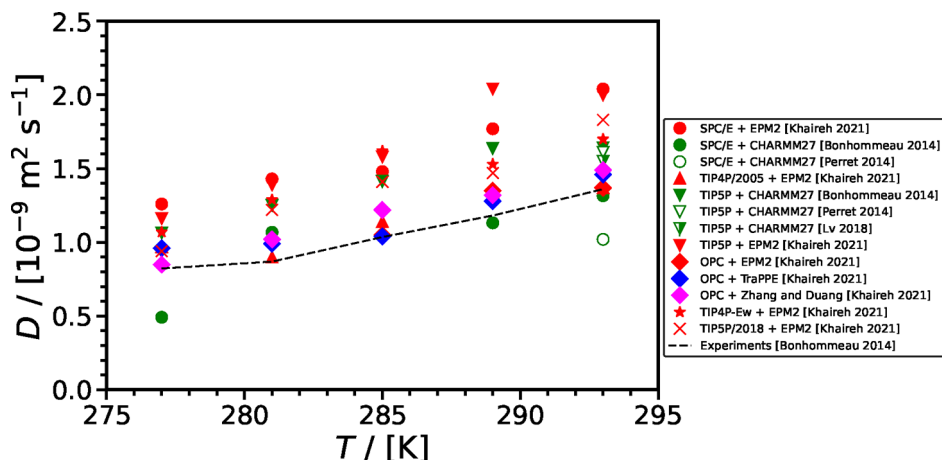


Figure 15. Comparison between computed^{40,224,225,256} and experimental²⁵⁶ self-diffusivities of CO_2 in carbonated alcoholic drinks as a function of temperature at 0.1 MPa.

discrepancy is observed between the data of Zhao and Jin,¹⁹³ and Zhao et al.^{241,242} Zhao and Jin¹⁹³ and Zhao et al.²⁴² reported data in the temperature range 673–973 K, while Zhao et al.²⁴¹ reported data at 600–670 K (close to the H₂O critical point). From Figure 14 it is evident that the data of Zhao and Jin¹⁹³ and Zhao et al.²⁴² fall in-between the correlation-lines corresponding to 150 and 250 MPa, while the simulations were performed in the range 25.3–28.4 MPa. Furthermore, for the MD data Zhao et al.,²⁴² focusing on the proximity of the H₂O critical point, the authors reported the diffusivity of CO₂ in H₂O at 620 K and 25.3312 MPa to be equal to $3.71 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while Moulton et al.⁴⁵ reported a diffusivity value equal to $50 \pm 4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 623 K and 20 MPa. Currently, the source of the discrepancy is not clear and further studies are required to resolve it.

2.2.8. Diffusivity of CO₂ in Aqueous Electrolyte Solutions. In Figure 15, intradiffusivity data from MD simulations^{40,224,225,256} are compared with experimental results from Bonhommeau et al.,²⁵⁶ in a carbonated hydroalcoholic solution (representing champagne) with mole fractions of CO₂, ethanol, and H₂O set at ca. 4.8×10^{-3} , 0.042, and 0.95, respectively, at 0.1 MPa and a temperature range of 277–293 K. While MD studies using the same force fields generally exhibit consistent results, a discrepancy arises between the intradiffusivities of CO₂ computed by Bonhommeau et al.²⁵⁶ and Perret et al.,⁴⁰ specifically when SPC/E is used for water and CHARMM for CO₂ and ethanol. Bonhommeau et al.²⁵⁶ argue that the improved equilibration method used in their study (replica exchange MD) is the cause of this discrepancy and their results are more accurate.

The investigation of Khaireh et al.²²⁵ shows the crucial role of the H₂O force field in determining the intradiffusivities of CO₂. The diffusivities computed using EPM2,¹⁹⁷ TraPPE,¹⁹⁸ and Zhang-Duan²⁵⁷ force fields are in agreement while the intradiffusivities computed using different water force fields show variations. The study by Lv et al.²²⁴ further emphasizes on this point, demonstrating agreement in the intradiffusivities computed in carbonated hydroalcoholic solution, cola (in this solution, ethanol was replaced with sucrose), and club soda (in this solution, ethanol was replaced with sodium bicarbonate) at 293 K and 0.1 MPa. Comparing with the experimental data from Bonhommeau et al.,²⁵⁶ OPC²¹⁴ and TIP4P/2005⁸⁵ H₂O models exhibit excellent agreement throughout the temperature range of 277–293 K, while the other H₂O force fields overestimate the self-diffusivity of CO₂. This is expected since these force fields (OPC²¹⁴ and TIP4P/2005⁸⁵) represent H₂O density and transport properties (viscosity and self-diffusivity of H₂O) much better than the other H₂O models (see Figure 11). We suggest the usage of OPC²¹⁴ and TIP4P/2005⁸⁵ force fields for the future MD studies, while caution is advised against SPC/E,²¹³ TIP4P-Ew,²⁵⁸ TIPSP,²¹⁵ and TIPSP/2018²⁵⁹ force fields.

García-Ratés et al.²⁶⁰ investigated the diffusivity of CO₂ in aqueous ionic solutions using MD simulations. The authors computed self- and MS diffusivities in brine for a temperature range of 333–453 K, a pressures range of 5–50 MPa, and a salinity range of 1–4 mol kg⁻¹. The results²⁶⁰ showed that both self- and MS diffusivities increase with increasing temperature, while an increase in salinity from 1 mol kg⁻¹ to 4 mol kg⁻¹ led to a decrease of 34–41%. Typically to aqueous systems, the authors²⁶⁰ show that pressure has not a significant impact on the diffusivities. Additionally, García-Ratés et al.²⁶⁰ developed a correlation linking MS diffusivities to self-diffusivities and rotational relaxation times, achieving a good agreement between predicted and computed MS diffusivities with an absolute

average deviation of 15.4%. These findings contribute insight into the complex interplay of temperature, salinity, and pressure on the diffusivity of CO₂ in brine which is relevant to CO₂ sequestration in deep saline aquifers.

Understanding the diffusivity of CO₂ in aqueous alkanolamine solutions is critical for absorption-based CO₂ capture processes.²⁶¹ Polat et al.⁷⁸ investigated the temperature and alkanolamine concentration dependencies of infinitely diluted CO₂ in aqueous monoethanolamine (MEA) solutions within a temperature range of 293–353 K and MEA concentrations ranging from 10 to 50 wt % using MD simulations. The results⁷⁸ show a significant effect of temperature and MEA concentration on the self-diffusivities of CO₂, with a 72–86% decrease in self-diffusivities from 10 wt % to 50 wt % MEA concentration in the solution. This study⁷⁸ further revealed that the temperature dependence of the self-diffusivities in 10 wt % aqueous MEA solutions are higher than that in 50 wt % solutions. Similar observations were made by Yiannourakou et al.¹⁸³ for CO₂ in 30 wt % aqueous *N*-methyldiethanolamine (MDEA) solutions, demonstrating an increase in self-diffusivities from $2.50 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 300 K to $1.03 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at 400 K. Polat et al.⁷⁷ expanded the exploration to unloaded and loaded aqueous MDEA mixtures, showing that CO₂ diffusion is 3.5 times faster in 10 wt % than in 50 wt % aqueous MDEA solutions within a temperature range of 288–333 K. Polat et al.⁷⁷ attributed the slower diffusion of CO₂ in concentrated MDEA solutions to stronger interactions between CO₂ and surrounding molecules (both water and MDEA). Additionally, investigations⁷⁷ into the self-diffusivities of CO₂ in loaded 50 wt % aqueous MDEA solutions revealed a decrease with increasing CO₂ loading, indicating that the CO₂ capture with aqueous MDEA solutions slows down as CO₂ loading increases. The research on CO₂ diffusivity in aqueous alkanolamine solutions remains limited, focusing primarily on two alkanolamines and solely on self-diffusivities. The diffusivity of CO₂ in aqueous solutions of other alkanolamines, such as diethanolamine (DEA) still remains unexplored, while comprehensive studies into collective diffusivities (Fick and MS) in CO₂/H₂O/alkanolamine mixtures are yet to be conducted, highlighting avenues for future research in the CO₂ capture field.

3. AQUEOUS CO₂ DIFFUSION IN CONFINED MEDIA

In applications such as gas separation and CCS in geological formations, CO₂ molecules are constrained by confined media. The confinement effect imposes a heterogeneous distribution of the fluid in such a way that the thermophysical properties and structure are very different from an unconfined homogeneous fluid. For instance, the solubility of confined CO₂ in H₂O is different than that of the unconfined CO₂ in H₂O. When confined by hydrophobic surfaces, a higher solubility is expected due to the coadsorption of CO₂ molecules, whereas a lower solubility is expected for the hydrophilic ones, because of the weak CO₂–H₂O interactions.^{262,263} Diffusion is also affected by confinement. Overall, CO₂ diffusivity is expected to decrease because the mobility of molecules is reduced; preferential adsorption and steric hindrance may further decrease diffusion.²⁶⁴

3.1. Experimental Studies. **3.1.1. Experimental Measurement Techniques.** Direct experimental measurements of the molecular diffusion of confined fluids are often infeasible or nontrivial.²⁶⁵ Nevertheless, trends can be observed through experiments, and macroscopic diffusion-related properties can be determined. Quasi-Elastic Neutron Scattering (QENS) can

be used in combination with MD simulations to investigate the stochastic motion of molecules. From the scattering signal, one can devise a model based on functions, such as Lorentzian and Gaussian, and fit parameters to determine diffusion coefficients, residence times, and correlation lengths.²⁶⁶

The transport diffusivity of pure CO₂ in silicalite has been studied with QENS and MD by Papadopoulos et al.²⁶⁷ The same order of magnitude was obtained by both methods, however, QENS diffusivities were higher at every condition studied. The trend with loading inside the zeolite was similar for QENS and MD. The dynamics of pure CO₂ with QENS has been investigated in other confining materials such as the zeolite AlPO₄-5²⁶⁸ and the metal–organic frameworks (MOF) MIL-140A(Zr)²⁶⁹ and UiO-66(Zr).²⁷⁰ The mixtures of CO₂ with CH₄,^{268,271,272} C₂H₆,^{273,274} and H₂²⁶⁹ have also been studied. To the best of our knowledge, the only work available on the diffusion of the mixture CO₂–H₂O studied with QENS is from Hunvik et al.²⁷⁵ These authors investigated the dynamics of the hydrated interlayer of hectorite with and without CO₂ using QENS techniques. The system has been dominated by jump-diffusion mechanisms, in which the molecule motion occurs via almost instantaneous jumps. Because individual molecule trajectories are indistinguishable, the system is characterized by a single random jump diffusion coefficient, a residence time, and a mean jump distance. Based on the diffusion parameters, the authors concluded that the dynamics in the interlayer of a hydrated smectite remains unchanged after exposure to CO₂.²⁷⁵

Nuclear magnetic resonance (NMR) may be applied to investigate dynamic properties. By signal attenuation, one can fit a model to determine diffusion coefficients. Bowers et al.²⁷⁶ have shown with NMR that CO₂ has a parallel preferential orientation when confined in the interlayer space of hectorites. The main CO₂ dynamics are characterized by fast-motion rotation to the normal surface at rates ca. 10⁵ Hz. Peksa et al.²⁷⁷ investigated the diffusion of pure CO₂ confined by DMOF-1 with the ¹³C pulsed field gradient (PFG) NMR technique. They discovered that CO₂ is highly mobile in this MOF with diffusion trace tensor of $(6.2 \pm 1.0) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The anisotropy (ratio between the parallel and perpendicular diffusion coefficient) is equal to 3.²⁷⁷ Using similar techniques, Forse et al.²⁷⁸ have shown that this anisotropy is equal to ca. 30 for the CO₂ diffusion in the Zn₂(dobpdc) MOF. The diffusion coefficient of CO₂ confined by pores of silica is at least 1 order of magnitude lower than in the bulk. By modifying the silica surface, further decrement in the CO₂ diffusivity occurs due to higher adsorption.²⁷⁹ Despite the numerous NMR studies of CO₂ diffusion in various confining materials,^{276–281} to the best of our knowledge no studies investigating the CO₂–H₂O mixture exist in the open literature.

Microfluidics can be applied along with fluorescence techniques to investigate CO₂ diffusion in aqueous mixtures. By the spatial evolution of the pH measured by fluorescence emissions, one determines the CO₂ concentration profile with time. The diffusion coefficient is obtained by fitting the profiles with analytical diffusion models.^{121,282} Sell et al.¹²¹ developed a microfluidic device capable of measuring diffusivity in less than 90 s. The authors determined the CO₂ diffusion coefficient in a wide range of pressure (0.5 to 5 MPa) and salinity (0 to 5 M NaCl) and showed that their results are in good agreement with previous experiments and models: CO₂ diffusivity is almost independent of the pressure, and decay exponentially with salinity. Peñas López et al.²⁸² have investigated the CO₂ radial diffusion from a CO₂ bubble to an air-saturated H₂O solution confined by a horizontal Hele-Shaw cell via pH-sensitive planar

laser-induced fluorescence (PLIF). Different analytical models were able to successfully describe the diffusion-driven transport, and the characteristic length of the isoconcentration front evolves proportionally to $\sqrt{Dt}$, with t being time.

Finally, chromatographic techniques may also provide insights into macroscopic diffusion. Suzuki et al.²⁸³ performed chromatographic experiments in a zeolite bed with different humidity contents. The authors showed that the contribution of the macropore diffusion on the interparticle diffusion is dominant compared to the micropore diffusion. The CO₂ interparticle diffusion in hydrophobic zeolites has shown no dependency on the moisture level.²⁸³

3.1.2. Core Flooding Experiments. Core flooding experiments are a common approach when the effect of confinement, via a porous medium, on different thermodynamic or transport properties is of interest. For the case of CO₂ diffusion in liquid H₂O under confinement, core flooding experiments usually provide an effective diffusivity, which is different than the molecular diffusivity in bulk fluids, that also includes the effect of the porous medium.

Macroscopically, core flooding experiments may also provide insights related to CO₂ transport in a confined environment, for instance, through the rock permeability calculation.^{284–286} Moortgat et al.²⁸⁷ have shown that, to represent the core-flooding experiments, the applied numerical model needs to take into account the CO₂ Fickian diffusion. Busch et al.²⁸⁸ measured the effective diffusion coefficient of CO₂ in a H₂O-saturated shale sample under subsurface conditions by fitting the cumulative amount of CO₂ passing through the pores to a nonstationary diffusion model. The diffusivity is estimated at 3.08 and $4.81 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the first and second run of the experiment, respectively. The difference between runs is attributed to CO₂ partial sorption in the first run. By comparing the effective diffusivity with the diffusion of CO₂ in bulk H₂O, the sample tortuosity is estimated to be between 40 and 70.²⁸⁸ Si et al.²⁸⁹ conducted a similar experimental study for the measurement of the effective diffusion coefficient of CO₂ in water-saturated coal.

Renner²⁹⁰ used Berea cores and examined the diffusivity of CO₂ in 0.25 N NaCl (i.e., 14.625 g per L H₂O) brines at 311 K and pressures up to 5.86 MPa. The author concluded that for the chosen conditions there was no difference identified between diffusion coefficients measured for vertical or horizontal positioning of the cores (i.e., the gravity-induced convection had minimal effects on the measured diffusivities). Shi et al.¹⁵⁴ reported experimental measurements for water-saturated or brine-saturated packs of two different porous materials. Namely, (i) 1.6 mm soda lime glass beads with 40% porosity and $250.11 \times 10^{-11} \text{ m}^2$ permeability, and 125–150 μm quartz particles with 45% porosity and $0.48 \times 10^{-11} \text{ m}^2$ permeability. Seyyedi et al.²⁹¹ performed experiments in brines (0–20 wt %) at temperatures in the range 311.15–331.15 K, in a bead pack cell, with 37% porosity and $2.95 \times 10^{-9} \text{ m}^2$ permeability. The authors used a mathematical model to account for the density-driven convection and investigated the effect of temperature and brine salinity on the convection mechanism. They reported that an increase in salinity results in reduction of the diffusion coefficient, while an increase in the temperature results in an increase of the diffusion coefficient, which is consistent with previous studies. Additionally, they reported that an increase in temperature or brine salinity has an unfavorable effect on the convection mechanism. Zhang et al.¹⁸² used Berea cores and examined the effect of the core permeability (10, 50, and 100

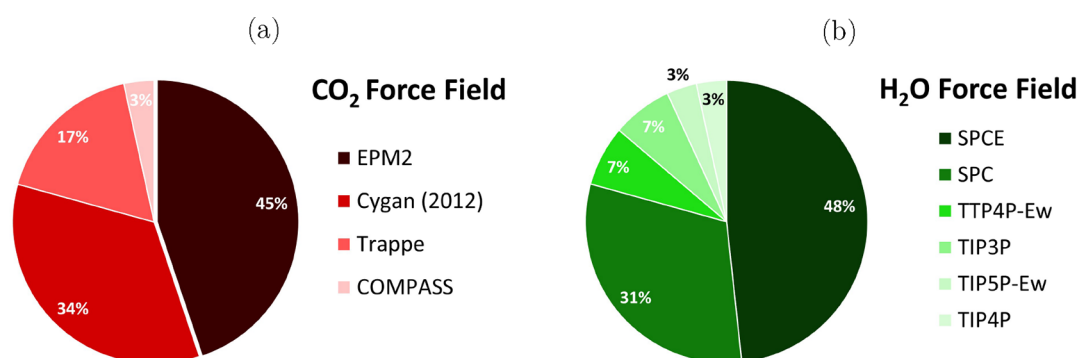


Figure 16. Overview of the relative popularity of (a) CO₂ and (b) H₂O force fields used in the literature for the computation of CO₂–H₂O diffusion in confinement.

mD) on the CO₂ diffusivity in brine-saturated (3 wt %) cores at T , P conditions equal to 290.15 K and 4 MPa, respectively. They reported effective diffusion coefficients of CO₂ in the brine-saturated cores equal to 1.22×10^{-15} , 3.87×10^{-15} , and 4.81×10^{-15} , m²/s for the aforementioned permeabilities, respectively. Li et al.²⁹² reported effective diffusion coefficients in brine-saturated (0.5–2 mol L⁻¹ NaCl) Berea cores. The authors examined temperatures in the range 313.15–373.15 K and pressures in the range 8.28–30.94 MPa, and provided empirical pressure–temperature-based correlations for the CO₂ diffusivities in brines under reservoir conditions. Li et al.¹⁵⁰ reported experiments using Berea and Bentheimer core samples. The authors introduced a new method for the measurement of effective gas diffusion coefficients in brine-saturated consolidated cores based on a radial diffusion model. To this purpose, mathematical models were developed to obtain the gas effective diffusion coefficient from the measured pressure decay curve. Li et al.¹⁵⁰ concluded that the diffusive tortuosity factor of the examined cores was about 10. Basilio et al.¹²⁴ used the pressure decay method to measure the molecular CO₂ diffusion coefficients in pure water, at 293.15 K, using capillary tubes, packed with glass beads with three different grain size ranges: (i) 45–90 μ m, (ii) 200–300 μ m, and (iii) 425–560 μ m. The use of capillary tubes in this experimental approach allows for the disregard of density-induced convection during the diffusion process. Moghaddam et al.²⁹³ used different unconsolidated sand packs with permeabilities in a range of ca. 3.1–2.546 m² to measure the effective CO₂ diffusion coefficients in pure water at 310.15 K. The experimental diffusivities were subsequently correlated with the dimensionless Rayleigh number.

3.1.3. The Challenge of Comparing Experimental and Computed Diffusivities in Confined Media. The comparison of diffusion data from experiments and theoretical models is not always straightforward. The multiple definitions of diffusivities (e.g., self-, Fickian, Maxwell-Stefan) makes the comparison even harder, since one needs to be very careful on how the diffusion coefficient is defined, which depends on the proposed driving force (concentration, mole fraction, or chemical potential). Only few techniques, such as NMR²⁹⁴ and QENS²⁹⁵ can provide essential insight into diffusion mechanisms under confinement. More difficulties emerge when comparing real materials (with defects, different geometries, shapes, and crystallographic planes) with the simulations, which are usually carried out with perfect materials (e.g., no defects). Due to this, the experimentally determined diffusion tensor is different from the diffusion tensor computed with MD simulations. The latter is a diagonal tensor even for anisotropic materials, whereas the

former exhibits off-diagonal components in anisotropic materials.²⁹⁶ This is a direct consequence of the spatial scale at which the experiment and the simulations are conducted. When confined in a idealized shape (e.g., slit, cylindrical, or spherical pores), the diffusion tensor of the fluid is necessarily diagonal.^{296,297} Another issue is related to Darcy's law, widely applied to describe porous media flow. For highly confined media with low permeability (e.g., some nanoporous materials), due to the strong adsorption, Darcy's law may fail, as shown via molecular simulations for kerogen.²⁹⁸ Such discrepancies between experiments and simulations could be tackled to some degree by a more systematic effort by the scientific community in determining diffusion coefficients, and transport properties more generally, in confined media.

3.2. Molecular Simulations. For a full description of the microscopic diffusion under confinement, molecular simulation techniques can be a very helpful approach. From MD simulations, we obtain the trajectories of the molecules from which the diffusion of each species can be computed. The initial configuration of MD simulations of confined fluids may be obtained with Grand-Canonical Monte Carlo (GCMC) simulations, in which the temperature T , the volume V , and the chemical potential of each species μ_i are fixed.^{264,299–302} At equilibrium, the chemical potential of confined species is equal to their chemical potential in the bulk, and the number of molecules is defined based on insertion/deletion techniques. Performing GCMC to generate initial configurations for MD simulations, one guarantees a confined fluid distribution that is in equilibrium with an unconfined fluid at the specified bulk pressure.

Via MD simulations, the diffusion of confined CO₂ has been investigated as part of various mixtures, such as shale gas,³⁰³ CH₄,^{304–306} n -C₄H₁₀,³⁰⁷ n -C₇H₁₆,³⁰⁸ n -C₈H₁₈,³⁰⁹ and ionic liquids.^{310,311} The diffusivity of pure CO₂ has also been investigated under confinement by different materials, such as MOF,^{312–314} graphene sheets,³¹⁵ zeolites,³¹⁶ calcites,^{317,318} silicalites,^{314,319} and clays.³²⁰ In this review, we focus only on the results related to diffusion of the confined mixture of CO₂ and H₂O.

3.2.1. Force Fields. As we extensively discussed earlier, in MD (and GCMC) simulations, accurate force fields are required for the description of the interactions between the species. Similarly to the bulk phase, to study transport properties of confined CO₂–H₂O mixtures, the EPM2¹⁹⁷ and SPCE²¹³ force fields for CO₂ and H₂O, respectively, are the ones more commonly used in the literature (see Figure 16). These force fields were developed to reproduce bulk properties at homogeneous

conditions, and thus, they may not always be a good representation of the interactions of the molecules in confinement, especially taking into account the solid–fluid interactions. Cygan et al.³²¹ have developed a fully flexible force field for CO₂ based on vibrational data of confined CO₂. This force field has been widely used to study CO₂ diffusion in confinement.^{263,264,301,322–328}

The choice of force field representing the confining material is also crucial. CLAYFF³²⁹ is the most used force field to represent natural confining media. CLAYFF has been shown to be suitable for representing hydrated minerals, such as hydroxides, oxyhydroxides, and clays, in contact with fluids. CLAYFF is based on metal–oxygen ionic interactions and the only bonded interactions are in the terminal groups.³²⁹ To investigate CO₂ diffusion under confinement, CLAYFF has been used to represent the mineral structure of montmorillonite,^{264,265,301,323,325,327} hectorite,³³⁰ beidellite,³⁰² forsterite,³³¹ kaolinite,²⁶² sepiolite,³²⁸ palygorkite,³²⁸ and hydrocalcite.³²² To represent kerogen³³² and calcite^{263,333,334} structures, COM-PASS²⁰⁴ and the force field developed by Xiao et al.³³⁵ are the ones commonly used.

To represent artificial materials, various force fields can be used. For carbon-derived materials such as carbon nanotubes^{300,336} the LJ carbon is commonly represented by the chargeless FF from Steele.³³⁷ The CVFF³³⁸ has also been applied to model graphene sheets.³³⁹ This force field, however, has been originally parametrized to represent proteins.³³⁸ Sizova et al.³⁴⁰ applied the Steele FF³³⁷ combined with the OPLS-AA³⁴¹ to represent, respectively, the carbon atoms and the functional groups in the structure of the CMK-5 mesoporous.

The representation of MOF usually is made by the generic DREIDING force field³⁴² and the universal force field (UFF).³⁴³ Both these models have already been used to investigate CO₂ diffusion.^{344–347} Bendt et al.³⁴⁴ devised a force field based on Density Functional Theory (DFT) calculations capable of better predicting the potential energy surface around the open metal sites of Mg-MOF-74.³⁴⁸ The authors have investigated the effect of accounting for flexibility in the solid framework on the CO₂ diffusion. Although the adsorption energy in the flexible material is about the same as in the rigid one, the equilibrium distance between guest molecules and the open metal site is enlarged in the former, which increases the diffusivity of CO₂ molecules when flexibility is taken into account.³⁴⁴

3.2.2. Methods. When confined, the fluid density is no longer spatially homogeneous, and the diffusion coefficient exhibits a tensorial nature. Following Einstein's method, diffusion coefficients may be obtained from the mean squared displacement evolution with time if the medium is homogeneous. For inhomogeneous fluids, however, Einstein's equation is no longer valid, not only because of the inherent inhomogeneity, but also because Einstein's solution to the mass balance equation is found by considering boundary conditions at infinity, which does not hold for confined systems. In this case, both parallel and perpendicular components of diffusion coefficients should be computed using other methods. For parallel self-diffusion coefficients, the method proposed by Liu et al.,³⁴⁹ based on the solution of the Smoluchowski equation and the calculation of the survival probability, is adequate and has been applied in the literature.^{317,350} Similar to Einstein's relation, the method is based on the computation of diffusivity from the mean squared displacement, but, to account for the medium inhomogeneity, the mean squared displacement must be divided by the survival

probability of molecules to stay in the reference layer in which the diffusivity is evaluated.

For the perpendicular self-diffusion coefficient, some methods have been proposed in the literature. Liu et al.³⁴⁹ proposed a method that requires two simulations in parallel, one of them using Langevin dynamics.⁶⁵ Mittal et al.³⁵¹ proposed a method based on a discretized version of Smoluchowski equation. The Mean First-Passage Time has been applied by von Hansen et al.³⁵² to compute the diffusion of H₂O in a lipid bilayer. Carmer et al.³⁵³ proposed the steady-state color reaction-counter-diffusion method. Finally, Franco et al.²⁹⁷ analytically solved the Smoluchowski equation deriving a method to compute the perpendicular self-diffusion coefficient. It is important to note that although these methods have been applied in the literature, many authors continue to apply Einstein's relation to compute diffusion coefficients in confined media. Overall, the perpendicular component of CO₂ diffusion is lower than the parallel one due to the constraints imposed by the surface in that direction.^{262,326,327,339} Usually, the diffusion coefficient tensor is dependent on the distance from the surface, in such a way that the Smoluchowski equation needs to be solved for each direction in layers parallel to the confining media. When a molecule goes from one layer to another, it no longer contributes to the calculation of the diffusion in its initial layer. This effect is accounted for by the survival probability of molecules in space.³⁴⁹

Using the method proposed by Liu et al.³⁴⁹ for the parallel self-diffusion coefficient, Chialvo et al.³⁵⁴ computed the H₂O and CO₂ self-diffusion coefficients parallel ($D_{\parallel}^s$) to a silica surface in a H₂O-rich environment. They have computed $D_{\parallel}^s$ in both external and internal (confined) interfacial regions. Externally, the diffusion coefficient of H₂O decreases monotonically with decreasing distance from the silica surface.^{263,354} In the confined region of hydrophobic surfaces, the diffusivity is no longer monotonic due to the local fluctuations of density and composition. Under severe confinement of hydrophobic silica (distance of 0.6 nm between plates), CO₂ concentrates in a single peak in the middle of the pore and achieves a diffusivity ($2.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) close to the bulk value ($3.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). Santos et al.³³⁴ have also computed the parallel diffusion of CO₂ with low H₂O concentration at calcite and silica surfaces, accounting for the inhomogeneity of the confined fluid. All other studies available on the confined CO₂–H₂O diffusion have computed the diffusion coefficients from the slope of the mean squared displacement with time, following Einstein's relation, which could lead to misleading conclusions and inaccurate results.

The self-diffusion coefficient relates to the thermal energy of particles through Brownian motion. The presence of other particles, especially a different component, may interfere with the particle motion. Transport diffusivity, such as Maxwell–Stephan or Fick diffusion coefficients, accounts for the influence of collective interactions on the fluid motion. Transport diffusion coefficients can be computed from EMD or NEMD. The former may converge very slowly because it needs to account for cross-correlation between all particles.³⁵⁵ Various nonequilibrium techniques may be applied to investigate diffusion flux under confinement. With gradient relaxation molecular dynamics (GRMD), an initial concentration gradient is established and the transport diffusivity is obtained by fitting the diffusion equation with the system relaxation with time.³⁵⁶ In the dual control volume grand canonical molecular dynamics (DCV-GCMD), two bulk reservoirs with distinct chemical

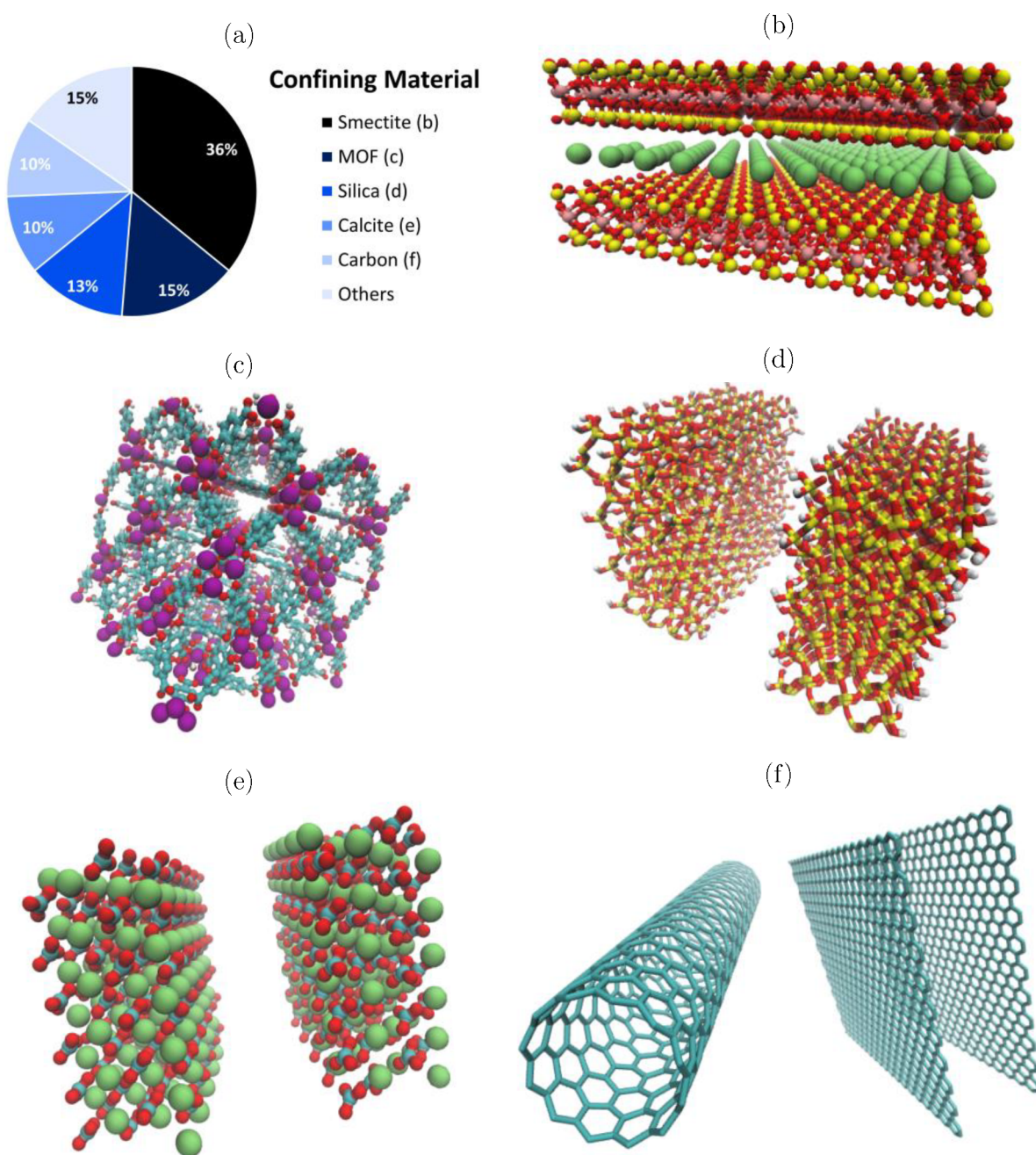


Figure 17. (a) Overview of the relative popularity of confining materials used in molecular simulations in the literature for the investigation of CO_2 – H_2O diffusion in confinement. An example of the structure of the main confining material is shown: (b) Ca-montmorillonite representing a smectite crystal; (c) UiO-66(Zr) MOF; (d) [001] quartz representing a silica crystal; (e) [1014] calcite crystal; and (f) carbon nanotube and graphene sheets representing carbon materials. The colors red, white, yellow, cyan, green, pink, and purple represent oxygen, hydrogen, silicon, carbon, calcium, aluminum, and zirconium atoms, respectively.

potential are coupled to opposite edges of the confined system; the chemical potential gradient is kept constant via particle creation/destruction in the reservoirs, in such a way that a steady state flux is established and the diffusion coefficients can be obtained.³⁵⁷ An external field (EF-NEMD) can also be applied in the fluid particles to induce a mass flux in a predefined direction.³⁵⁸ Care should be taken because the effect of an external field on the interaction between particles may not be negligible.³⁵⁵

Magnin et al.³⁴⁶ have computed both self- and MS diffusivity of CO_2 and H_2O confined by a MOF using Einstein's method (EMD) and applying a constant force on the guest molecules

(NEMD), respectively. They found that $D_{\text{MS}}^{\text{CO}_2} \approx D_{\text{CO}_2}^s$, which indicates that for CO_2 the cross-interaction effects on diffusion may be negligible compared to the strong effect imposed by the confinement. The same does not apply for H_2O at all conditions: by increasing the pressure, and consequently the loading, the self-diffusivity deviates from the Maxwell-Stefan one, and collective interactions may no longer be neglected.³⁴⁶ Yang et al.³⁰⁰ related the self- and transport diffusion coefficients in the CO_2 – H_2O mixture confined in carbon nanotubes (CNT). The authors have used the pure component sorption and diffusion data, and the saturation loading, and derived a loading-

independent self-exchange coefficient. They found that the MS diffusivity of CO₂ is almost independent of the loading. Overall, good agreement is obtained with the correlation. At low loading (or high H₂O content), this approach is less reliable.³⁰⁰

As in the bulk phase, finite-size effects may also be present when computing diffusivities under confinement. Considering z as the confinement direction, Simonnin et al.³⁵⁹ have shown that for a LJ fluid the use of periodic boundary conditions in x and y directions leads to finite-size effects due to the hydrodynamic interactions between periodic images and the constraint of total momentum conservation. Elongated simulation boxes in x and y directions ($L_x \approx L_y \gg L_z$) should be used to avoid such effects. When this is not an option (it is often computationally expensive), analytical expressions may be applied to correct diffusion coefficients.^{249,359} To the best of our knowledge, there is no investigation available in the literature regarding finite-size effects on CO₂ diffusion under confinement.

3.2.3. Confinement in Natural Media. The effect of confinement on CO₂ depends on the confining material. Figure 17 shows the distribution of confining media used to investigate the CO₂ diffusion in studies available in the literature.

3.2.3.1. Smectites. Smectites are the most studied material due to their importance in carbon sequestration applications. This clay is a layered aluminosilicate composed of one octahedral (O) sheet with Al as central atom and two adjacent tetrahedral (T) sheets with Si, creating a T–O–T structure. Some of these central atoms are substituted by divalent metals. This creates a partial negative charge in the structure that is balanced by positive counterions located in the interlayer region between two T–O–T structures.³²³ Because of the high hydration energy of counterions, smectites may swell to accommodate H₂O molecules in the interlayer. It has been experimentally observed that hydrated smectites may also swell in contact with CO₂, depending on the initial confined H₂O concentration.³⁶⁰ The confinement effect in these conditions is significant, and the molecules distribute themselves in one or two layers.³²¹

The different types of smectite can be classified depending on the main substitution of metal atoms and its location.³⁰² Montmorillonite (MMT) is the most common smectite and also the most investigated one in regards to CO₂ diffusion.^{264,265,299,301,302,323,325,327,361} CO₂ diffusion has also been investigated in the interlayer of hectorite (HEC)^{275,326,330} and beidellite (BEI).³⁰²

The basal d -spacing in the interlayer depends on its relative humidity.^{301,323} For a monolayer (1W), a bilayer (2W), and three layer (3W) H₂O arrangement, the basal d -spacing is expected to be around 12, 15, and 18.5 Å, respectively.³⁶² Care should be taken when defining the basal d -spacing in MD simulations because not all hydrate states are stable for all clays.³⁶¹ By predefining the basal d -spacing, the final equilibrated composition may not correspond to a thermodynamically stable state.²⁶⁴ From MD and MC simulations, the stability of the clay can be analyzed through the swelling free energy.^{299,323}

Swelling may also occur due to the intercalation of CO₂ molecules within interlayers.^{323,330} At low CO₂ concentration and low hydration state, CO₂ molecules organize themselves parallel to the surface.^{276,325,330} By increasing the H₂O concentration, CO₂ adopts other orientations, with some of them pointing perpendicular to the surface.^{322,330} Swelling is not always expected to happen due to CO₂ intercalation. No evidence of swelling is observed in the presence of CO₂ for 1W Na-HEC.²⁷⁵ The effect of swelling increases CO₂ diffusivity in

the interlayers of smectites.^{301,322–324,327} Transition from 1W to 2W hydration state increases both CO₂ and H₂O mobility. The increment is more pronounced on CO₂ diffusivity because molecules are no longer trapped in a single preferential orientation.³²⁴ At the same hydration state, H₂O mobility is higher at lower concentrations of CO₂ due to the hindering caused by the latter.^{327,361} Kadoura et al.²⁶⁴ showed that for a fixed basal d -spacing, CO₂ diffusivity decreases with loading of both CO₂ and H₂O due to steric hindrance, but does not depend significantly on the loading of CH₄. Both CO₂ and H₂O molecules simultaneously adsorb in the clay surface and occupy the center region of the interlayer, whereas CH₄ does not present preferential adsorption. Therefore, the effect of both H₂O and CO₂ loading on the CH₄ diffusion is more pronounced than the effect of CH₄ loading on CO₂ diffusion.²⁶⁴

The ions in the interlayer reduce the diffusivity of both H₂O and CO₂.^{263,363} Severe confinement at 1W structure decreases the mobility of ions the most due to the strong electrostatic interactions with the mineral wall (the diffusion coefficient can be up to 4 orders of magnitude lower than the bulk).³⁰¹ Different cations may occupy the interlayer space to balance the surface charge. By fixing an ion-independent basal d -spacing, Kadoura et al.³⁰¹ have concluded that the diffusion of CO₂ is mostly independent of the cation type. Cations with different hydration energies could lead to different hydration and swelling of the clay, which may affect the diffusion of CO₂.³²⁴ The residence time between CO₂ and ions is short, and the activation energy for H₂O molecules to move out of the first coordination shell of ions is 5 times larger than the activation energy for CO₂.^{325,330} The CO₂–ion interaction is weak compared to their respective interaction with H₂O molecules. Due to the repulsions, CO₂ may change the clay wettability.³²⁴ In the presence of CO₂, ion migration to the clay basal surface may screen part of the surface charge, increasing the surface hydrophobicity.³²³

Zhang et al.³²⁷ have performed a compression test in MMT intercalated with CO₂ and H₂O by deforming the cell parameters. The self-diffusion coefficient of both species decreases drastically with compression loading and approaches zero at the end of the test. The mineral stiffness is increased by the process of intercalation of both CO₂ and H₂O.³²⁷

Owusu et al.²⁶⁵ have investigated the diffusion of different gases (CO₂ included) in H₂O confined by MMT. By increasing the pore size, CO₂ diffusion coefficient converges asymptotically to CO₂ unconfined diffusion. The diffusion is inversely proportional to the hydrodynamic radius of the gas. The authors have investigated the temperature influence on diffusion. As expected, by increasing temperature, the mobility of both CO₂ and H₂O increases. The diffusion activation energy is changed by the confinement: for polyatomic molecules such as CO₂ and CH₄, the activation energy is higher than in the bulk H₂O,²⁶⁵ which means that CO₂ diffusion is less dependent on temperature under confinement.

Figure 18 shows a compilation of the results reported for CO₂ diffusion coefficient in the interlayer of MMT. $\ln D_{\text{CO}_2}^s$ is plotted as a function of $1/T$ to verify the correspondence to Arrhenius equation (i.e., $D = D_0 \exp\left(-\frac{E_a}{RT}\right)$). A wide range of diffusivities is obtained for similar temperatures and hydration states. The main factors that may cause this dispersion are the fluid composition and density, the force field selection, the definition of the basal distance, and the method of computing the diffusion coefficient. At the same temperature and hydration state (2W), Kadoura et al.²⁶⁴ have obtained diffusion coefficients different

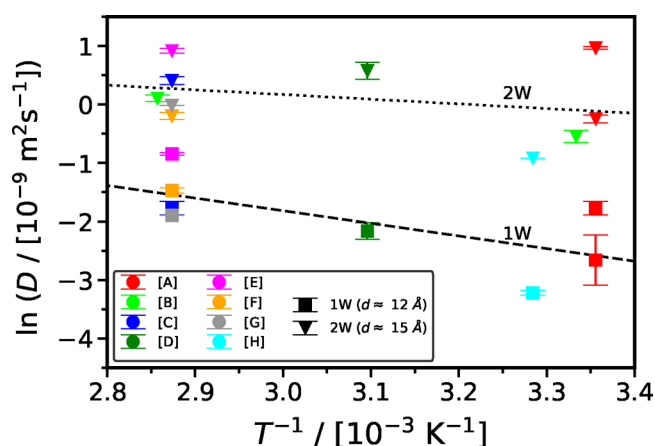


Figure 18. CO₂ self-diffusion coefficient in Na-MMT at different temperatures for the 1W (square symbols) and 2W (triangle symbols) hydration states. The black dashed and dotted lines represent linear interpolation of Arrhenius equation for the 1W and 2W states, which are given by $\ln D/D_0 = -2157.2/T + 4.7$ and $\ln D/D_0 = -798.1/T + 2.6$, respectively, where $D_0 = 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Legend: [A] Kadoura et al.,²⁶⁴ [B] Owusu et al.,²⁶⁵ [C] Botan et al.,²⁹⁹ [D] Kadoura et al.,³⁰¹ [E] Makaremi et al.,³⁰² [F] Myshakin et al.,³²³ [G] Rahromostaqim and Sahimi,³²⁴ and [H] Zhang et al.³²⁷

from each other by a factor of 3. The lower the H₂O concentration (400 compared to 600 kg m⁻³), the higher the diffusivity. The number of H₂O and CO₂ molecules should be defined in GCMC simulations before the MD simulation, to avoid simulation artifacts caused by an arbitrary choice of the number of particles. The usual basal *d*-space definition is the pore distance plus half the width of each T–O–T structure. Owusu et al.²⁶⁵ have considered only the pore distance, which could cause some disparity when compared to other works if no correction is made. Finally, if the perpendicular component is accounted for in the trace of the diffusion coefficient,³²⁷ then lower values are obtained compared with the parallel-only diffusion coefficients. By linear interpolation of the $\ln D_{\text{CO}_2}$ vs $1/T$ plot, the activation energy (E_a) of CO₂ diffusion in the 1W and 2W hydration states are 17.9 and 6.6 kJ mol⁻¹, respectively. The activation energy computed by Owusu et al.²⁶⁵ for CO₂ diffusion in MMT is ca. 11.1 kJ mol⁻¹ (no difference caused by the pore size was accounted for).

3.2.3.2. Calcite. Despite the abundance of carbonate-bearing subsurface formations, only a few works have investigated the diffusion of CO₂ confined by calcite.^{263,317,318,322,334} CO₂ solubility is reduced by the hydrophilic surface of calcite and the presence of salts, such as NaCl, may further reduce it.²⁶³ H₂O at low concentrations increases CO₂ diffusion by displacing CO₂ toward the center of the pore due to H₂O preferential adsorption.^{333,334} Increasing the concentration of both components, the species mobility decreases due to steric hindrance and molecular collisions.^{322,333} For CO₂ confined between parallel calcite minerals, an anisotropy in the CO₂ parallel diffusion coefficients is observed due to the calcite plane morphology.³¹⁷ The same anisotropy is also observed in the CO₂–H₂O mixture.^{333,334}

3.2.3.3. Silica. CO₂ diffusion has been also investigated in silica nanopores.^{328,334,340,354} The mobility of CO₂ increases in regions with larger pores. For this reason, CO₂ diffusion is higher in sepiolite channels than in palygorskite,³²⁸ and larger in mesopores than micropores of the SBA-15 structure.³⁴⁰ Molecules located close to the porous medium surface have

low mobility. The displacement of CO₂ molecules caused by low concentrations of H₂O in hydrophilic surfaces increase CO₂ diffusivity.^{334,340} Under severe confinement (6 Å), CO₂ diffusion coefficient is five times higher in hydrophobic silica than in the hydrophilic silica because of the lower H₂O content.³⁵⁴

3.2.3.4. Other Materials. Others confining materials include kerogen,³³² kaolinite,²⁶² forsterite,³³¹ Illite,³²⁴ and zeolites.³⁶⁴ As with the materials discussed earlier, the diffusivity of CO₂ increases with temperature in kerogen. In the presence of H₂O, adsorption of CO₂ onto functional groups of kerogen is reduced.³³² The hydrophobic surfaces of kaolinite promote a slightly higher parallel diffusion of CO₂ than the hydrophilic surfaces for pressures up to 35 MPa.²⁶² Rahromostaqim and Sahimi³²⁴ have investigated CO₂–H₂O diffusion confined by mixed layers of MMT and Illite, a mica mineral. They showed that the swelling and ion hydration depends on the charge location of the mineral. Within the bilayer space, the diffusivities of both CO₂ and H₂O increase with the H₂O-to-CO₂ ratio.³²⁴ Kerisit et al.³³¹ have studied the behavior of CO₂–H₂O in the interface of a forsterite mineral. A phase separation occurs, and a H₂O film forms at this mineral surface. The diffusivity of CO₂ and H₂O are similar in both aqueous and CO₂-rich phase. In the transition interface region, CO₂ is less hydrated by other H₂O molecules compared to their hydration in the bulk region, which results in a higher CO₂ diffusivity than H₂O diffusivity in this region.³³¹ Wang et al.³⁶⁴ have investigated the diffusion of flue gas (CO₂, NO, NO₂, N₂, O₂, SO₂ and H₂O) in zeolites (13X and 5A). The authors reported a correlation between the guest molecule size and its diffusivity, with triatomic molecules obtaining a lower diffusion coefficient. Due to the strong binding force between water molecules and the zeolite framework, no detectable H₂O diffusion was obtained with reasonable accuracy. As expected, the higher the temperature or the pore sizes (zeolite 13X), the higher the mobility and the diffusion coefficient of all molecules.³⁶⁴

3.2.4. Confinement in Artificial Media. **3.2.4.1. Metal–Organic Frameworks.** MOFs are crystal-like structures composed of metal clusters and organic linkers. Due to their potential to separate CO₂ from flue gas, the diffusion of CO₂ in various MOFs at different conditions have been investigated.^{344–347} The diffusion behavior of CO₂ in this confining medium depends on the crystal structure and the loading.

Diffusion and adsorption show opposite trends, i.e., the species with higher adsorption energy tend to have lower mobility. Mera et al.³⁴⁷ investigated the diffusion of the CO₂–N₂–H₂O mixture in three MOFs (IRMOF-1, Cu-BTC, and MIL-47). Although Cu-BTC has the narrowest pores, the reduction in pure CO₂ diffusion is higher in the confinement imposed by MIL-47 due to the stronger interactions between the adsorbate and the framework. In the presence of H₂O, CO₂ diffusion coefficient in MIL-47 is increased by 1 order of magnitude. The competition between CO₂ and H₂O for the active sites increases the mobility of both species. The opposite occurs in the mixture diffusion in Cu-BTC, in which the species have a lower diffusivity compared to its pure components diffusion.³⁴⁷

Magnin et al.³⁴⁵ investigated the CO₂ diffusion in UiO-66 at different loadings of CO₂ and H₂O. At lower pressures (lower loadings), CO₂ preferentially adsorbs in the tetrahedral cages and the diffusion mechanism is mainly cage hopping.^{345,346} By increasing CO₂ loading, its mobility is reduced due to the increase of CO₂–CO₂ collisions and reduction in the MOF free

volume. In a different MOF, CALF-20, further increment in CO₂ loading could actually increase CO₂ diffusivity because of the presence of more than one CO₂ per cage could make their interaction with the solid surface weaker.³⁴⁶

In UiO-66 MOF, H₂O acts as an extra sorbent medium for CO₂ diffusion. The tortuosity created by the H₂O network, the CO₂–H₂O attractive interactions, and the occupied pore volume at high H₂O loading are some of the reasons for the reduction in CO₂ mobility in the presence of H₂O.³⁴⁵ In CALF-20, the enthalpies of adsorption of CO₂ and H₂O have similar magnitudes, which results in similar values for their diffusion coefficients.³⁴⁶ On the other hand, in the Mg-MOF-74, where the adsorption energy between water and the open metal sites is stronger, CO₂ diffusion coefficient can be an order of magnitude higher than H₂O.³⁴⁴

Darcy's law describing the fluid flow in the porous media, fails to predict the fluid transport in nanopores by neglecting the adsorption. Magnin et al.³⁴⁵ have computed the permeance, which corrects Darcy's law, using the confined fluid diffusivity. From the nano-Darcy expression, they show that the macroscopic fluid flow in UiO-66 MOF decreases with H₂O loading, following the behavior predicted by the diffusion mechanisms.³⁴⁵

Figure 19 shows at which conditions the CO₂ diffusion in MOFs has been investigated by the studies available in literature. The CO₂ mole fraction here accounts only for the presence of CO₂ and H₂O as guest molecules (not accounting for the N₂ in the work of Mera et al.,³⁴⁷ for instance). The focus so far has been mainly on temperatures ca. 300 K and low loadings (low pressure), with few exceptions. In the future, it could be interesting to further investigate the temperature and pressure effects, because by changing these conditions one can control the adsorption/release of guest molecules in gas capture applications.

3.2.4.2. Carbon Materials. Carbon nanotubes (CNTs) allow for faster CO₂ diffusion compared to other nanoporous materials.³³⁶ The larger the pore, the higher the CO₂ mobility.^{300,336,339} Contrary to other materials, CO₂ diffusion coefficients in CNTs is almost space-independent. Svoboda et al.³³⁶ attribute the abnormal higher diffusivity close to the wall to the CO₂ parallel orientation to the nanotube. The effect of H₂O on CO₂ diffusion is a balance between CO₂ displacement and CO₂–H₂O interactions.^{300,336} Because these interactions are stronger than CH₄–H₂O interactions, the effect of preadsorbed H₂O is less pronounced on CO₂ diffusion than on methane diffusion.³⁰⁰ In hydrophobic carbon mesoporous surfaces, such as CMK-5, at high pressures (high loading) the CO₂ diffusivity is decreased in the presence of H₂O due to the reduction in the pore free volume.³⁴⁰ In most cases, the mobility of species increases with temperature. Zhao et al.³³⁹ discovered, however, that the diffusion coefficient of hydrogen decreases with temperature in the mixture of CO₂–H₂–H₂O confined by graphene sheets. The increment in the thermal motion of CO₂ and H₂O molecules with temperature acts like an extra obstruction to small H₂ molecules.³³⁹

4. OUTLOOK

In light of the discussion we provided in this review and the currently available data (experimental and MD) on the diffusivity of CO₂ in H₂O, we propose several promising directions for future research for both cases of diffusivity in bulk or under confinement.

4.1. CO₂–H₂O Diffusion in Bulk.

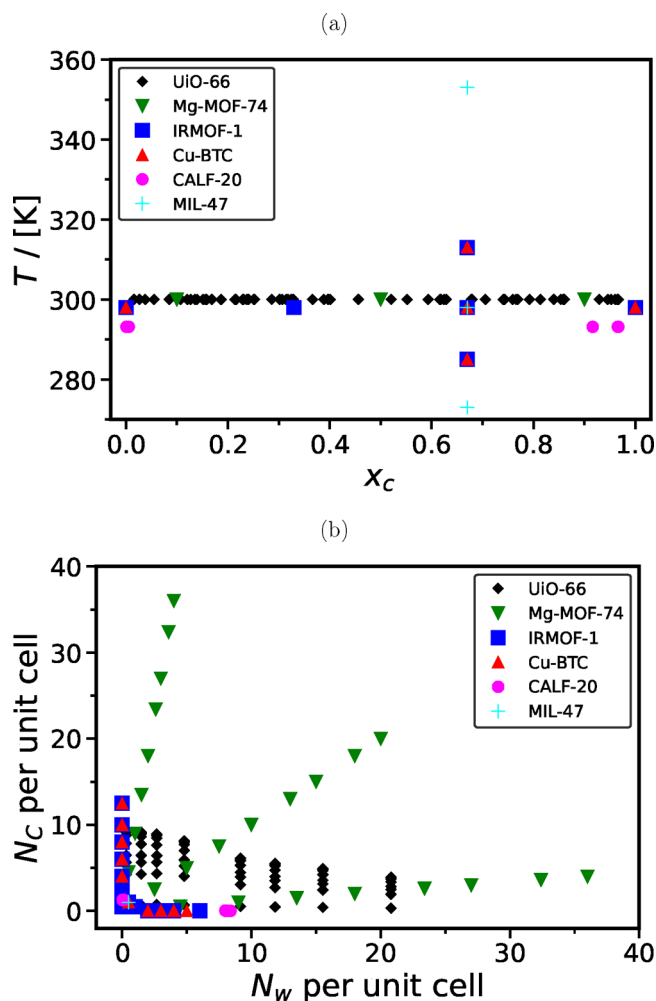


Figure 19. Conditions with available data in the literature for CO₂ diffusion confined in metal organic frameworks UiO-66,³⁴⁵ IRMOF-1,³⁴⁷ Cu-BTC,³⁴⁷ MIL-47,³⁴⁷ Mg-MOF-74,³⁴⁴ and CALF-20.³⁴⁶ (a) Temperature as a function of CO₂ composition ($x_{\text{CO}_2} = N_{\text{CO}_2} / (N_{\text{CO}_2} + N_{\text{H}_2\text{O}})$), and (b) loading as a function of the number of CO₂ and H₂O per unit cell.

- The effect of pressure on the diffusion of CO₂ in brines needs to be further investigated via: (i) additional experimental measurements, and/or (ii) extensive MD simulations;
- Additional experimental measurements for CO₂ diffusion in brines are required to provide adequate data for the development of accurate correlations. Emphasis should be given to aqueous salt-solutions (other than NaCl solutions), as well as to geologic formation brines;
- In addition to useful engineering-type correlations of the experimental data, there is a need for the development of theoretically based models for the diffusivity of CO₂ in pure H₂O and brines;
- A call for closer collaboration between experimental and simulation groups is stressed to rigorously validate simulation results, thereby deepening the insights into CO₂ diffusion in H₂O. Currently in literature, for many systems the experimental data are insufficient for validating the results from MD studies, especially at high temperatures and pressures. An enhanced synergy

between experiments and simulations can pave the way for more accurate simulations of CO₂ in H₂O;

- Polarizable force fields may offer the potential for a more precise representation of electrostatic interactions in aqueous solutions of CO₂, increasing the accuracy of MD simulations.^{216–218,365,366} Simulations are needed toward this direction since no data exist for the diffusivity of CO₂ in H₂O using polarizable force fields;
- Ab initio MD (AIMD) simulation is another possible method to study the diffusivity of CO₂ in H₂O, yielding a more comprehensive understanding of electronic structure in the solution.³⁶⁷ Although AIMD simulations have already been used to investigate the reaction mechanism and dynamics of CO₂ in different solvents,^{367–372} their applicability to computing transport properties is largely hindered by the significant additional computational cost, compared to classical MD, that does not allow for accessing the time scale required to capture the diffusive regime. Nevertheless, with the ever-increasing computational power being available, AIMD could be an interesting route to explore further;
- Introducing machine learning techniques into force field parametrization is possible to increase the predictive accuracy by discerning patterns in extensive data sets.³⁷³ This field is already very active, nevertheless, more efforts can focus on the CO₂–H₂O system;
- Currently, the behavior of CO₂ diffusivity at near-critical H₂O is not well understood. Additional MD simulations are required to produce the necessary data at these conditions. An advancement in this area will facilitate the refinement of the engineering-type correlations, and thus, allow for the development of more accurate predictive tools.

4.2. CO₂–H₂O Diffusion under Confinement.

- Experimental investigation of the mixture diffusion mechanisms with techniques such as QENS and NMR would be a powerful route to explore;
- When performing MD simulations, care should be taken to choose the initial configuration and the method. We advocate the use of GCMC to determine the composition and loading for a given state, and the use of methods that account for the nonhomogeneity of the confined fluid to compute the diffusion coefficients;
- From a methodological perspective, the study of transport diffusion coefficients using NEMD simulations to account for the collective transport and the investigation of possible finite-size effects in the confined CO₂ diffusion is an interesting future directive;
- Diffusion within confining materials, such as smectites, have been extensively studied. Others, however, such as calcite, which is a mineral abundant in subsurface formations, needs further investigation since it is important for many applications, e.g., CCS.

5. CONCLUSIONS

In this review paper, experimental data for the diffusion coefficient of CO₂ in pure H₂O are collected and discussed in detail. The experimental data are used to develop simple and computationally efficient correlations. These correlations are applicable to temperatures from 273 K and 0.1 MPa to 473 K and pressures up to 45 MPa. At this pressure and temperature range, the diffusion coefficient of CO₂ in H₂O has a very weak

dependence on pressure. Therefore, the proposed correlations are only temperature-dependent. The proposed correlations could be useful for engineering calculations that are related to a number of industrial and environmental processes. Finally, experimental data for the diffusion coefficient of CO₂ in brines are collected and their dependency on temperature, pressure and salinity have been thoroughly examined and reported.

Along with the experimental data, in this review, a detailed discussion on the available MD studies of CO₂ diffusivity in aqueous solutions is provided. The focus is on the force field combinations, the data for diffusivities at low and high pressures, the finite-size effects, and the correlations using MD data. The vast majority of the available MD studies of CO₂ diffusivity in H₂O report data at the infinite dilution limit (i.e., 1 to 5 solute molecules). The very few data available for higher CO₂ compositions are also provided and useful analysis is performed. A short discussion related to CO₂ diffusivity in carbonated hydroalcoholic drinks is also available.

For certain applications, e.g., CCS, a confining structure can constrain the CO₂ mobility, and consequently reduce CO₂ diffusion coefficients. Here, the main methods to compute the diffusivity of confined CO₂ are reviewed and the main natural and artificial confining media (i.e., smectites, calcites, silica, MOFs, and carbon materials), focusing primarily on MD simulations and secondarily on experimental studies are discussed. Smectites were found to be the most studied material due to their swelling, which generates an interlayer space capable of intercalating CO₂ and H₂O. The diffusion of CO₂ and H₂O under confinement is driven by a balance between adsorption and steric hindrance. For hydrophilic surfaces, water at lower concentrations increases CO₂ mobility due to preferential adsorption of H₂O. Based on the analysis and discussion, an outlook containing possible, useful, future research paths for advancing the field of CO₂ diffusivity in H₂O at the bulk phase and in confinement is devised.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.3c00778>.

Raw experimental and simulation data shown in the figures, along with the available statistical uncertainties (XLSX)

■ AUTHOR INFORMATION

Corresponding Authors

Othonas A. Moulτος — *Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical Engineering, Delft University of Technology, 2628CB Delft, The Netherlands*; orcid.org/0000-0001-7477-9684; Email: o.moultos@tudelft.nl

Ioannis N. Tsimpanogiannis — *Chemical Process & Energy Resources Institute (CPERI)/Centre for Research & Technology Hellas (CERTH), 57001 Thessaloniki, Greece*; orcid.org/0000-0002-3466-1873; Email: i.n.tsimpanogiannis@certh.gr

Luís Fernando Mercier Franco — *Universidade Estadual de Campinas (UNICAMP), Faculdade de Engenharia Química, Campinas CEP: 13083-852, Brazil*; Email: lmfranco@unicamp.br

Authors

H. Mert Polat – Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical Engineering, Delft University of Technology, 2628CB Delft, The Netherlands

Felipe M. Coelho – Universidade Estadual de Campinas (UNICAMP), Faculdade de Engenharia Química, Campinas CEP: 13083-852, Brazil; orcid.org/0000-0002-7572-1991

Thijs J. H. Vlugt – Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical Engineering, Delft University of Technology, 2628CB Delft, The Netherlands; orcid.org/0000-0003-3059-8712

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jced.3c00778>

Author Contributions

[†]These authors contributed equally to this work.

Notes

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