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### A molecular dynamics simulation study

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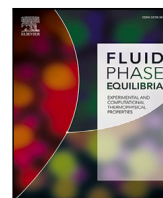
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# Densities, viscosities, and diffusivities of loaded and unloaded aqueous CO<sub>2</sub>/H<sub>2</sub>S/MDEA mixtures: A molecular dynamics simulation study

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## ABSTRACT

Experimentally measuring the diffusivities of CO<sub>2</sub> and H<sub>2</sub>S in aqueous alkanolamine solutions presents an extremely challenging task. To overcome this challenge, we performed Molecular Dynamics (MD) simulations to study the effects of temperature and *N*-methyldiethanolamine (MDEA) concentration on self-diffusivities of CO<sub>2</sub> ( $D_{\text{CO}_2}$ ) and H<sub>2</sub>S ( $D_{\text{H}_2\text{S}}$ ) in aqueous MDEA solutions. We compute the densities and viscosities of aqueous MDEA solutions for an MDEA concentration range of 10–50 wt% and a temperature range of 288–333 K showing an excellent agreement with experimental data from literature. We compute the self-diffusivity of MDEA ( $D_{\text{MDEA}}$ ) in aqueous MDEA solutions and our findings show that the computed values of  $D_{\text{MDEA}}$  are in excellent agreement with experimental and simulation results from literature. The self-diffusivities  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in aqueous MDEA solutions are computed for a wide range of temperatures and MDEA concentrations and our results show that both  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  depend significantly on temperature and MDEA concentration. We also show that both CO<sub>2</sub> and H<sub>2</sub>S diffuse slower in aqueous MDEA solutions than in aqueous MEA solutions. By comparing the radial distribution functions of CO<sub>2</sub>, H<sub>2</sub>S, water, and MDEA, we show that H<sub>2</sub>S has stronger interactions with the surrounding molecules than CO<sub>2</sub>, which makes H<sub>2</sub>S diffuse slower in aqueous MDEA solutions. We also investigate the densities and viscosities of acid gas loaded aqueous MDEA solutions and self-diffusivities of the reaction products of CO<sub>2</sub> and H<sub>2</sub>S with aqueous MDEA solutions. We show that the self-diffusivities of CO<sub>2</sub>-loaded solutions significantly decrease with increasing CO<sub>2</sub> loading while the self-diffusivities of H<sub>2</sub>S-loaded solutions do not change with changing H<sub>2</sub>S loading. Our results will be helpful in the design and optimization of acid gas removal units.

## 1. Introduction

Natural gas combustion produces much lower particulate matter emissions and has the highest energy output per CO<sub>2</sub> emitted compared to other fossil fuels [1–3]. Therefore, natural gas has the potential to be a transition fuel that will decrease CO<sub>2</sub> emissions until large scale usage of renewable energy sources becomes feasible [4–6]. Using steam methane reforming [7–9], natural gas can also be used to produce hydrogen, an energy carrier with high gravimetric energy density and near-zero greenhouse gas emissions [10]. Unfortunately, 40% of the known natural gas sources have high concentrations of acid gases, specifically, more than 2 mol % of CO<sub>2</sub> and 100 ppm of H<sub>2</sub>S [11]. Some reservoirs of natural gas in Southeast Asia and Australia can even have CO<sub>2</sub> concentrations of up to 80% [12]. CO<sub>2</sub> and H<sub>2</sub>S can cause corrosion of the pipelines [13,14], and therefore,

these components must be removed from the natural gas streams. Also, for safety reasons, H<sub>2</sub>S must be removed since it is a toxic gas [15]. For transportation in pipelines, CO<sub>2</sub> and H<sub>2</sub>S concentrations should be lower than 2 mol % and 4 ppm [16], respectively. In liquefied natural gas (LNG), CO<sub>2</sub> concentrations should be lower than 50 ppm [12] to eliminate the blockages caused by solid CO<sub>2</sub> in the liquefaction process. To this end, several different processes can be used to remove acid gases from natural gas streams such as membrane-based separation [17,18], cryogenic distillation [19,20], direct conversion of H<sub>2</sub>S to elemental sulfur [21,22], adsorption-based separation [23–25], and absorption-based separation [11].

Absorption-based separation is commonly preferred as it is a mature and reliable process which also results in very low amounts of

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absorbed (lost) methane [26–28]. This process uses liquid solvents to remove CO<sub>2</sub> and H<sub>2</sub>S from natural gas streams [11,27,29,30], usually aqueous alkanolamine solvents which can absorb acid gases by physical and/or chemical absorption [11,26]. In absorption-based separation of acid gases, the natural gas stream flows through a high pressure column (usually at pressures of 20–100 bar [31]) at temperatures in the range of 313–353 K [32]. The acid gases come in contact with the solvent and are absorbed into the liquid phase. Another advantage of the absorption-based separation process is that the liquid solvents can be regenerated at high temperature (typically at 363–383 K) and reused. To optimize this process, process simulation software is typically used [33–36] which requires parameters such as the diffusion coefficients of the acid gases, and the viscosity and the density of the solvent [37]. Therefore, accurate knowledge of these properties is crucial for the process design of both the absorption and regeneration stages. Since CO<sub>2</sub> and H<sub>2</sub>S react with the solvent, it is extremely challenging to experimentally measure their diffusivities in aqueous alkanolamine solvents. For this reason, estimates of the diffusion coefficients of acid gases are obtained by performing experiments with surrogate non-reacting molecules such as N<sub>2</sub>O instead of CO<sub>2</sub> [38–40]. For example, Sada et al. [41] estimated the diffusion coefficient of CO<sub>2</sub> in aqueous solutions of different alkanolamines by measuring the diffusion coefficient of N<sub>2</sub>O in these solutions. For more examples of the CO<sub>2</sub>/N<sub>2</sub>O analogy, the reader is referred to Refs. [38,42,43].

Molecular dynamics (MD) simulations with classical force fields are widely used to compute thermodynamic and transport properties (e.g., viscosities, densities, diffusion coefficients, phase equilibria) of aqueous solutions [2,44–54]. The main advantage of MD simulations for computing the diffusion coefficients of acid gases in aqueous alkanolamine solutions is that the reactions in the liquid phase are not considered, therefore, there is no need for surrogate non-reacting molecules in these simulations. Also, experiments can be expensive, time consuming, and dangerous at high pressures and temperatures. Despite the importance of thermodynamic and transport properties of these systems, literature data on the diffusion coefficients of CO<sub>2</sub> and H<sub>2</sub>S, and their temperature and alkanolamine concentration dependency, are scarce. To validate the CO<sub>2</sub>/N<sub>2</sub>O analogy, Chen et al. [39] computed the diffusion coefficients of CO<sub>2</sub> and N<sub>2</sub>O in aqueous monoethanolamine (MEA) solutions at 303 K. Melnikov et al. [55] computed the diffusion coefficients of CO<sub>2</sub> in aqueous MEA solutions for different loadings of CO<sub>2</sub> at 313 K. Yiannourakou et al. [11] computed the diffusion coefficients of *N*-methyldiethanolamine (MDEA) and CO<sub>2</sub> in 30 wt% MDEA/water solutions for a temperature range of 300–400 K. Recently, we computed viscosities of aqueous MEA solutions and self-diffusion coefficients of CO<sub>2</sub> and H<sub>2</sub>S in 10–50 wt% MEA/water solutions at 293–353 K [2]. In line with experimental data, we showed that the MEA concentration in the solution significantly affects the self-diffusion coefficients of both CO<sub>2</sub> and H<sub>2</sub>S [2].

Here, the self-diffusion coefficients of CO<sub>2</sub> and H<sub>2</sub>S in aqueous MDEA solutions are computed for a wide range of temperatures and MDEA concentrations. We focus on MDEA solutions because it is a commonly used alkanolamine for selective acid gas removal from natural gas and biogas streams [56]. To validate the accuracy of the interaction potentials for the aqueous solutions of acid gases, we first computed self-diffusion coefficients of CO<sub>2</sub> and H<sub>2</sub>S in pure water. Next, we computed the densities of aqueous MDEA solutions for a temperature range of 288–333 K and an MDEA concentration range of 10–50 wt% MDEA and compared our results with experimental data from literature. By introducing a scaling factor of 0.9 to the point charges of MDEA, we show that we can accurately compute the density of aqueous MDEA solutions. To validate the force field selection for MDEA, we compute viscosities of aqueous MDEA solutions for a temperature range of 288–333 K and an MDEA concentration range of 10–50 wt% MDEA, and compare the computed viscosities with experimental data from literature. We further validate the force field for MDEA by computing the self-diffusion coefficient of MDEA and comparing it with available

data from literature. Next, the self-diffusion coefficients of CO<sub>2</sub> and H<sub>2</sub>S in aqueous MDEA solutions are computed for a temperature range of 288–333 K and an MDEA concentration range of 10–50 wt% MDEA. Using radial distribution functions of the acid gases, water, and MDEA, we investigated the structural changes in the solutions as a function of MDEA concentration. Finally, we investigated the diffusivities of the acid gases and the reaction products from acid gas absorption in aqueous MDEA solutions (bicarbonate (HCO<sub>3</sub><sup>-</sup>), bisulfide (CO<sub>3</sub><sup>2-</sup>), and protonated MDEA (MDEAH<sup>+</sup>) ions) as a function of acid gas loading in 50 wt% MDEA/water solutions at 313 K. The accurate knowledge of the self-diffusivities of the reaction products in acid gas loaded aqueous MDEA solutions is important since this shows how the mass transfer of these species change with changing acid gas loading [57–60].

Our results will be helpful in the optimization of an acid gas removal unit of a plant treating natural gas and biogas, and we anticipate that our study will motivate further research in computing transport properties of acid gases and the reaction products from acid gas absorption in aqueous alkanolamine solutions.

This article is organized as follows: the simulation methods and force fields are explained in Section 2. We discuss the results from our simulations and the comparison with available data from literature in Section 3. Our main findings are summarized in Section 4.

## 2. Simulation methods

All MD simulations in this study are performed using LAMMPS (version 2 June 2022) [61] on the DelftBlue supercomputer [62]. The widely used TIP4P/2005 classical force field [63] is used to model water. For CO<sub>2</sub> and H<sub>2</sub>S, we use the TraPPE force field [64,65]. For the interactions between water and CO<sub>2</sub>, we used the cross-interaction parameters optimized by Orozco et al. [66]. In our simulations, water, CO<sub>2</sub>, and H<sub>2</sub>S are considered nearly-rigid by using strong bond-stretching and bond-bending potentials. For water, CO<sub>2</sub>, and H<sub>2</sub>S molecules, bond-stretching and bond-bending coefficients are set to 1000 kcal Å<sup>-2</sup> and 1000 kcal, respectively (see Tables S9 and S10 of the Supplementary Material for the functional forms of these potentials). For the Lennard-Jones (LJ) and bonded (bonds, angles, and dihedrals) interactions of MDEA, MDEAH<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and SH<sup>-</sup>, the OPLS-AA force field [67,68] is utilized. We used two sets of parameters for the N–C–O dihedral of MDEA as the parameters for this dihedral are not available in the OPLS-AA force field: (1) the parameters from Cornell et al. [69] and (2) the parameters from Orozco et al. [70]. The difference in the development of the parameters from Cornell et al. [69] and Orozco et al. [70] is that the first one was parameterized for proteins, nucleic acids, and organic molecules, while the latter was parameterized for alkanolamines by adjusting the densities, vapor pressures, excess enthalpies, and viscosities of six different alkanolamines which is more relevant to the system of our interest.

The point charges of MDEA, MDEAH<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and SH<sup>-</sup> molecules are computed using quantum chemical calculations performed with Gaussian09 [71] with the 6-311+G(2d,2p) basis set at the second order Møller-Plesset perturbation (MP2) [72] level of theory, by means of a Natural bond orbital (NBO) analysis [73,74]. To obtain accurate densities for aqueous MDEA solutions, the point charges of MDEA molecules are scaled by 0.9 after comparison with experimental data from literature, in line with the previous work on the effect of the scaled charges on transport properties of molecules/ions [2,75–78]. Note that the charge scaling factor validated for aqueous alkanolamine solutions can be used to obtain accurate densities and viscosities of pure alkanolamine solutions as shown in our previous study [2]. To obtain accurate densities and viscosities for CO<sub>2</sub>/H<sub>2</sub>S-loaded aqueous MDEA solutions, we scaled the point charges of the reaction products from CO<sub>2</sub> (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>S (MDEAH<sup>+</sup> and SH<sup>-</sup>) absorption by 0.90 and 0.75, respectively. The point charges of water, CO<sub>2</sub>, and H<sub>2</sub>S are not scaled. For this purpose, we use a scaling factor  $\chi_i^j$ , where  $i$  shows the parameter that is scaled and  $j$  represents the specific

**Table 1**

Number of MDEA and water molecules in MD simulations for different concentrations of MDEA in aqueous MDEA solutions. The average simulation box sizes are computed at 313 K and 1 bar.

MDEA concentration/[wt.%]	Number of MDEA molecules	Number of water molecules	Average box size/[Å]
0	0	700	27.6
10	12	688	28.4
20	25	675	29.4
30	43	657	30.1
40	64	636	31.5
50	92	608	32.6

interaction or molecule for the scaling. For example, a scaling factor of  $\chi_{\text{MDEA}}^q = 0.9$  means that the point charges of MDEA molecule were scaled (multiplied) by 0.9. Note that there are more fundamental methods to adjust the point charges (and therefore the dipole moment) of the molecules with point charges computed by quantum chemistry such as the Quantum Mechanical Bespoke approach [79], the Polarization-Consistent Approach [79], and the Self-Consistent Electrostatic Embedding approach [80]. However, in this work, we adopted scaling the point charges of the molecules as it has been shown to produce accurate self-diffusivities [2,47,48,81–83] and to be consistent with our previous work [2]. All force field parameters are tabulated in the Supplementary Material (Tables S1–S21 of the Supplementary Material).

The LJ interactions of unlike atom types are computed using the Lorentz–Berthelot mixing rules [84] unless specified otherwise. In all MD simulations, the LJ interactions are truncated at 12 Å and analytic tail corrections [85] are applied to energies and pressures. Electrostatic interactions are computed using the Particle-Particle Particle-Mesh (PPPM) method with a relative precision of  $10^{-5}$ . The 1–4 LJ and electrostatic intramolecular interactions are scaled by a factor of 0.5 [67,68].

The initial configurations for MD simulations were generated by randomly inserting molecules in a cubic simulation box with a size of 45–55 Å, depending on the MDEA concentration in the solution. The number of molecules of water and MDEA for all systems studied are shown in Table 1. The composition of the simulation box for the acid gas-loaded 50 wt% MDEA/water solutions at 313 K is computed using CASpy [86], an open-source software for computing speciation at reaction equilibrium that we recently developed. To this purpose, we followed the procedure explained in Ref. [86] and computed the composition in CO<sub>2</sub>-loaded 50 wt% MDEA/water solutions and H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions using the correlations for experimental reaction equilibrium constants reported by Plakia et al. [87]. The compositions of the simulation box of CO<sub>2</sub>-loaded 50 wt% MDEA/water solution and H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions at 313 K are reported in Tables S22 and S23 of the Supplementary Material.

To compute the self-diffusivities of CO<sub>2</sub> or H<sub>2</sub>S, two solute molecules are used to improve statistics. Although two molecules of free CO<sub>2</sub> or H<sub>2</sub>S are higher than the solubility of CO<sub>2</sub> or H<sub>2</sub>S in the aqueous MDEA solutions [86], we did not encounter any agglomeration of these species in the time period of our MD simulations. Note that the computed self-diffusion coefficients of the acid gases are practically equal to transport diffusion coefficients since CO<sub>2</sub> and H<sub>2</sub>S are at the infinite dilution limit [88]. We start the MD simulations with an equilibration stage of 0.5 ns with a timestep of 1 fs in the *NPT* ensemble. The Nosé-Hoover thermostat (with a coupling constant of 10 fs) and barostat (with a coupling constant of 1000 fs) are used to maintain constant temperature and pressure, respectively. Consecutively, another equilibration stage of 1 ns with a timestep of 1 fs is performed in the *NVT* ensemble. Finally, production runs of 20 ns are performed in the *NVE* ensemble to compute all properties of interest.

The On-the-Fly Calculation of Transport Properties (OCTP) plugin [89] in LAMMPS is used to compute viscosities, self-diffusivities,

and center-of-mass radial distribution functions (RDFs). The OCTP plugin [89] computes transport properties with the order-*n* [84,90] algorithm using Einstein relations. The center-of-mass RDFs computed by the OCTP plugin are corrected for finite-size effects [89]. For details about these computations the reader is referred to Ref. [89]. In this work, all reported self-diffusivities are corrected for finite-size effects using [91–94]:

$$D_i = D_i^{\text{MD}} + \frac{\xi k_B T}{6\pi\eta L} \quad (1)$$

where  $D_i$  is the self-diffusivity of species *i* at the thermodynamic limit,  $D_i^{\text{MD}}$  is the self-diffusivity of species *i* computed from the MD simulation,  $\xi$  is a constant equal to 2.837297 for a cubic simulation box,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity computed from the MD simulation, and  $L$  is the length of the simulation box. Note that the computed viscosities do not show any finite-size effects [91,92,95]. The standard deviations for densities, viscosities, and self-diffusion coefficients are computed from seven independent simulations each one starting from a different initial configuration. The average values and uncertainties shown in this work are computed from five independent simulations. Average number of hydrogen bonds between water-MDEA and MDEA-MDEA pairs are computed using VMD Hydrogen Bonds plugin [96] with a cutoff distance of 3.5 Å and a cutoff angle of 30° [97]. To quantify the agreement between the computed values (of density, viscosity, and diffusivity) and experimental values from literature, the coefficient of determination ( $R^2$ ) scores are computed using:

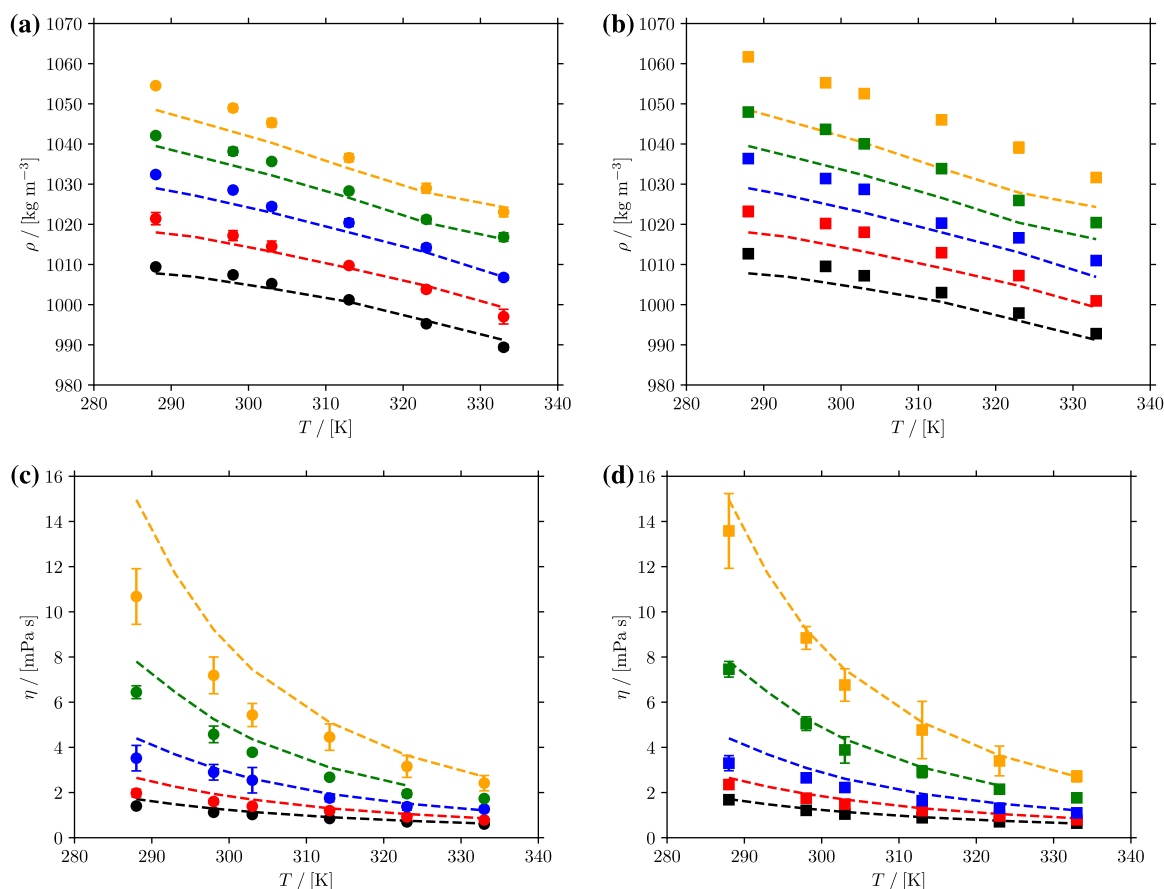
$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{i,\text{exp}} - y_{i,\text{sim}})^2}{\sum_{i=1}^n (y_{i,\text{exp}} - \bar{y}_{\text{exp}})^2} \quad (2)$$

where  $n$  is the number of data points,  $y_{i,\text{exp}}$  is the experimental value from literature,  $y_{i,\text{sim}}$  is the computed value, and  $\bar{y}_{\text{exp}}$  is the arithmetic average of the experimental values from literature. An  $R^2$  score of 1 means that the agreement between simulations and experiments is perfect.

### 3. Results and discussion

#### 3.1. Densities and viscosities of aqueous MDEA solutions

To validate the force fields for water, CO<sub>2</sub>, and H<sub>2</sub>S, we first compute the diffusion coefficients of CO<sub>2</sub> ( $D_{\text{CO}_2}$ ) and H<sub>2</sub>S ( $D_{\text{H}_2\text{S}}$ ) in pure water. Fig. S3 of the Supplementary Material shows the comparison between the computed and experimental [98,99] self-diffusivities  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in pure water as a function of temperature. Our results show that the computed values of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in pure water are in excellent agreement with the experimental results from literature [98,99] as the maximum deviations are 12% and 10% for  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$ , respectively. This shows that the force fields chosen for CO<sub>2</sub>, H<sub>2</sub>S, and water accurately describe the interactions in aqueous solutions of CO<sub>2</sub> and H<sub>2</sub>S. Therefore, we then proceeded with investigating the accuracy of the OPLS-AA force field [67,68] (with point charges computed by quantum chemistry calculations) for MDEA. We used two different sets of parameters for N–C–O dihedrals of MDEA molecule as the parameters for this dihedral are not available in the OPLS-AA force field: (1) from Cornell et al. [69], and (2) from Orozco et al. [70]. The main difference between these two sets of parameters for N–C–O dihedral is that the parameters from Cornell et al. [69] was developed for proteins, nucleic acids, and organic molecules, while the parameters from Orozco et al. [70] was developed for alkanolamines. Note that the dihedral reported by Orozco et al. [70] is ca. 2.5 times stiffer (i.e. the barrier for dihedral rotation is 2.5 times higher) than the dihedral reported by Cornell et al. [69] (Fig. S4 of the Supplementary Material). We computed the densities of aqueous MDEA solutions as a function of temperature and MDEA concentration in the solution using  $\chi_{\text{MDEA}}^q = 1.0$ . Fig. S5 of the Supplementary Material shows the comparison between the computed (with unscaled point charges  $\chi_{\text{MDEA}}^q =$



**Fig. 1.** Computed and experimental [98] (a,b) densities and (c,d) viscosities of aqueous MDEA solutions as a function of temperature at 1 bar. (a,c) show the densities and viscosities computed using the parameters from Cornell et al. [69] for N–C–O dihedral of MDEA; (b,d) show the densities and viscosities computed using the N–C–O dihedral parameters from Orozco et al. [70]. Note that the point charges of MDEA are scaled with 0.9, i.e.  $\chi_{\text{MDEA}}^q = 0.9$ . Dashed lines represent experimental results from Al-Ghawas et al. [98]. Color code: black: 10 wt% MDEA/water; red: 20 wt% MDEA/water; blue: 30 wt% MDEA/water; green: 40 wt% MDEA/water; orange: 50 wt% MDEA/water.

1.0) and experimental [98] densities of aqueous MDEA solutions. Our results show that the computed densities are significantly overestimated and the deviations between the computed and experimental densities increase with increasing MDEA concentration in the solution. As it has been shown that the point charges computed using quantum chemical calculations typically overestimate electrostatic interactions and the scaled point charges provide a better representation of the potential energy surface of the molecules/ions [77,100–105], we scaled the point charges of MDEA by 0.9 ( $\chi_{\text{MDEA}}^q = 0.9$ ). Fig. 1 shows the computed and experimental densities of aqueous MDEA solutions (with  $\chi_{\text{MDEA}}^q = 0.9$ ) for the temperature range 288–333 K at 1 bar. Our results show that the computed densities using both sets of parameters for the N–C–O dihedral agree very well with the experimental densities from literature [98] with a maximum deviation of 1.3%. The deviation between the experimental data and the computed densities using the parameters from Cornell et al. [69] is 0.1–0.5% (Fig. 1(a)), while the respective deviation is between 0.2–1.3% when the parameters from Orozco et al. [70] are used (Fig. 1(b)). The deviations between the simulations and experimental densities from literature for both dihedral parameters are larger than the standard errors as the standard errors for calculated values of densities are ca. 0.05%. For the dihedral parameters from Orozco et al. [70], the difference between the computed and experimental densities increases with increasing MDEA concentration in the solution. As the densities computed using both set of parameters are in excellent agreement (with a maximum deviation of 1.3%) with experimental data from literature [98], we computed viscosities of aqueous MDEA solutions and compared them with available data from literature.

Fig. 1(c) and Fig. 1(d) show the comparison between the computed (using the same two dihedral parameters discussed earlier) and experimental [98] viscosities of aqueous MDEA solutions for an MDEA concentration range of 10–50 wt% MDEA, and a temperature range of 288–333 K. Our results show that the viscosities computed using both set of parameters for N–C–O dihedral underestimate experimental [98] viscosities of aqueous MDEA solutions. The viscosities computed using the parameters from Orozco et al. [70] underestimate experimental results [98] (average absolute deviation of 8.4%) less as the density of aqueous MDEA solutions are higher (due to the 2.5 times stiffer N–C–O dihedral, see Fig. S4 of the Supplementary Material) compared to the ones obtained using the parameters from Cornell et al. [69] (average absolute deviation of 13.3%). Note that the average absolute deviation for the viscosities computed using the dihedral parameters from Cornell et al. [69] are larger than the average standard error of 8.3% while the average standard error for viscosities computed using the dihedral parameters from Orozco et al. [70] (8.7%) is slightly higher than the average absolute deviation between simulations and experimental values from literature. To quantify the agreement between the simulations and experimental values from literature, we also computed the  $R^2$  scores. Our findings show that the viscosities computed using the parameters from Cornell et al. [69] for the N–C–O dihedral of MDEA and experimental results [98] have an  $R^2$  of 0.88, while the  $R^2$  score of the viscosities computed using N–C–O dihedral parameters optimized by Orozco et al. [70] and experimental results [98] is 0.98. Indicatively, the viscosities computed using the N–C–O dihedral parameters from Cornell et al. [69] are between 0.6–1.4 mPa s and 2.4–10.7 mPa s at 288–333 K for 10 wt% MDEA/water

and 50 wt% MDEA/water solutions, respectively. The viscosities computed using the N–C–O parameters from Orozco et al. [70] vary between 0.6–1.7 mPa s and 2.7–13.6 mPa s at 288–333 K for 10 wt% MDEA/water and 50 wt% MDEA/water solutions, respectively. For the same temperature range, experimental viscosities [98] are between 0.6–1.7 mPa s and 2.7–14.9 mPa s for 10 wt% MDEA/water and 50 wt% MDEA/water solutions, respectively. Both the  $R^2$  scores and deviations from experiments show that the simulations agree well with experiments from literature when the parameters from Orozco et al. [70] for N–C–O dihedral are used to predict viscosities of aqueous MDEA solutions.

### 3.2. Diffusivities of MDEA, CO<sub>2</sub>, and H<sub>2</sub>S in aqueous MDEA solutions

We further investigate the transport properties of aqueous MDEA solutions by computing the self-diffusion coefficients of MDEA ( $D_{\text{MDEA}}$ ) in the solution. Fig. 2 shows the values of  $D_{\text{MDEA}}$  computed using the two different sets of parameters for N–C–O dihedral for MDEA concentrations in the range of 10–50 wt%, and the comparison with experimental data from Snijder et al. [106] and MD simulation data from Yiannourakou et al. [11] (with the PCFF+ force field reported in ref [107]) for 30 wt% MDEA/water solutions. As expected, our data show that  $D_{\text{MDEA}}$  decreases with increasing MDEA concentration in the solution (Fig. 2). The values of  $D_{\text{MDEA}}$  in the 10 wt% MDEA/water solutions are ca. 3–9 and 3–6 times higher compared to the 50 wt% MDEA/water solutions for the values computed using the parameters from Cornell et al. [69] and Orozco et al. [70], respectively, for the temperature range 288–333 K. Fig. 2(a) shows that the values of  $D_{\text{MDEA}}$  computed using the parameters from Cornell et al. [69] for the N–C–O dihedral are in agreement with the experimental results from Snijder et al. [106] and computational results from Yiannourakou et al. [11] (with an  $R^2$  score of 0.80) for 30 wt% MDEA/water solutions except for the data point at 333 K. The value of  $D_{\text{MDEA}}$  computed using the parameters from Cornell et al. [69] for N–C–O dihedral is  $7.94 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at 333 K while the experimental value for the same temperature is  $9.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . As shown in Fig. 2(b), the values of  $D_{\text{MDEA}}$  computed using the parameters from Orozco et al. [70] agree very well with the experimental and MD data from literature [11,106] ( $R^2$  score = 0.94). The values of  $D_{\text{MDEA}}$  computed using the optimized N–C–O dihedral parameters from Orozco et al. [70] are between  $3.92 \times 10^{-10}$ – $8.89 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in 30 wt% MDEA/water solution at 303–333 K, while the experimental values [106] for the same temperature range and solution vary between  $4.6 \times 10^{-10}$ – $9.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . This shows that the N–C–O dihedral parameters from Orozco et al. [70] perform better than the ones by Cornell et al. [69]. Based on the force field validation for the densities (Fig. 1(a,b)), viscosities (Fig. 1(c,d)) and  $D_{\text{MDEA}}$ , we hereafter adopt the parameters by Orozco et al. [70] for the N–C–O dihedral MDEA to compute the diffusivities of the acid gases in aqueous MDEA solutions.

Interestingly, MDEA diffuses slightly faster in 30 wt% MDEA/water solutions at 333 K ( $D_{\text{MDEA}} = 8.89 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) compared to MEA in 30 wt% MEA/water solutions ( $D_{\text{MEA}} = 7.54 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) from our previous study [2] despite the similar viscosities of both solutions (1.1 mPa s for 30 wt% MDEA/water solutions while 1.2 mPa s for 30 wt% MEA/water solutions [2] at 333 K). Although one would expect the opposite since MEA is smaller and lighter than MDEA (molar mass of MDEA and MEA are  $119.163 \text{ g mol}^{-1}$  and  $61.08 \text{ g mol}^{-1}$ , respectively), comparing solutions with same alkanolamine weight percentages may be misleading as the mole fractions of these components in these solutions are quite different (mole fraction of MDEA ( $X_{\text{MDEA}} = 0.06$  in 30 wt% MDEA/water solution while mole fraction of MEA ( $X_{\text{MEA}} = 0.11$  in 30 wt% MEA/water solution). Fig. S6 of the Supplementary Material compares  $D_{\text{MDEA}}$  and  $D_{\text{MEA}}$  [2] for similar mole fractions of alkanolamine ( $X_{\text{MDEA}} = 0.13$  in 50 wt% MDEA/water vs.  $X_{\text{MEA}} = 0.11$  in 30 wt% MEA/water solution) in the solution as a function of temperature. Compared to a similar mole fraction of MDEA in MDEA/water

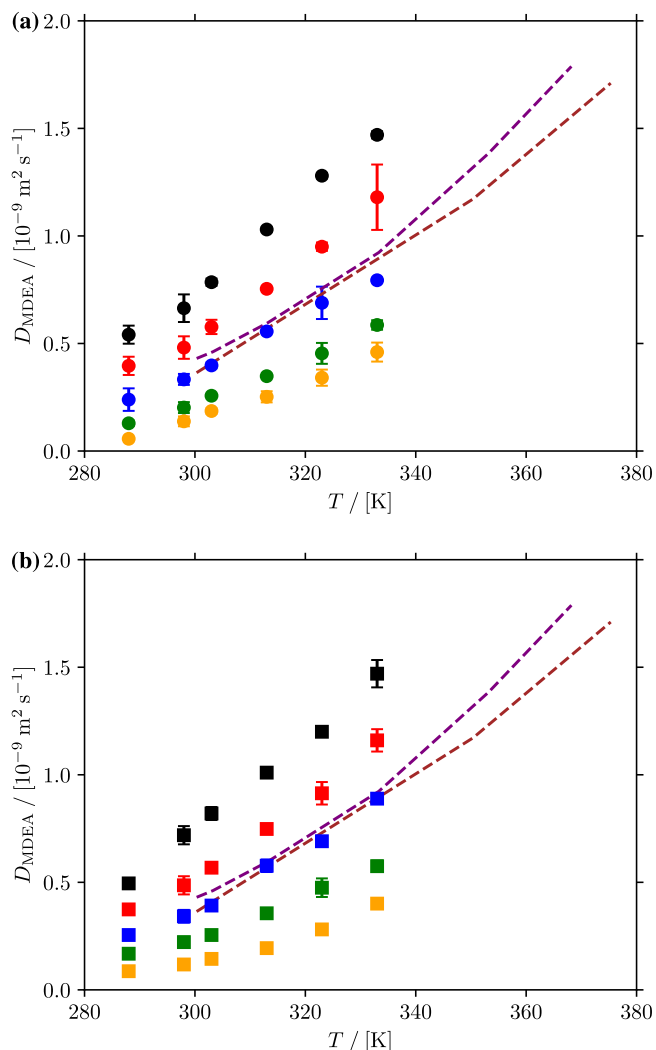


Fig. 2. Computed and experimental [11,106] self-diffusivities  $D_{\text{MDEA}}$  in aqueous MDEA solutions as a function of temperature at 1 bar. (a) shows the values of  $D_{\text{MDEA}}$  computed using the parameters from Cornell et al. [69] for N–C–O dihedral of MDEA while (b) shows the values of  $D_{\text{MDEA}}$  computed using the N–C–O dihedral from Orozco et al. [70]. Note that the point charges of MDEA are scaled by 0.9, i.e.  $X_{\text{MDEA}}^q = 0.9$ , and all self-diffusivities are corrected for finite-size effects using Eq. (1). Dashed lines represent experimental results in 30 wt% MDEA/water solutions from Snijder et al. [106] (purple) and simulation results from Yiannourakou et al. [11] (brown). The color code follows that of Fig. 1.

solutions, MEA molecules diffuse ca. 2–4 times faster in 30 wt% MEA/water solutions than MDEA molecules in 50 wt% MDEA/water solutions for a temperature range of 288–333 K.

We compute the values of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  as a function of MDEA concentration in the solution and temperature using MD simulations. Fig. 3 shows the simulation results and comparisons with the available experimental data from literature [98]. To the best of our knowledge, no experimental or modeling data on the diffusivity of H<sub>2</sub>S in aqueous MDEA solutions have been reported. Using the CO<sub>2</sub>/N<sub>2</sub>O analogy [38, 39] (by measuring the diffusivity of N<sub>2</sub>O), Al-Ghawas et al. [98] estimated the values of  $D_{\text{CO}_2}$  to be in the ranges  $1.2 \times 10^{-9}$ – $3.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $3.8 \times 10^{-10}$ – $1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  in 10 wt% MDEA/water and 50 wt% MDEA/water solutions, respectively, at temperatures ranging from 288 to 323 K. For the same temperature range, we computed  $D_{\text{CO}_2}$  to be  $1.29 \times 10^{-9}$ – $2.87 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $3.54 \times 10^{-10}$ – $9.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in 10 wt% MDEA/water and 50 wt% MDEA/water solutions, respectively. This clearly shows that our data are in agreement with the values of the self-diffusivity of CO<sub>2</sub>,  $D_{\text{CO}_2}$ , estimated using CO<sub>2</sub>/N<sub>2</sub>O

analogy [98]. Note that Chen et al. [39] investigated the validity of  $\text{CO}_2/\text{N}_2\text{O}$  analogy by computing the Henry coefficients and self-diffusivities of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  in water, ethanol, n-heptane, and aqueous MEA solutions, and concluded that the assumption holds for 30 wt% MEA/water solutions at 303 K. Also, Kohns et al. [40] stated that the analogy is valid for  $\text{CO}_2$  in pure water and ethanol, while it is not valid for  $\text{CO}_2$  in binary mixtures of water and ethanol. We also compare the computed values of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in aqueous MDEA solutions with the ones in aqueous MEA solutions from our previous study [2]. Fig. S7 of the Supplementary Material shows the comparison of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in aqueous MDEA and aqueous MEA solutions. When solutions with similar mole fractions of MDEA and MEA are compared,  $\text{CO}_2$  diffuses ca. 1 – 3 times slower in aqueous MDEA solutions than in aqueous MEA solutions. For example, we computed  $D_{\text{CO}_2}$  as  $5.19 \times 10^{-10}$ – $9.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at 298 – 323 K in 50 wt% MDEA/water solution while the respective value in 30 wt% MEA/water solution at the same temperature range is  $1.38 \times 10^{-9}$ – $2.00 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . This is expected since the viscosity of 50 wt% MDEA/water solution is ca. 3 times higher than the viscosity of 30 wt% MEA/water solution at 298 – 323 K and the self-diffusivities of solutes depend highly on the viscosity of the solution. The comparison of the self-diffusivities  $D_{\text{H}_2\text{S}}$  in MEA/water and MDEA/water solutions (Fig. S7(b)) shows a similar difference between the two solutions, i.e.  $\text{H}_2\text{S}$  diffuses ca. 2 times faster in 30 wt% MEA/water solutions than in 50 wt% MDEA/water solutions.

As shown in Fig. 3, the self-diffusivities  $D_{\text{CO}_2}$  in aqueous MDEA solutions are slightly larger than the self-diffusivities  $D_{\text{H}_2\text{S}}$  at the same conditions. Note that the differences between the computed values of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  are statistically important as the differences are larger than the error bars.  $\text{H}_2\text{S}$  diffuses slower in aqueous MDEA solutions despite its lower molar mass ( $M_{\text{H}_2\text{S}} = 34.1 \text{ g mol}^{-1}$  vs.  $M_{\text{CO}_2} = 44.01 \text{ g mol}^{-1}$ ) compared to  $\text{CO}_2$  because  $\text{H}_2\text{S}$  can form hydrogen bonds with both water and MDEA molecules [2,108–110] and it is a more spherical molecule than  $\text{CO}_2$ . The values of both  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  decrease with increasing MDEA concentration in the solution. For example, both  $\text{CO}_2$  and  $\text{H}_2\text{S}$  diffuse ca. 3.5 times faster in 10 wt% MDEA/water solutions than in 50 wt% MDEA/water solutions. Our results also show that the temperature dependency of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  changes significantly with MDEA concentration in the solution. The slope of  $D_{\text{CO}_2}$  ( $D_{\text{H}_2\text{S}}$ ) as a function of temperature is 2.6 (1.8) times higher in 10 wt% MDEA/water solution than in the 50 wt% MDEA/water solution. The same trend can also be seen in the values of  $D_{\text{CO}_2}$  estimated by Al-Ghawaz et al. [98] using the  $\text{CO}_2/\text{N}_2\text{O}$  analogy.

The temperature dependence of the self-diffusion coefficients can be described with an Arrhenius equation [2], the Speedy-Angell power equation [111], or the Vogel-Tamann-Fulcher (VTF) equation [112]. We fit the values of  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  to an Arrhenius equation [2], the Speedy-Angell power equation [111], and the VTF equation [112] for an MDEA concentration range of 10 – 50 wt% MDEA and a temperature range of 288 – 323 K. The functional forms of these equations are shown in the Supplementary Material. Table 2 and 3 show Arrhenius fit parameters for  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$ , respectively. The Speedy-Angell and VTF equation fit parameters for  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  are tabulated in Tables S24-S27 of the Supplementary Material. Figures S8–S10 of the Supplementary Material show the fits to Arrhenius equation, Speedy-Angell power equation, and VTF equation. The activation energies for diffusion ( $E_A$ ) for both  $\text{CO}_2$  and  $\text{H}_2\text{S}$  increase with MDEA concentration in the solution which also indicates slower diffusion of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  with increasing MDEA concentration (see Table 2 and 3).

### 3.3. Structure of aqueous $\text{CO}_2/\text{H}_2\text{S}/\text{MDEA}$ mixtures

In Fig. 4, the center-of-mass RDFs of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  with water and MDEA are shown at 313 K and 1 bar. Our findings show that as the MDEA concentration in the solution increases, the first and second peaks in both  $\text{CO}_2$ -MDEA and  $\text{H}_2\text{S}$ -MDEA RDFs shift to lower values of intermolecular distance, indicating stronger interactions between

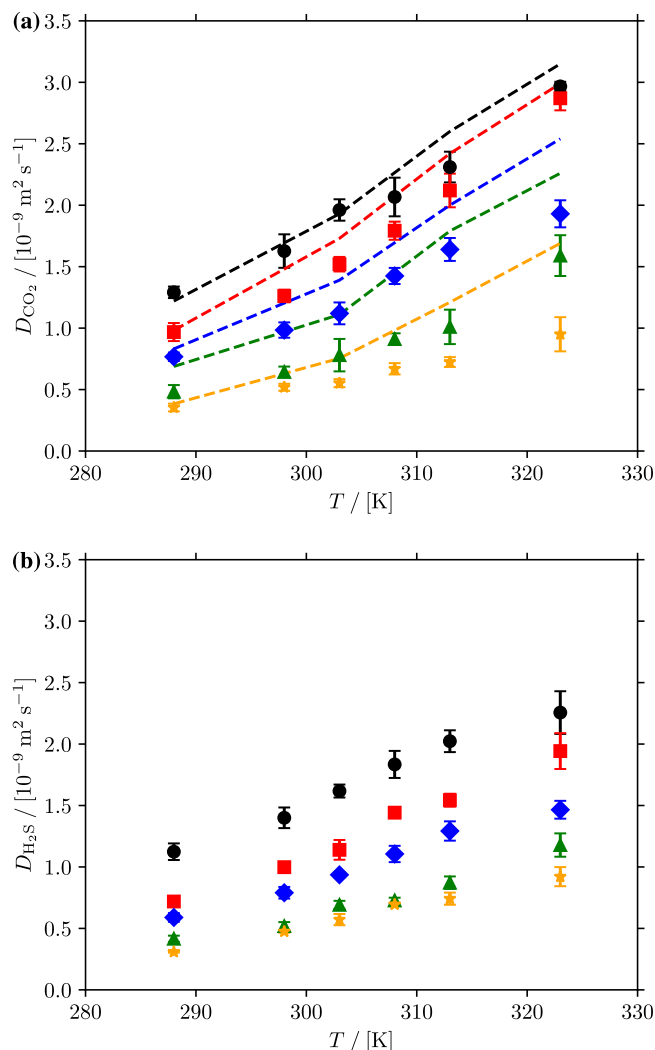


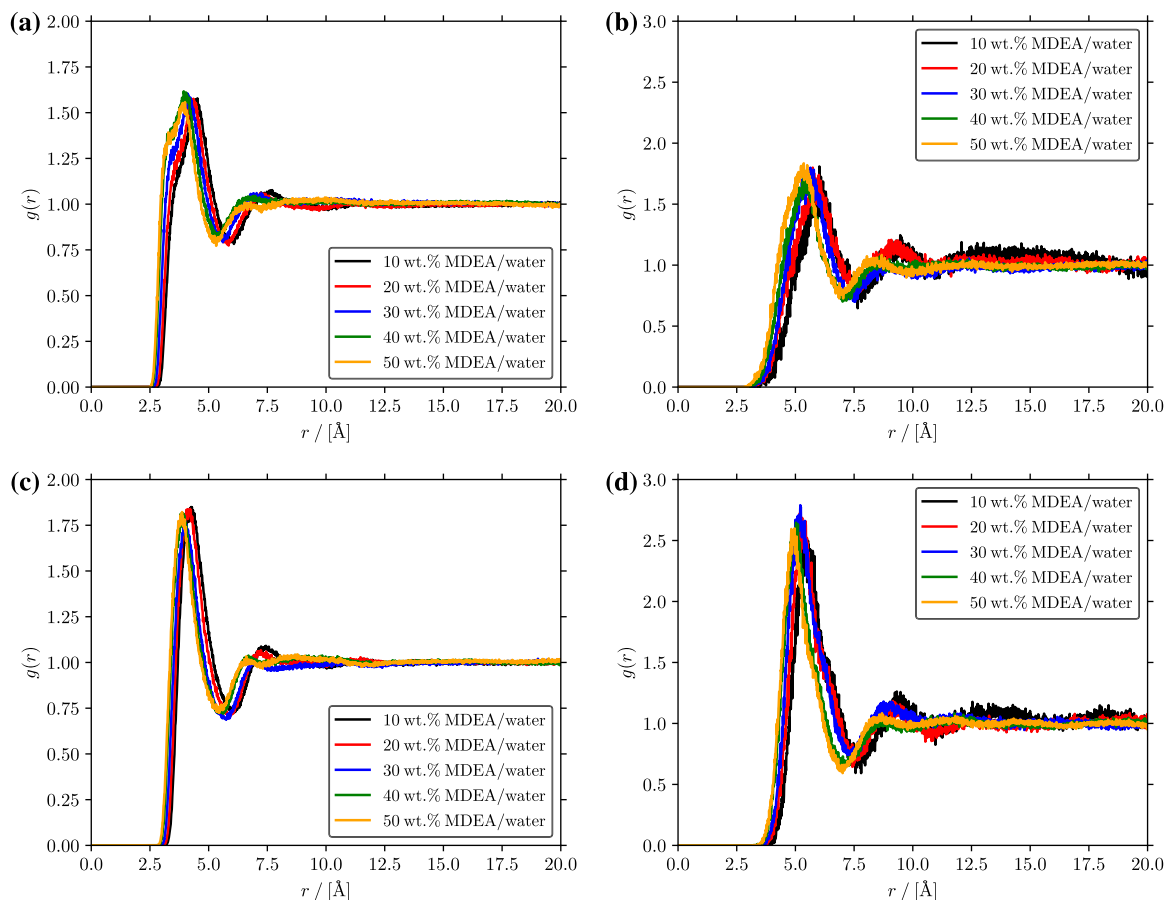
Fig. 3. Computed and experimental [98] (a) self-diffusivities of  $\text{CO}_2$  and (b) computed self-diffusivities of  $\text{H}_2\text{S}$  in aqueous MDEA solutions as a function of temperature and MDEA concentration at 1 bar. Note that the point charges of MDEA are scaled with 0.9, i.e.  $z_{\text{MDEA}}^q = 0.9$ , and all self-diffusivities are corrected for finite-size effects using Eq. (1). The TraPPE force field [64,65] was used for  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . In (a), dashed lines represent experimental results from Al-Ghawaz et al. [98]. The color code follows that of Fig. 1.

Table 2

Arrhenius fit parameters (pre-exponential factors ( $D_0$ ) and activation energies ( $E_A$ )) and coefficients of determinations ( $R^2$ ) for  $D_{\text{CO}_2}$  in aqueous MDEA solutions with different MDEA concentrations.

MDEA concentration/[wt.%]	$D_0/[\text{m}^2 \text{ s}^{-1}]$	$E_A/[\text{kJ mol}^{-1}]$	$R^2$
10	$2.71 \times 10^{-6}$	18.33	0.991
20	$3.51 \times 10^{-5}$	25.28	0.997
30	$4.97 \times 10^{-6}$	21.02	0.975
40	$5.78 \times 10^{-5}$	28.28	0.981
50	$2.25 \times 10^{-6}$	20.87	0.991

acid gases and MDEA. However, the intensities of the first peaks in  $\text{H}_2\text{S}$ -MDEA RDFs are higher than those of  $\text{CO}_2$ -MDEA RDFs, indicating stronger  $\text{H}_2\text{S}$ -MDEA interactions than  $\text{CO}_2$ -MDEA interactions. The same trend is observed for the  $\text{CO}_2$ -water and  $\text{H}_2\text{S}$ -water RDFs, where the position of the first and second peaks shift to lower values with increasing MDEA concentration, and the intensities of the first peaks in  $\text{H}_2\text{S}$ -water RDFs are higher than those of  $\text{CO}_2$ -MDEA RDFs. Overall, these findings suggest that  $\text{H}_2\text{S}$  has stronger interactions with the



**Fig. 4.** Radial distribution functions of (a) CO<sub>2</sub>-water, (b) CO<sub>2</sub>-MDEA, (c) H<sub>2</sub>S-water, and (d) H<sub>2</sub>S-MDEA at 313 K and 1 bar. For water, the TIP4P/2005 force field [63] was used while for MDEA, we used OPLS-AA force field [67,68] with point charges computed from quantum chemistry. Note that the point charges of MDEA are scaled by 0.9, i.e.  $\chi_{\text{MDEA}}^q = 0.9$ . For CO<sub>2</sub> and H<sub>2</sub>S, the TraPPE force field [64,65] was used.

**Table 3**

Arrhenius fit parameters (pre-exponential factors ( $D_0$ ) and activation energies ( $E_A$ )) and coefficients of determinations ( $R^2$ ) for  $D_{\text{H}_2\text{S}}$  in aqueous MDEA solutions with different MDEA concentrations.

MDEA concentration/[wt.%]	$D_0$ /[m <sup>2</sup> s <sup>-1</sup> ]	$E_A$ /[kJ mol <sup>-1</sup> ]	$R^2$
10	$6.79 \times 10^{-7}$	15.24	0.976
20	$5.59 \times 10^{-6}$	21.34	0.986
30	$2.34 \times 10^{-6}$	19.70	0.972
40	$8.82 \times 10^{-6}$	23.98	0.988
50	$3.04 \times 10^{-6}$	21.68	0.973

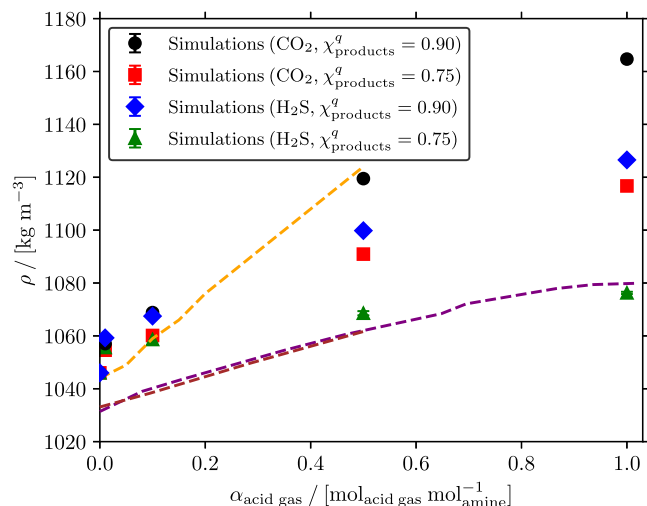
surrounding molecules (MDEA and water) than CO<sub>2</sub>. This is probably the reason why H<sub>2</sub>S diffuses slower than CO<sub>2</sub> in aqueous MDEA solutions (Fig. 3). We also compute the average number of hydrogen bonds between water-MDEA and MDEA-MDEA pairs in aqueous MDEA solutions as a function of MDEA concentration at 313 K and 1 bar (Fig. S11 of the Supplementary Material). Our results show that the average number of hydrogen bonds for both water-MDEA and MDEA-MDEA pairs decrease with increasing MDEA concentration in the solution.

### 3.4. Densities, viscosities, and diffusivities of acid gas-loaded aqueous MDEA solutions

The densities, viscosities, and self-diffusivities of the reaction products are of primary importance in the optimization of the mass transfer in acid gas loaded aqueous MDEA solutions [57–60]. Here, we investigate the densities, viscosities, and self-diffusivities of CO<sub>2</sub> and H<sub>2</sub>S loaded aqueous MDEA solutions at 313 K as this is a typical operation temperature in acid gas removal units [32]. We compute

the densities of CO<sub>2</sub>- or H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions at 313 K by using two different scaling factors for the point charges of the reaction products of CO<sub>2</sub> absorption (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>S absorption (MDEAH<sup>+</sup> and SH<sup>-</sup>), see Tables S23 and S24 of the Supporting Material:  $\chi_{\text{products}}^q = 0.90$  and  $\chi_{\text{products}}^q = 0.75$ . Note that for the point charges of MDEA, we use  $\chi_{\text{MDEA}}^q = 0.90$  in all simulations. Fig. 5 shows the comparison between the computed and experimental [113–115] densities of CO<sub>2</sub>- and H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions at 313 K and 1 bar. Our findings show that the computed densities of CO<sub>2</sub>-loaded solutions agree well with the experimental data from literature [113] when the point charges of the reaction products (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) are scaled by 0.90. When the point charges of the reaction products (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) are scaled by 0.90, the computed densities show an average absolute deviation of 0.8% and a maximum deviation of 1.2%. When a scaling factor of 0.75 is used for the point charges of MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>, the computed densities of CO<sub>2</sub>-loaded solutions agree less well with the experimental data [113] with an average absolute deviation of 1.3% and a maximum deviation of 3%. However, following the trend in experimental densities of CO<sub>2</sub>-loaded solutions in Fig. 5, it is clear that a scaling factor of 0.9 for the reaction products results in more accurate computed densities than a scaling factor of 0.75 at CO<sub>2</sub> loading of 1 mol<sub>CO<sub>2</sub></sub> mol<sub>amine</sub><sup>-1</sup>. The computed densities of H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions have average absolute deviations of 3.6% and 1%, and maximum deviations of 4.3% and 2% when scaling factors of  $\chi_{\text{products}}^q = 0.90$  and  $\chi_{\text{products}}^q = 0.75$  are used, respectively. Our findings show that a scaling factor of  $\chi_{\text{products}}^q = 0.90$  results in accurately predicted densities for CO<sub>2</sub>-loaded 50 wt% MDEA/water solutions, while the computed densities of H<sub>2</sub>S-loaded solution have a better agreement with the experimental data [114,115] when a scaling factor of  $\chi_{\text{products}}^q = 0.75$  is used.

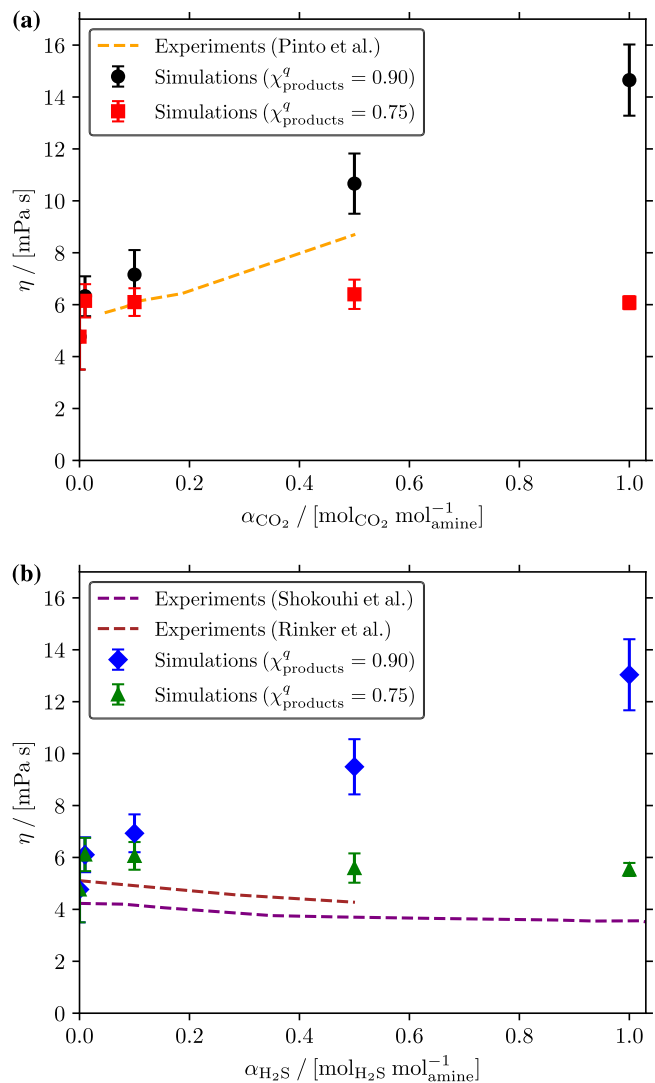




**Fig. 5.** Densities of acid-gas loaded 50 wt% MDEA/water solutions as a function of acid gas loading at 313 K and 1 bar. The orange dashed line represents experimental densities of CO<sub>2</sub>-loaded 50 wt% MDEA solutions from Weiland et al. [113], while the purple and brown dashed lines represent experimental densities of H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions from Shoukouhi et al. [114] and Rinker et al. [115], respectively. Note that the point charges of MDEA are scaled by 0.9, i.e.  $\chi_{\text{MDEA}}^q = 0.9$ . The point charges of the reaction products of CO<sub>2</sub> absorption (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>S absorption (MDEAH<sup>+</sup> and SH<sup>-</sup>) are scaled by either 0.9 or 0.75, i.e.  $\chi_{\text{products}}^q = 0.9$  or  $\chi_{\text{products}}^q = 0.75$ . For CO<sub>2</sub> and H<sub>2</sub>S, the TraPPE force field [64,65] was used.

We compute the viscosities of CO<sub>2</sub> and H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions at 313 K and 1 bar using two different scaling factors for the point charges of reaction products from CO<sub>2</sub> and H<sub>2</sub>S absorption,  $\chi_{\text{products}}^q = 0.90$  and  $\chi_{\text{products}}^q = 0.75$ , and compared the computed viscosities with experimental data from literature [114–116]. Fig. 6 shows the comparison between the computed and experimental [114–116] viscosities of acid gas-loaded 50 wt% MDEA/water solutions at 313 K and 1 bar. For CO<sub>2</sub>-loaded solutions, our findings show that the computed viscosities agree well with the experimental data from Pinto et al. [116] when a scaling factor of  $\chi_{\text{products}}^q = 0.90$  is used, capturing the increasing viscosity of the solutions with increasing CO<sub>2</sub> loading. However, the computed viscosities are significantly underestimated when  $\chi_{\text{products}}^q = 0.75$  is used, especially at high CO<sub>2</sub> loadings. The computed viscosities of H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions agree well when a scaling factor of  $\chi_{\text{products}}^q = 0.75$ , while a scaling factor of  $\chi_{\text{products}}^q = 0.90$  results in significant overestimation of the computed viscosities. Our simulations also capture the effect of slightly decreasing viscosity of the solutions with increasing H<sub>2</sub>S loading. Therefore, we decided to compute the self-diffusivities of free CO<sub>2</sub>, MDEAH<sup>+</sup>, and HCO<sub>3</sub><sup>-</sup> in CO<sub>2</sub>-loaded 50 wt% MDEA/water solutions using a scaling factor of  $\chi_{\text{products}}^q = 0.90$ , while using a scaling factor of  $\chi_{\text{products}}^q = 0.75$  for the MD simulations of H<sub>2</sub>S-loaded solutions. The reason for scaling down the point charges of the reaction products of H<sub>2</sub>S absorption (SH<sup>-</sup> and MDEAH<sup>+</sup>) to a greater extent compared to those of the reaction products of CO<sub>2</sub> absorption (HCO<sub>3</sub><sup>-</sup> and MDEAH<sup>+</sup>) may be attributed to quantum chemistry calculations overestimating the electrostatic interactions of SH<sup>-</sup> ion more than the electrostatic interactions of HCO<sub>3</sub><sup>-</sup> ion. This may be due to the greater polarity of SH<sup>-</sup> ion compared to the HCO<sub>3</sub><sup>-</sup> ion.

Fig. 7 shows the computed self-diffusivities of free CO<sub>2</sub>, free H<sub>2</sub>S, and the reaction products of CO<sub>2</sub> or H<sub>2</sub>S absorption in 50 wt% MDEA/water solutions at 313 K and 1 bar. To the best of our knowledge, the data of self-diffusivities of the reaction products in CO<sub>2</sub> or H<sub>2</sub>S loaded aqueous MDEA solutions reported here are the first in literature. For CO<sub>2</sub>-loaded aqueous MDEA solutions, our results show that for free CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and MDEAH<sup>+</sup>, the self-diffusivities show a decreasing trend with increasing CO<sub>2</sub> loading. For all species, the self-diffusivities



**Fig. 6.** Comparison of the computed and experimental [114–116] viscosities of (a) CO<sub>2</sub>-loaded and (b) H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions as a function of acid gas loading at 313 K and 1 bar. Note that the point charges of MDEA are scaled with 0.9, i.e.  $\chi_{\text{MDEA}}^q = 0.9$ . The point charges of the reaction products of CO<sub>2</sub> absorption (MDEAH<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>) and H<sub>2</sub>S absorption (MDEAH<sup>+</sup> and SH<sup>-</sup>) are scaled by either 0.9 or 0.75, i.e.  $\chi_{\text{products}}^q = 0.9$  or  $\chi_{\text{products}}^q = 0.75$ . For CO<sub>2</sub> and H<sub>2</sub>S, the TraPPE force field [64,65] was used.

in CO<sub>2</sub>-loaded 50 wt% MDEA/water solutions decrease by ca. 50% from a CO<sub>2</sub> loading of 0.01 mol<sub>CO<sub>2</sub></sub> mol<sub>amine</sub><sup>-1</sup> to 1 mol<sub>CO<sub>2</sub></sub> mol<sub>amine</sub><sup>-1</sup>. This is expected since the viscosities of the CO<sub>2</sub>-loaded solutions increase with increasing CO<sub>2</sub> loading (Fig. 6(a)). However, the self-diffusivities of free H<sub>2</sub>S, SH<sup>-</sup>, and MDEAH<sup>+</sup> are not affected by the changes in H<sub>2</sub>S loading. The self-diffusivities of H<sub>2</sub>S and H<sub>2</sub>S related reaction products also follow the same trend as the viscosities of H<sub>2</sub>S-loaded 50 wt% MDEA/water solutions (Fig. 6(b)) and the viscosities of H<sub>2</sub>S-loaded solutions also showed minimal change with changing H<sub>2</sub>S loading. Our results indicate that the absorption of CO<sub>2</sub> slows down with increasing CO<sub>2</sub> loading whereas the absorption of H<sub>2</sub>S does not exhibit the same behavior. This may be due the linear shape of the SH<sup>-</sup> ion (as opposed to the spherical HCO<sub>3</sub><sup>-</sup> ion) and a speculative proposition; a proton hopping mechanism between SH<sup>-</sup> and water molecules where the ion acts as a proton hole [117,118].

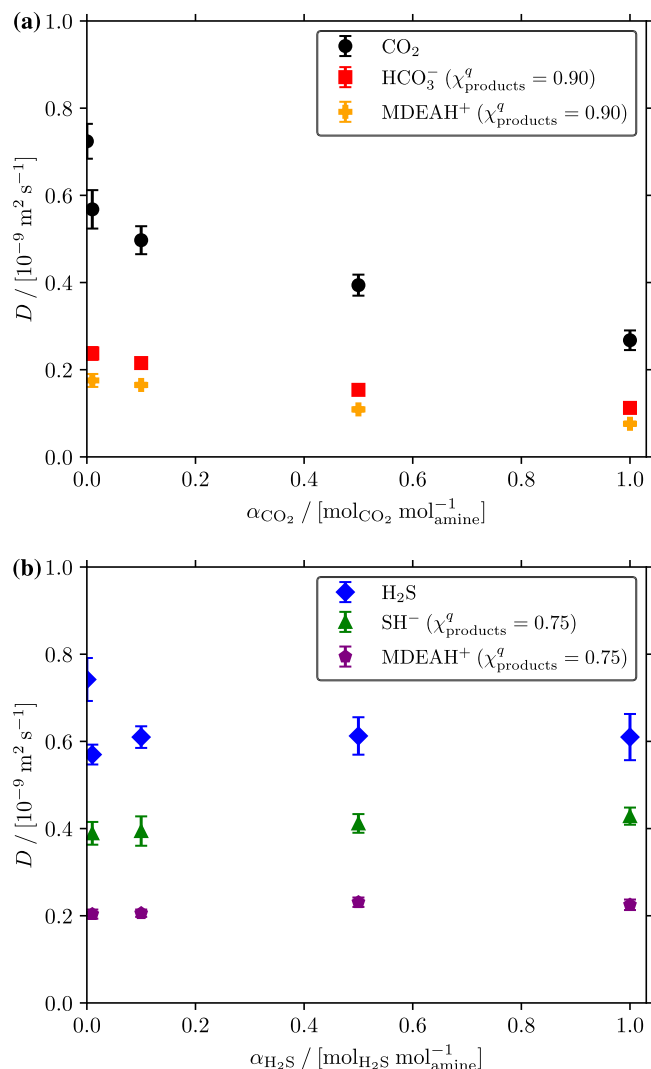


Fig. 7. Self-diffusivities of free acid gases and the reaction products from acid gas absorption in (a)  $\text{CO}_2$ -loaded and (b)  $\text{H}_2\text{S}$ -loaded 50 wt% MDEA/water solutions as a function of acid gas loading at 313 K and 1 bar. Note that the point charges of MDEA are scaled with 0.9, i.e.  $\chi_{\text{MDEA}}^q = 0.9$ . The point charges of the reaction products of  $\text{CO}_2$  absorption ( $\text{MDEAH}^+$  and  $\text{HCO}_3^-$ ) and  $\text{H}_2\text{S}$  absorption ( $\text{MDEAH}^+$  and  $\text{SH}^-$ ) are scaled by 0.9 and 0.75, respectively. All self-diffusivities are corrected for finite-size effects using Eq. (1). For  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , the TraPPE force field [64,65] was used.

#### 4. Conclusions

In this study, the effects of temperature and MDEA concentration in aqueous MDEA solutions on the values of the self-diffusivities  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  were investigated using classical MD simulations. First, we computed the densities of aqueous MDEA solutions for a temperature range of 288 – 333 K and an MDEA concentration of 10 – 50 wt% MDEA using two different sets of parameters for the N–C–C–O dihedral in MDEA, showing excellent agreement with experimental data from literature. We also computed the viscosities of aqueous MDEA solutions and showed that the computed viscosities agree well with experimental results from literature when the dihedral parameters from Orozco et al. [70] and a point charge scaling factor of 0.9 for MDEA are used. To validate that the diffusion of MDEA molecules are accurately captured in the MD simulations, we computed  $D_{\text{MDEA}}$  in aqueous MDEA solutions for a wide range of temperatures and MDEA concentrations and compared our data with available data in literature, showing a good agreement. Next, we computed  $D_{\text{CO}_2}$  and  $D_{\text{H}_2\text{S}}$  in aqueous MDEA solutions. Our findings showed that both  $\text{CO}_2$

and  $\text{H}_2\text{S}$  diffuse 3.5 times faster in 10 wt% MDEA/water solutions than in 50 wt% MDEA/water solutions and  $\text{H}_2\text{S}$  diffuse slower than  $\text{CO}_2$  in aqueous MDEA solutions. We also investigated the RDFs between  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , water, and MDEA molecules and showed that the interactions between  $\text{H}_2\text{S}$  and the surrounding molecules are stronger than those between  $\text{CO}_2$  and the surrounding molecules which explains why  $\text{H}_2\text{S}$  diffuse slower than  $\text{CO}_2$  in these solutions. Our results also showed that the interactions between the acid gases and surrounding molecules are stronger with increasing MDEA concentration in the solution. Finally, we investigated the impact of acid gas loading on the densities, viscosities and self-diffusivities (of acid gases and reaction products) in 50 wt% MDEA/water solutions at 313 K and 1 bar. The densities, viscosities, and self-diffusivities in the acid gas loaded aqueous MDEA solutions are important for the modeling of the mass transfer in loaded solutions. Comparing the computed densities and viscosities of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ -loaded solutions with experimental data from literature showed that two different point charge scaling factors are needed to accurately compute the densities and viscosities of acid gas-loaded aqueous MDEA solutions. When a scaling factor of 0.90 for the point charges of reaction products of  $\text{CO}_2$  absorption ( $\text{HCO}_3^-$  and  $\text{MDEAH}^+$ ) and a scaling factor of 0.75 for those of  $\text{H}_2\text{S}$  absorption ( $\text{SH}^-$  and  $\text{MDEAH}^+$ ) are used, we showed that the viscosities of  $\text{CO}_2$ -loaded aqueous MDEA solutions increase with increasing  $\text{CO}_2$  loading while the viscosities do not show a significant change with changing  $\text{H}_2\text{S}$  loading in  $\text{H}_2\text{S}$ -loaded solutions. For the first time in literature, we computed the self-diffusivities of free  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{MDEAH}^+$  in  $\text{CO}_2$ -loaded 50 wt% MDEA/water solutions, and free  $\text{H}_2\text{S}$ ,  $\text{SH}^-$ , and  $\text{MDEAH}^+$  in  $\text{H}_2\text{S}$ -loaded 50 wt% MDEA/water solutions at 313 K. Our results showed that the self-diffusivities in  $\text{CO}_2$ -loaded solutions significantly decrease with increasing  $\text{CO}_2$  loading while the self-diffusivities in  $\text{H}_2\text{S}$ -loaded solutions did not change significantly with changing  $\text{H}_2\text{S}$  loading in the solution which indicates that  $\text{CO}_2$  absorption slows down with increasing  $\text{CO}_2$  loading while this is not the case for  $\text{H}_2\text{S}$  absorption.

#### CRedit authorship contribution statement

**H. Mert Polat:** Simulations, Data analysis, Writing of original and revised manuscript. **Casper van der Geest:** Simulations, Data analysis. **Frédéric de Meyer:** Data analysis, Co-supervision of project, Proof-reading of original and revised manuscript. **Céline Houriez:** Data analysis, Co-supervision of project, Proof-reading of original and revised manuscript. **Thijs J.H. Vlugt:** Data analysis, Co-supervision of project, Writing of original and revised manuscript. **Othonas A. Moultsos:** Conceptualization, Data curation, Main supervision of the project, Writing of original and revised manuscript.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.fluid.2023.113913>.

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