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# Interfacial Tensions, Solubilities, and Transport Properties of the H<sub>2</sub>/H<sub>2</sub>O/NaCl System: A Molecular Simulation Study

W. A. van Rooijen,<sup>§</sup> P. Habibi,<sup>§</sup> K. Xu, P. Dey, T. J. H. Vlugt, H. Hajibeygi, and O. A. Moulτος\*Cite This: <https://doi.org/10.1021/acs.jced.2c00707>

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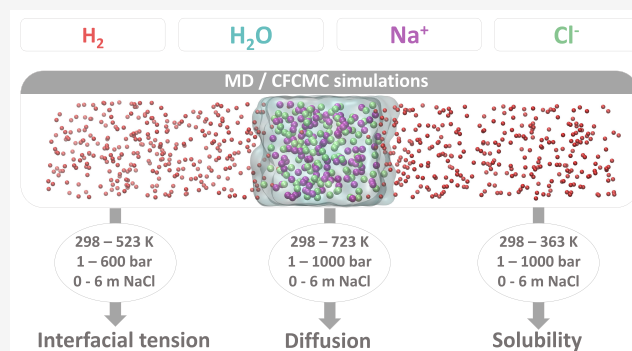
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**ABSTRACT:** Data for several key thermodynamic and transport properties needed for technologies using hydrogen (H<sub>2</sub>), such as underground H<sub>2</sub> storage and H<sub>2</sub>O electrolysis are scarce or completely missing. Force field-based Molecular Dynamics (MD) and Continuous Fractional Component Monte Carlo (CFCMC) simulations are carried out in this work to cover this gap. Extensive new data sets are provided for (a) interfacial tensions of H<sub>2</sub> gas in contact with aqueous NaCl solutions for temperatures of (298 to 523) K, pressures of (1 to 600) bar, and molalities of (0 to 6) mol NaCl/kg H<sub>2</sub>O, (b) self-diffusivities of infinitely diluted H<sub>2</sub> in aqueous NaCl solutions for temperatures of (298 to 723) K, pressures of (1 to 1000) bar, and molalities of (0 to 6) mol NaCl/kg H<sub>2</sub>O, and (c) solubilities of H<sub>2</sub> in aqueous NaCl solutions for temperatures of (298 to 363) K, pressures of (1 to 1000) bar, and molalities of (0 to 6) mol NaCl/kg H<sub>2</sub>O. The force fields used are the TIP4P/2005 for H<sub>2</sub>O, the Madrid-2019 and the Madrid-Transport for NaCl, and the Vrabec and Marx for H<sub>2</sub>. Excellent agreement between the simulation results and available experimental data is found with average deviations lower than 10%.



## 1. INTRODUCTION

Due to the vastly growing global energy demand and the resulting climate change, a transition from fossil-fuel based energy production to clean renewable energy production is crucial.<sup>1,2</sup> As a green energy carrier, hydrogen (H<sub>2</sub>) plays a crucial role in this transition because of its high gravimetric energy density and clean combustion products.<sup>3–5</sup> Important technologies in the H<sub>2</sub> value chain include underground H<sub>2</sub> storage<sup>6–9</sup> and H<sub>2</sub>O electrolysis.<sup>10,11</sup> To enable the design and optimization of these technologies, accurate knowledge of thermodynamic, interfacial, and transport properties of H<sub>2</sub> is essential.<sup>9,12–15</sup> More specifically, the diffusivities and solubilities of H<sub>2</sub> in aqueous solutions, and the interfacial tensions of H<sub>2</sub> gas in contact with aqueous electrolyte solutions are crucial properties. The interplay of these properties determines the efficiency of the technologies, and allows for accurate predictions of the processes involved, which are, e.g., required for safety. These properties depend on pressure, temperature, and salt concentration.<sup>16</sup> H<sub>2</sub> technologies cover a wide range of operational conditions. For example, in underground H<sub>2</sub> storage sites, the pressure, temperature, and salt molality can be as high as 300 bar, 333 K, and 5 mol NaCl/kg H<sub>2</sub>O, respectively.<sup>7</sup> Typically, H<sub>2</sub>O electrolyzers operate at atmospheric pressure, temperatures of ca. (348 to 372) K, and molalities of ca. (3 to 4) electrolyte/kg H<sub>2</sub>O.<sup>17,18</sup> Other types of electrolysis require much higher pressures and temperatures, i.e., up to 700 bar and 1400 K, respectively.<sup>19–21</sup> Thus, to cover the conditions for important H<sub>2</sub> applications, the

interfacial tensions, self-diffusivities, and solubilities need to be available for a very wide range of pressures, temperatures, and salt concentrations.

Traditionally, these thermophysical properties are measured experimentally.<sup>22–24</sup> Nevertheless, only a small number of experimental studies on the interfacial tension of H<sub>2</sub>/pure H<sub>2</sub>O<sup>22,25–28</sup> is available, while only two studies report measurements of interfacial tension of H<sub>2</sub>/aqueous solutions (with NaCl and NaCl+KCl).<sup>27,28</sup> These experiments are performed by using the capillary rise<sup>29</sup> and the pendant drop<sup>25,27,28,30</sup> techniques. Interfacial tensions of H<sub>2</sub>/aqueous solutions are reported for temperatures up to 423 K, pressures up to 345 bar, and molalities of up to 5 mol (NaCl + KCl)/kg H<sub>2</sub>O. As far as the solubility of H<sub>2</sub> in aqueous NaCl solutions is concerned, for an overview of the available experimental data the reader is referred to the works of Chabab et al.,<sup>31</sup> Torin-Ollarves and Trusler,<sup>32</sup> and Ansari et al.<sup>33</sup> Although a lot of experimental data are available for H<sub>2</sub> in pure H<sub>2</sub>O, solubility measurements of H<sub>2</sub> in aqueous NaCl solutions are scarce, and in many cases conflicting.<sup>23,31,34–38</sup> The two main sources of

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experimental data of solubilities of H<sub>2</sub> in aqueous solutions at concentrations above 1 mol NaCl/kg H<sub>2</sub>O, at temperatures above 300 K, and at pressures above 10 bar by Torin-Ollarves and Trusler,<sup>32</sup> and Chabab et al.<sup>31</sup> show conflicting results as the measured solubilities differ by ca. 30%. For the self-diffusivity of H<sub>2</sub> in H<sub>2</sub>O, experimental data are available<sup>24,39–46</sup> but mostly at atmospheric pressure and for limited temperatures below 340 K. Similarly to the solubilities, the experimental measurements also differ by up to 70%. To the best of our knowledge, no experimental data are available for the self-diffusivity of H<sub>2</sub> in aqueous NaCl solutions.

Based on the available experimental data, it is evident that only a limited range of the required interfacial tensions, solubilities, and self-diffusivities of the H<sub>2</sub>/H<sub>2</sub>O/NaCl system has been measured, while in some cases, there are significant discrepancies between the data reported from different sources. The reason for the scarcity of and deviation in the data may be that experimental measurements are rather challenging and expensive to perform, especially at high pressures and temperatures. To this end, a widely used complementary approach for obtaining thermophysical data is molecular simulation, especially at conditions which are challenging for experimental measurements.

Numerous studies have used Molecular Dynamics (MD) to compute the interfacial tension of gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>) and liquids (e.g., hydrocarbons) in contact with H<sub>2</sub>O (pure or saline).<sup>47–57</sup> However, no molecular simulation studies on the interfacial tension of H<sub>2</sub> and aqueous solutions are available. MD simulations have also been performed to compute self-diffusivities (i.e., self-diffusion coefficients) of H<sub>2</sub> in pure H<sub>2</sub>O.<sup>58–62</sup> Recently, Tsimpanogiannis et al.<sup>60</sup> reported such data for pressures in the range of (1 to 2000) bar and temperatures in the range of (275 to 975) K spanning vapor, liquid, and supercritical H<sub>2</sub>O. The Marx,<sup>63</sup> Vrabec,<sup>64</sup> Buch,<sup>65</sup> Hirschenfelder,<sup>66</sup> Cracknell,<sup>67</sup> and Silvera-Goldman<sup>68</sup> H<sub>2</sub> force fields were used in combination with the TIP4P/2005<sup>69</sup> H<sub>2</sub>O force field. The Buch<sup>65</sup> and Vrabec<sup>64</sup> H<sub>2</sub> force fields were shown to yield the best agreement with experimental data. In contrast, self-diffusivities of H<sub>2</sub> in aqueous NaCl solutions computed from MD simulations have not yet been reported, while there are a few studies available reporting computations of self-diffusivities of CO<sub>2</sub> in aqueous NaCl solutions.<sup>70–73</sup> Lopez-Lazaro et al.<sup>74</sup> have computed solubilities of H<sub>2</sub> in aqueous NaCl solutions using Monte Carlo (MC) simulations for molalities up to a maximum of 2 mol NaCl/kg H<sub>2</sub>O. To the best of the authors' knowledge, this was the only molecular simulation study on H<sub>2</sub> solubilities in aqueous NaCl solutions. Molecular simulations have been used for computing solubilities of other gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>) in water and aqueous NaCl solutions.<sup>52,57,75–77</sup>

Despite the urgency and importance of reliable data of interfacial tension of H<sub>2</sub> in contact with aqueous NaCl solutions, self-diffusivity of H<sub>2</sub> in aqueous NaCl solutions, and solubility of H<sub>2</sub> in aqueous NaCl solutions, only very limited experimental and simulation studies are available. The objective of this work is to generate reliable data for these properties for a wide range of conditions relevant to H<sub>2</sub> technologies, such as underground H<sub>2</sub> storage and H<sub>2</sub>O electrolysis. We present new data sets of (a) interfacial tensions of H<sub>2</sub> and aqueous NaCl solutions for temperatures, pressures, and molalities of (298 to 523) K, (1 to 600) bar, and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively, (b) self-diffusivities of H<sub>2</sub> in aqueous NaCl solutions for temperatures, pressures, and

molalities of (298 to 723) K, (1 to 1000) bar, and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively, and (c) solubilities of H<sub>2</sub> in aqueous NaCl solutions for temperatures, pressures, and molalities of (298 to 363) K, (1 to 1000) bar and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively. The interfacial tensions and self-diffusivities are computed using MD simulations, and the solubilities are computed using CFCMC<sup>78–80</sup> simulations. Densities and viscosities of the aqueous NaCl solutions are also computed for a wide range of conditions and are compared to available experimental data. The TIP4P/2005<sup>69</sup> force field is used for H<sub>2</sub>O, the Madrid-2019<sup>81</sup> force field for NaCl, and the Vrabec<sup>64</sup> and Marx<sup>63</sup> force fields are used for H<sub>2</sub>. A modified version of the Madrid-2019 force field by Vega and co-workers<sup>82</sup> (i.e., the Madrid-Transport<sup>77,82</sup>), optimized for viscosities of aqueous NaCl solutions for salinities up to the experimental solubility limit, is also used.

The paper is structured as follows. Details of the force fields used and the molecular simulation techniques are given in section 2. In section 3, the computed interfacial tensions, viscosities, densities, self-diffusivities, and solubilities obtained are presented and compared with experimental data when possible. Finally, concluding remarks are presented in section 4. All data computed in this study are provided in a tabulated format as Supporting Information.

## 2. METHODOLOGY

**2.1. Force Fields.** The four-site TIP4P/2005<sup>69</sup> force field is used to model H<sub>2</sub>O. Previous studies have shown that this force field can accurately capture thermodynamic, transport, and interfacial properties of pure H<sub>2</sub>O and H<sub>2</sub>O/NaCl solutions in contact with gases for a wide range of conditions.<sup>47,49,60,83–88</sup> For the Na<sup>+</sup> and Cl<sup>−</sup> ions, the Madrid-2019<sup>81</sup> force field is used, which is parametrized for the TIP4P/2005 H<sub>2</sub>O model.<sup>89</sup> A new version of the Madrid-2019 force field (i.e., Madrid-Transport force field<sup>77,82</sup>) is currently being developed by Vega and co-workers,<sup>82</sup> which performs better for transport properties, especially at high NaCl molalities. The difference of Madrid-Transport from Madrid-2019 is that ion charges are scaled by 0.75 instead of 0.85, and the Lennard-Jones (LJ) parameters are slightly altered. Interfacial tensions and self-diffusivities are computed using the single-site Vrabec<sup>64</sup> H<sub>2</sub> force field, while for the solubilities of H<sub>2</sub> in the aqueous NaCl solutions the three-site Marx<sup>63</sup> model is used. Tsimpanogiannis et al.<sup>84</sup> showed that the Vrabec<sup>64</sup> H<sub>2</sub> force field yields very accurate self-diffusivities of H<sub>2</sub> in pure TIP4P/2005 H<sub>2</sub>O. The solubilities computed using the Vrabec<sup>64</sup> force field deviate from experimental data of H<sub>2</sub> in pure water by ca. 50%. In sharp contrast, the solubilities computed using the Marx<sup>63</sup> force field show excellent agreement with experimental data. A comparison of the solubilities computed using the Marx and Vrabec force fields in pure TIP4P/2005 H<sub>2</sub>O are listed in Table S1 and shown in Figure S1 of the Supporting Information. At low temperatures, H<sub>2</sub> exhibits quantum effects which can be accounted for by using potentials such as the Feynman-Hibbs effective interaction potential.<sup>90–92</sup> At the temperatures considered in this work (i.e., 298 K and above) these quantum effects can be neglected.<sup>93</sup> All force field parameters are listed in Tables S2–S5 in the Supporting Information. A list of the chemical formulas, CAS numbers, and force fields of all species studied here is shown in Table 1.

**2.2. Molecular Simulation Details.** **2.2.1. MD Simulations.** The MD simulations are used to calculate (a) the

**Table 1. Details of All the Species Simulated in This Work**

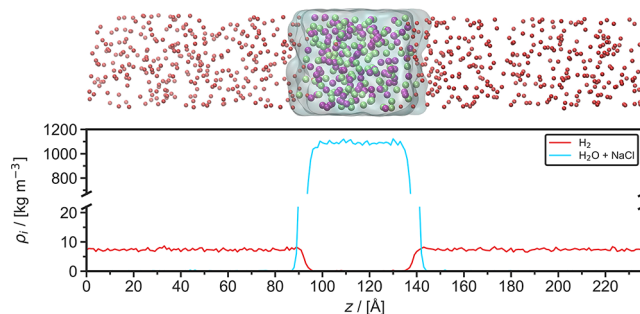
Component	Chemical formula	CAS number	Force field
Water	H <sub>2</sub> O	7732-18-5	TIP4P/2005 <sup>69</sup>
Hydrogen	H <sub>2</sub>	133-74-0	Vrabc64
Hydrogen	H <sub>2</sub>	133-74-0	Marx <sup>63</sup>
Sodium	Na <sup>+</sup>	7440-23-5	Madrid-2019 <sup>81</sup>
Sodium	Na <sup>+</sup>	7440-23-5	Madrid-Transport <sup>77,82</sup>
Chloride	Cl <sup>-</sup>	7782-50-5	Madrid-2019 <sup>81</sup>
Chloride	Cl <sup>-</sup>	7782-50-5	Madrid-Transport <sup>77,82</sup>

interfacial tensions of H<sub>2</sub> in contact with aqueous NaCl solutions, (b) self-diffusivities of H<sub>2</sub> in aqueous NaCl solutions, (c) densities, and (d) viscosities of aqueous NaCl solutions. For all MD simulations, the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)<sup>94</sup> is used (version 29 Sep 2021). For the integration of the equations of motion, the velocity-Verlet algorithm is used with a time step of 1 fs. The bond length and bending angle of H<sub>2</sub>O are fixed using the SHAKE algorithm.<sup>94,95</sup> The intermolecular interactions are described by Lennard-Jones and Coulombic interaction potentials. The Lorentz–Berthelot combining rules<sup>96</sup> are used for interactions between different types of molecules, with the exception of Na<sup>+</sup>–H<sub>2</sub>O, Na<sup>+</sup>–Cl<sup>-</sup>, and Cl<sup>-</sup>–H<sub>2</sub>O LJ interactions as specified in Table S5. Long-range electrostatic energies are computed using the particle–particle particle–mesh (PPPM) method<sup>97,98</sup> with a relative error<sup>99</sup> of 10<sup>-5</sup>. The temperature and pressure are regulated by the Nosé–Hoover thermostat and barostat.<sup>97</sup> Initial configurations are created using the PACKMOL software.<sup>100</sup> Periodic boundary conditions are imposed in all directions. All MD simulations for a specific set of conditions are repeated 5 times using different initial velocity distributions from which the average quantities are calculated. The reported uncertainties are standard deviations from the results of these 5 simulations.

**2.2.2. Computation of Interfacial Tension.** The following procedure is used for computing the interfacial tensions: An initial configuration is created by combining separately equilibrated bulk phases of aqueous sodium chloride solutions and H<sub>2</sub> gas. An equilibration run of 5 ns is carried out in the *NPT* ensemble using anisotropic pressure coupling, i.e., only the *z*-direction of the simulation box is allowed to fluctuate. The last 2 ns of the equilibration run are used to calculate the average simulation box dimensions, which are used for an equilibration run of 3 ns in the *NVT* ensemble. Next, production runs of 2 ns are carried out for computing the interfacial tension. In all simulations, 2088 H<sub>2</sub>O molecules are used. Depending on the pressure, the number of H<sub>2</sub> molecules varied between 64–640. 0–188 Na<sup>+</sup> and Cl<sup>-</sup> ions are used, depending on the molality. The exact numbers of species along with the simulation box sizes for all simulations are listed in Table S6 of the Supporting Information. A cutoff radius of 12 Å is used for the short-range LJ and short-range electrostatic energies. Because the system is inhomogeneous, analytic corrections were not used. Instead, long-range LJ and electrostatic interactions are computed using the Particle–Particle Particle–Mesh (PPPM) method.<sup>97,98,101</sup> For the real and reciprocal space computations for the dispersion part of the PPPM method the desired accuracies are set to 0.0001 and 0.002, respectively. A relative error of 10<sup>-5</sup> is used for the long-range electrostatic energies. The adequacy of the PPPM method for computing the LJ interactions was recently

validated by Salehi et al.<sup>102</sup> in interfacial MD simulations of deep eutectic solvents with water.

Figure 1 (top panel) shows a typical MD simulation snapshot at *T* = 343 K, *P* = 100 bar, and *m* = 3 mol NaCl/kg



**Figure 1.** Top: Typical snapshot from a Molecular Dynamics simulation used to calculate the interfacial tension of H<sub>2</sub> and an aqueous NaCl solution (3 mol NaCl/kg H<sub>2</sub>O) at 343 K and 100 bar. H<sub>2</sub> molecules are represented by red spheres, Na<sup>+</sup> and Cl<sup>-</sup> are represented by purple and green spheres, respectively, H<sub>2</sub>O is represented by the transparent blue surface. Bottom: Density profile in the *z*-direction of H<sub>2</sub> and the aqueous NaCl solution of the same simulation, averaged over 1 ns. *z* is the direction perpendicular to the interface.

H<sub>2</sub>O. The bulk liquid H<sub>2</sub>O phase containing the Na<sup>+</sup> and Cl<sup>-</sup> ions, which is shown as the transparent blue surface, occupies a domain of ca. 40 × 40 × 40 Å<sup>3</sup> in the middle of the simulation box. H<sub>2</sub> gas is in contact with the liquid phase from both sides, in the *z*-direction. This creates two H<sub>2</sub>/H<sub>2</sub>O interfaces perpendicular to the *z*-direction. The density profile of this system, averaged over 1 ns, is shown in Figure 1 bottom panel.

The interfacial tension  $\gamma$  is calculated from the principal components of the diagonal elements of the stress tensor ( $P_{zz}$ ,  $P_{xx}$ , and  $P_{yy}$ ):<sup>103</sup>

$$\gamma = \frac{1}{2}h_z \left[ P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right] \quad (1)$$

where  $h_z$  is the simulation cell length in the *z*-direction.

**2.2.3. Computation of Self-Diffusivities and Viscosities.** The scheme used for computing self-diffusivities and viscosities follows from ref 104. Initially, energy minimization of the system is performed, followed by equilibration runs in the *NPT* and *NVT* ensembles for 1–2 ns. Next, production runs in the *NVT* ensemble for 10 ns are carried out. The system consists of 700 H<sub>2</sub>O molecules, 2 H<sub>2</sub> molecules, and 0–76 Na<sup>+</sup> and Cl<sup>-</sup> ions, depending on the molality. The exact numbers of species used for every state point are provided in Table S7 of the Supporting Information. A cutoff radius of 10 Å is used for Lennard-Jones and electrostatic interactions. Analytic tail corrections for energies and pressures are applied.

To compute the self-diffusivities and the shear viscosities, the OCTP plugin<sup>104</sup> in LAMMPS is used. In this plugin, the Einstein relations are used in combination with the order-*n* algorithm<sup>97</sup> as implemented by Dubbeldam et al.<sup>105</sup> Self-diffusivity  $D_i$  of species *i* is computed based on the mean-squared displacements using

$$D_i = \lim_{t \rightarrow \infty} \frac{1}{6N_i t} \left\langle \sum_{j=1}^{N_i} (\mathbf{r}_{j,i}(t) - \mathbf{r}_{j,i}(0))^2 \right\rangle \quad (2)$$

where  $r_{j,i(t)}$  is the position vector of the  $j$ th molecule of species  $i$  at time  $t$  and  $N_i$  is the number of molecules of species  $i$ . All self-diffusivities in this work are corrected for finite-size effects using the Yeh-Hummer equation:<sup>106–108</sup>

$$D = D_i + \frac{k_B T \xi}{6\pi\eta L} \quad (3)$$

where  $D$  is the finite-size corrected self-diffusivity,  $T$  is the temperature in K,  $\xi$  is a dimensionless constant equal to 2.837298,  $\eta$  is the shear viscosity from eq 4, and  $L$  is the simulation box length. In this work, the finite-size correction magnitude was ca. 5–10% of the computed self-diffusivities.

Shear viscosity  $\eta$  is computed from

$$\eta = \lim_{t \rightarrow \infty} \frac{1}{10 \cdot 2t} \frac{V}{k_B T} \left\langle \sum_{\alpha\beta} \left( \int_0^t P_{\alpha\beta}^{\text{os}}(t') dt' \right)^2 \right\rangle \quad (4)$$

where

$$P_{\alpha\beta}^{\text{os}} = \frac{P_{\alpha\beta} + P_{\beta\alpha}}{2} - \delta_{\alpha\beta} \left( \frac{1}{3} \sum_k P_{kk} \right) \quad (5)$$

where  $V$  is the volume of the system,  $k_B$  is the Boltzmann constant,  $P_{\alpha\beta}^{\text{os}}$  denotes the components of the traceless pressure tensor,  $\delta_{\alpha\beta}$  is the Kronecker delta, and  $\langle \dots \rangle$  indicates an ensemble average. The computation of  $\eta$  does not depend on the size of the system.<sup>109–111</sup>

**2.2.4. Computation of Solubilities.** Continuous Fractional Component Monte Carlo<sup>78–80</sup> simulations in the isobaric–isothermal (CFCNPT) ensemble are used to compute solubilities and excess chemical potentials of  $\text{H}_2$  in NaCl solutions. The open-source Brick-CFCMC software<sup>78,112,113</sup> is used for all simulations. A 10 Å cutoff radius is used for both the LJ and Coulombic interactions. The Ewald summation with a relative precision of  $10^{-6}$  is used for the electrostatics. Analytic tail corrections for energies and pressures are applied.<sup>97</sup> The infinite dilution excess chemical potential of  $\text{H}_2$  can be computed using a single “fractional” molecule of  $\text{H}_2$ . Fractional molecules have their interactions scaled with a continuous order parameter  $\lambda$ .<sup>78,93</sup> In CFCNPT simulations,  $\lambda$  ranges from 0 to 1.  $\lambda = 0$  indicates that the fractional molecule does not interact with the surrounding molecules/atoms (i.e., the fractional molecule behaves as an ideal gas molecule), and  $\lambda = 1$  corresponds to full interactions. For the specifics regarding the scaling of the interactions the reader is referred elsewhere.<sup>114–116</sup> To improve the sampling in the  $\lambda$ -space, a biasing weight function ( $W(\lambda)$ ) is created using the Wang–Landau algorithm.<sup>117,118</sup> This biasing weight function is used to ensure a flat probability distribution in the  $\lambda$ -space ( $p_{\text{obs}}(\lambda)$ ). To compute the probability of occurrence of each  $\lambda$  value, a histogram with 100 bins is used. The Boltzmann averaged probability distributions of  $\lambda$  ( $p(\lambda)$ ) can be computed using<sup>77,119</sup>

$$p(\lambda) = \frac{\langle p_{\text{obs}}(\lambda) \exp[-W(\lambda)] \rangle}{\langle \exp[-W(\lambda)] \rangle} \quad (6)$$

The Boltzmann sampled probability distribution of  $\lambda$  ( $p(\lambda)$ ) can be related to the infinite dilution chemical potential ( $\mu^{\text{ex}}$ ) using<sup>77,78,119</sup>

$$\mu^{\text{ex}} = -k_B T \ln \frac{p(\lambda = 1)}{p(\lambda = 0)} \quad (7)$$

where  $p(\lambda = 1)$  and  $p(\lambda = 0)$  are the Boltzmann averaged probability distributions of  $\lambda$  at 1 and 0, respectively.

Five  $\times 10^5$  equilibration cycles, and  $5 \times 10^5$  production cycles are performed for all simulations. A cycle contains  $N$  number of trial moves, with  $N$  being the total number of molecules, with a minimum of 20. The following probabilities are used for selecting the trial moves: 35% translations, 29% rotations, 1% volume changes, 25%  $\lambda$  changes, and 10% reinsertions of the fractional molecules at random locations inside the simulation box. The maximum displacements for molecule translations, volume changes, rotations, and  $\lambda$  changes are adjusted to obtain ca. 50% acceptance. Another method that can be used to compute  $\mu^{\text{ex}}$  is the Widom’s Test Particle Insertion method (WTPI).<sup>96,97,120,121</sup> In dense fluid phases WTPI yields inaccurate results compared to the CFCMC method as successful insertion of test particles is a highly unlikely event due to the significant potential energy increase in case of overlap with other particles.<sup>78,122</sup>

The solubilities of  $\text{H}_2$  in aqueous NaCl solutions are computed at temperatures in the range (298 to 363) K and at  $\text{H}_2$  partial pressures of 1, 10, 100, 400, and 1000 bar. At  $\text{H}_2$  partial pressures of 1 and 10 bar, the  $\text{H}_2$  solubilities are computed using Henry coefficients ( $H$ ):

$$H = \lim_{f_i \rightarrow 0} \frac{f_i}{\langle \rho_{\text{H}_2, \text{L}} \rangle / \rho_0} \quad (8)$$

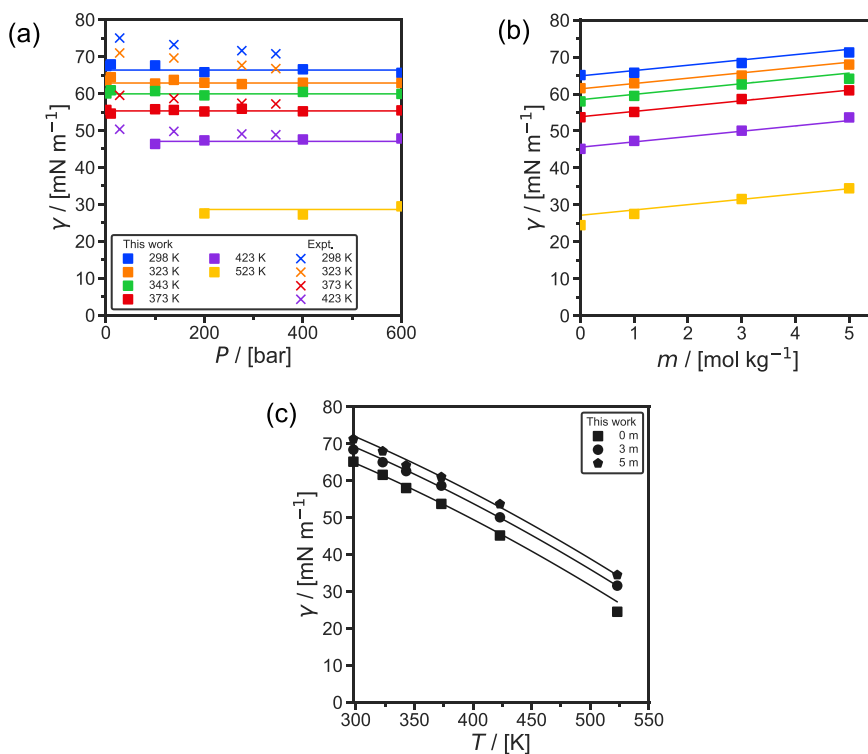
where  $f_i$  is the fugacity of  $\text{H}_2$  in the gas phase,  $\langle \rho_{\text{H}_2, \text{L}} \rangle$  is the average number density of  $\text{H}_2$  in the aqueous solution in units of  $1/\text{m}^3$ , and  $\rho_0$  is a reference number density in the same unit as  $\rho_{\text{H}_2, \text{L}}$  (set to 1 molecule per  $\text{m}^3$ ).<sup>119</sup> At  $\text{H}_2$  partial pressures of 1 and 10 bar, the fugacity coefficient of  $\text{H}_2$  is assumed to be 1 (i.e., the fugacity of  $\text{H}_2$  is equal to the partial pressure of  $\text{H}_2$ ). The validity of eq 8 at  $\text{H}_2$  partial pressures of 1–100 bar is discussed in Figure S3 of the Supporting Information. From the MC simulations,  $H$  can be computed using<sup>119</sup>

$$H = \rho_0 k_B T \exp \left[ \frac{\mu_{\text{H}_2, \text{L}}^{\text{ex}}}{k_B T} \right] \quad (9)$$

where  $\mu_{\text{H}_2, \text{L}}^{\text{ex}}$  is the infinite dilution chemical potential of  $\text{H}_2$  in the aqueous solution. A single fractional molecule of  $\text{H}_2$ , 300  $\text{H}_2\text{O}$  molecules, and varying number of NaCl molecules depending on the molality (ranging from 0 to 6 mol NaCl/kg  $\text{H}_2\text{O}$ ) are used to compute  $\mu_{\text{H}_2, \text{L}}^{\text{ex}}$ . The exact numbers of ions used for each molality are listed in Table S8 of the Supporting Information. To calculate solubilities of  $\text{H}_2$  in aqueous NaCl solutions at pressures of 100, 400, and 1000 bar, the chemical potentials of  $\text{H}_2$  in the liquid and in the gas phase are equated at constant pressure and temperature. The chemical potential of  $\text{H}_2$  in the gas phase ( $\mu_{\text{H}_2, \text{G}}$ ) is equal to<sup>97</sup>

$$\mu_{\text{H}_2, \text{G}} = \mu_{\text{H}_2}^0 + k_B T \ln \left( \frac{\langle \rho_{\text{H}_2, \text{G}} \rangle}{\rho_0} \right) + \mu_{\text{H}_2, \text{G}}^{\text{ex}} \quad (10)$$

where  $\mu_{\text{H}_2}^0$  is the reference state of the chemical potential,  $\langle \rho_{\text{H}_2, \text{G}} \rangle$  is the average number density of  $\text{H}_2$  in the gas phase in units of  $1/\text{m}^3$ , and  $\mu_{\text{H}_2, \text{G}}^{\text{ex}}$  is the excess chemical potential of  $\text{H}_2$  in the gas phase. At pressures above 100 bar and at temperatures between (298 to 363) K, the gas phase contains very few  $\text{H}_2\text{O}$  molecules (a  $\text{H}_2\text{O}$  mole fraction below 0.01).<sup>93</sup>



**Figure 2.** MD results of interfacial tension  $\gamma$  of  $\text{H}_2$  and aqueous NaCl solutions using the NaCl Madrid-2019<sup>81</sup> force fields, the TIP4P/2005<sup>69</sup>  $\text{H}_2\text{O}$  force field, and the Vrabec<sup>64</sup>  $\text{H}_2$  force field (a) as functions of pressure  $P$  for temperatures in a range of (298 to 523) K with a molality  $m$  of 1 mol NaCl/kg  $\text{H}_2\text{O}$  in combination with the experimental results of Hosseini et al.,<sup>27</sup> (b) as functions of molality at a pressure of 200 bar of the solution for similar temperatures, and (c) as functions of temperature at a pressure of 200 bar and molalities of (0 to 6) mol NaCl/kg  $\text{H}_2\text{O}$ . The statistical uncertainties are comparable to or smaller than the symbols and can be found in Table S9 of the Supporting Information. The error bars have been omitted for clarity. The solid lines represent fits using eq 13 for temperatures in the range of (298 to 523) K.

$\mu_{\text{H}_2,\text{G}}^{\text{ex}}$  is calculated in separate CFCNPT simulations, containing a single fractional molecule of  $\text{H}_2$ , and 300  $\text{H}_2$  molecules in the gas phase. At conditions where the gas phase is nonideal and the  $\text{H}_2\text{O}$  content in the gas phase is not negligible (i.e., temperatures above 363 K and pressures above 100 bar), Gibbs ensemble simulations can be performed to simulate the gas and the liquid phase simultaneously.<sup>93</sup> These simulations are beyond the scope of this work. The chemical potential of  $\text{H}_2$  in the liquid phase ( $\mu_{\text{H}_2,\text{L}}$ ) is equal to<sup>97</sup>

$$\mu_{\text{H}_2,\text{L}} = \mu_{\text{H}_2}^0 + k_{\text{B}}T \ln \left( \frac{\langle \rho_{\text{H}_2,\text{L}} \rangle}{\rho_0} \right) + \mu_{\text{H}_2,\text{L}}^{\text{ex}} \quad (11)$$

$\langle \rho_{\text{H}_2,\text{L}} \rangle$  can be computed by equating eq 10 and eq 11. The mole fractions of  $\text{H}_2$  ( $x_{\text{H}_2}$ ) in aqueous NaCl solutions are computed using

$$x_{\text{H}_2} = \frac{\langle \rho_{\text{H}_2,\text{L}} \rangle \langle V \rangle}{N_{\text{H}_2\text{O}} + N_{\text{NaCl}} + \langle \rho_{\text{H}_2,\text{L}} \rangle \langle V \rangle} \quad (12)$$

where  $\langle V \rangle$  is the average volume of the simulation box, computed in the CFCNPT ensemble.  $N_{\text{H}_2\text{O}}$  and  $N_{\text{NaCl}}$  are the numbers of  $\text{H}_2\text{O}$  and NaCl molecules in the simulation box, respectively. For each condition (concentration, temperature, and pressure), 20 independent simulations are performed. These 20 simulations are divided into 5 blocks from which the Boltzmann sampled probability distributions of  $\lambda$  ( $p(\lambda)$ ) are averaged. The averaged distributions ( $p(\lambda)$ ) of all blocks are

used to compute mean values and standard deviations for the excess chemical potentials and solubilities of  $\text{H}_2$ .

### 3. RESULTS AND DISCUSSION

**3.1. Interfacial Tensions.** Figure 2 shows the computed interfacial tensions of  $\text{H}_2/\text{H}_2\text{O}/\text{NaCl}$  as a function of pressure (Figure 2a), molality (Figure 2b) at temperatures in the range of (298 to 523) K, and as a function of temperature (Figure 2c) for molalities in the range of (0 to 6) mol NaCl/kg  $\text{H}_2\text{O}$ . Tabulated raw data of the interfacial tension along with their statistical uncertainties are listed in Table S9 of the Supporting Information. Figure 2a and 2c also show the available experimental data from Hosseini et al.<sup>27</sup> For the whole range of conditions a close agreement with the experimental results is found. The MD results differ on average 6.4% from the experimental values. The simulations at 523 K cannot be directly validated due to lack of experimental data.

The interfacial tensions computed in this work are fitted to an engineering equation:

$$\gamma = c_1 + c_2 m + c_3 T^{c_4} \quad (13)$$

where  $c_1$ ,  $c_2$ ,  $c_3$ , and  $c_4$  are fitting parameters, which are listed in Table 2. Equation 13 is valid for temperatures, pressures, and molalities of (298 to 523) K, (1 to 600) bar, and (0 to 6) mol NaCl/kg  $\text{H}_2\text{O}$ , respectively. The results of this engineering equation are shown as solid lines in Figure 2. Equation 13 is a very good fit to MD results, and can be used for calculating values at a specific combination of conditions in a fast and reliable way.

**Table 2. Parameters of eq 13 for Predicting Interfacial Tension of H<sub>2</sub> in Contact with Aqueous NaCl Solutions<sup>a</sup>**

$c_1/[\text{mN/m}]$	89.6
$c_2/[(\text{mN}\cdot\text{kg}_{\text{H}_2\text{O}})/(\text{m}\cdot\text{mol}_{\text{NaCl}})]$	1.44
$c_3/[\text{mN}/(\text{m}\cdot\text{K}^{1.65})]$	$-2.04 \times 10^{-3}$
$c_4/[-]$	1.65

<sup>a</sup>Values obtained using the NaCl Madrid-2019<sup>81</sup> force fields, TIP4P/2005<sup>69</sup> H<sub>2</sub>O force field, and Vrabec<sup>64</sup> H<sub>2</sub> force field. These parameters are valid for NaCl molalities of (0 to 6) mol NaCl/kg H<sub>2</sub>O, temperatures of (298 to 523) K, and pressures of (1 to 600) bar.

As shown in Figure 2a, no significant pressure dependence of interfacial tension is observed. The data of experimental studies also show no significant or small pressure dependences.<sup>22,25,27,28</sup> In particular, Higgs et al.<sup>28</sup> did not observe a significant pressure dependence for H<sub>2</sub> in contact with aqueous NaCl solutions. Other studies observed a small decrease in interfacial tension of H<sub>2</sub> and pure H<sub>2</sub>O<sup>22,25,27</sup> and H<sub>2</sub> and aqueous (NaCl+KCl) solutions.<sup>27</sup> Interestingly, the pressure dependence of H<sub>2</sub>/H<sub>2</sub>O interfacial tension is small compared to the CO<sub>2</sub>/H<sub>2</sub>O<sup>123–125</sup> and CH<sub>4</sub>/H<sub>2</sub>O<sup>51,126,127</sup> systems. This is because the interfacial tension is related to the density difference between the two phases.<sup>16</sup> The change in density difference between H<sub>2</sub> and H<sub>2</sub>O is very small at varying pressures because the density of H<sub>2</sub> is very low in comparison to H<sub>2</sub>O, and H<sub>2</sub>O is almost incompressible at these pressures.

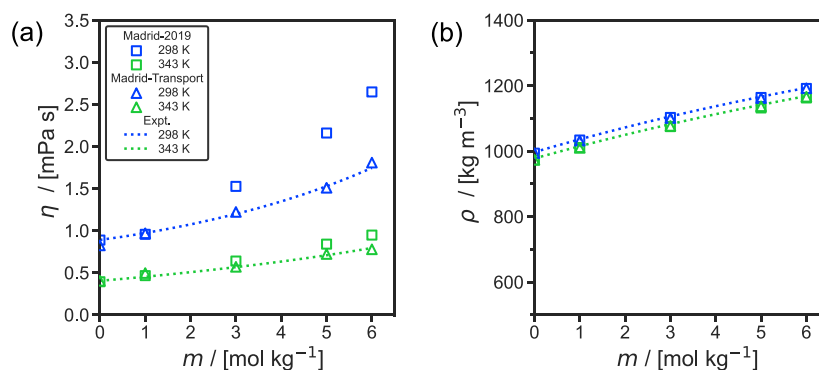
As shown in Figure 2b, the interfacial tension increases linearly with solution molalities, in agreement with the available experimental data.<sup>27</sup> This behavior is also observed for other gases such as CO<sub>2</sub> and CH<sub>4</sub>.<sup>128–130</sup> This increase is mainly due to the increased density of saline H<sub>2</sub>O compared to pure H<sub>2</sub>O as well as the arrangement of cations and anions at the interface.<sup>129,131–135</sup> The hydrogen bond network of H<sub>2</sub>O is strengthened by cations,<sup>132–134</sup> while anions cause the opposite effect.<sup>132–134</sup> Therefore, cations are absorbed into the bulk phase while anions are depleted from the bulk phase. This phenomenon can be observed in Figure S2 of the Supporting Information, where it is shown that the number density of Cl<sup>−</sup> ions at the interface is higher than Na<sup>+</sup> ions, and Na<sup>+</sup> ions are drawn into the bulk phase. The strengthening of the hydrogen bond network of H<sub>2</sub>O leads to an increase in interfacial tension.<sup>129,131</sup>

In Figure 2c, a nonlinear decrease of interfacial tension with temperature can be observed. This is in line with the

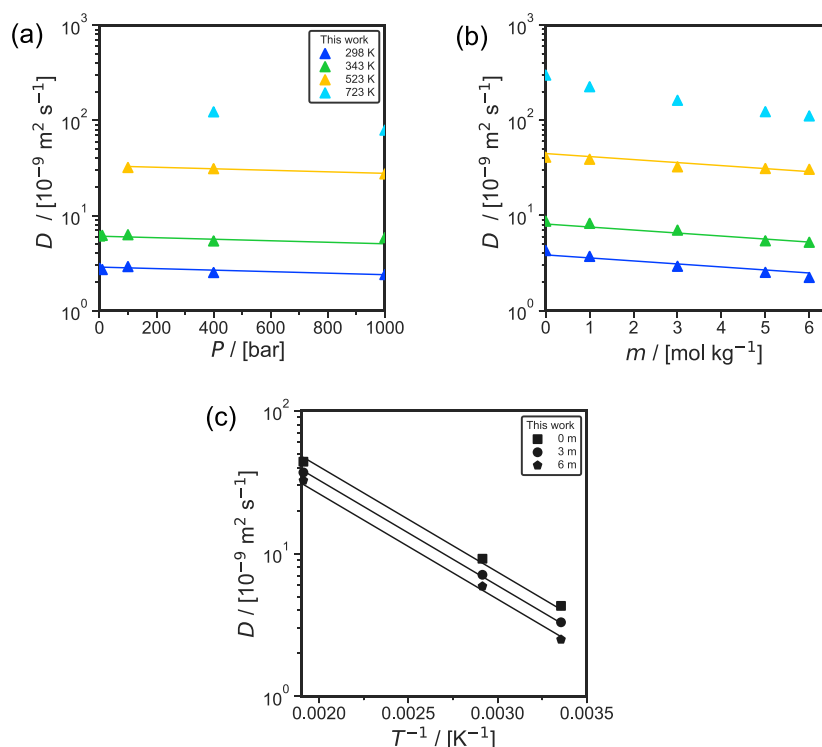
experimental data of Chow et al.<sup>25</sup> In sharp contrast, Hosseini et al.<sup>27</sup> reported a linear decrease of interfacial tension with temperature. The fact that interfacial tension depends nonlinearly on the density difference between the two phases in contact<sup>16</sup> combined with the nonlinear effect of temperature on the density difference between H<sub>2</sub> and H<sub>2</sub>O, results in the expectation that the interfacial tension is also nonlinearly related to temperature. Therefore, the observed nonlinear relationship between interfacial tension and temperature in our results is expected.

**3.2. Viscosities and Densities.** Figure 3 shows the computed densities and viscosities of aqueous NaCl solutions as functions of NaCl molalities at 298 and 343 K. The densities are computed from the average volume calculated from the NPT ensemble. Equation 4 is used to compute the viscosities. Densities and viscosities of aqueous NaCl solutions have a weaker dependence on pressure (in the range of 0–1000 bar) compared to temperature and NaCl molalities. Figures S4 and S5 in the Supporting Information show the densities and the viscosities as functions of pressure. The results for the Madrid-2019<sup>81</sup> and the Madrid-Transport<sup>77,82</sup> NaCl force fields are shown in Figure 3. Laliberté<sup>136</sup> and Laliberté and Cooper<sup>137</sup> developed models on the basis of experimental data for viscosities and densities, respectively. These fits are shown in Figure 3. The raw data of these properties, as well as their statistical uncertainties, are listed in Table S10 of the Supporting Information. Both the Madrid-2019<sup>81</sup> and Madrid-Transport<sup>77,82</sup> capture the experimental data of density very accurately (within 1%). As shown in Figure 3a, the Madrid-Transport<sup>77,82</sup> force field yields a better agreement with the experimental data of viscosity compared to the Madrid-2019<sup>81</sup> force field. The discrepancy between the two force fields starts at molalities above 2 mol NaCl/kg H<sub>2</sub>O. The viscosities computed using the Madrid-2019 force field deviate on average ca. 20% from the experimental data, while this deviation is only ca. 3% when the Madrid-Transport force field is used. Based on the excellent performance of Madrid-Transport in reproducing experimental viscosities, which is necessary for reliable diffusivity predictions,<sup>138</sup> only this force field was used for computing the self-diffusivities of H<sub>2</sub> in NaCl solutions.

**3.3. Self-Diffusivities of H<sub>2</sub>.** Figure 4 shows the computed finite-size corrected self-diffusivities of H<sub>2</sub> in aqueous NaCl solutions as a function of (a) pressure, (b) NaCl molality, and



**Figure 3.** Computed (a) viscosities  $\eta$  and (b) densities  $\rho$  of aqueous NaCl solutions as a function of molality  $m$  (mol NaCl/kg H<sub>2</sub>O) at a pressure of 1 bar and temperatures of 298 and 343 K. The fit to the experimental data is created by (a) Laliberté<sup>136</sup> and (b) Laliberté and Cooper.<sup>137</sup> The statistical uncertainties can be found in Table S10 of the Supporting Information. The error bars are smaller or comparable to the symbol size and have been omitted for clarity.



**Figure 4.** Computed finite-size corrected self-diffusivities ( $D$ ) of  $\text{H}_2$  in aqueous NaCl solutions (a) with a molality ( $m$ ) of 5 mol NaCl/kg  $\text{H}_2\text{O}$  solution as a function of pressure  $P$  for temperatures of (298 to 723) K, (b) at a pressure of 400 bar as a function of  $m$  of the solution for the similar temperatures, and (c) as a function of the reciprocal temperature at a pressure of 100 bar. The results are obtained using the NaCl Madrid-Transport<sup>77,82</sup> force fields, TIP4P/2005<sup>69</sup>  $\text{H}_2\text{O}$  force field, and Vrabec<sup>64</sup>  $\text{H}_2$  force field. The statistical uncertainties are comparable to or smaller than the symbols and can be found in Table S11 of the Supporting Information. The solid lines are fits calculated using eq 14 for temperatures of (298 to 523) K. Data points at a temperature of 723 K and a pressure of 400 bar are excluded from the fit because  $\text{H}_2\text{O}$  is supercritical at these conditions.

(c) temperature. These simulation are performed with the Madrid-Transport<sup>77,82</sup> force field for NaCl, the TIP4P/2005<sup>69</sup>  $\text{H}_2\text{O}$ , and the Vrabec<sup>64</sup> force field for  $\text{H}_2$ . All the self-diffusivities of  $\text{H}_2$  computed in this work are listed in Tables S11 and S12 of the Supporting Information. Simulations using the Madrid-2019<sup>81</sup> NaCl force field are performed for comparison. These data are shown in Table S12 of the Supporting Information.

The self-diffusivities of  $\text{H}_2$  shown in Figure 4 are fitted to an engineering correlation:

$$D = c_1 \exp \left[ c_2 m + c_3 \left( \frac{1}{T} \right) + c_4 P \right] \quad (14)$$

where  $c_1$ ,  $c_2$ ,  $c_3$ , and  $c_4$  are fitting parameters, which are listed in Table 3. As shown in Figure 4, this correlation provides an excellent fit for the MD results. Note that eq 14 is only valid for conditions at which  $\text{H}_2\text{O}$  is in the liquid phase, and therefore, data points at temperatures of 723 K or higher are excluded as the solution is in the supercritical phase. In this work, self-diffusivities for temperatures of 723 K and pressures lower than 400 bar are not calculated, because at those conditions,  $\text{H}_2\text{O}$  is in the gas phase. Equation 14 is an empirical model.

In Figure 4a a weak pressure dependence of the self-diffusivities of  $\text{H}_2$  is observed. The logarithm of the self-diffusivities decays linearly with respect to variations in pressure, similarly to what is reported by Tsimpanogiannis et al.<sup>84</sup> The pressure dependence of the self-diffusivities of  $\text{H}_2$  is more significant at 723 K (Figure 4a) as the solution is more

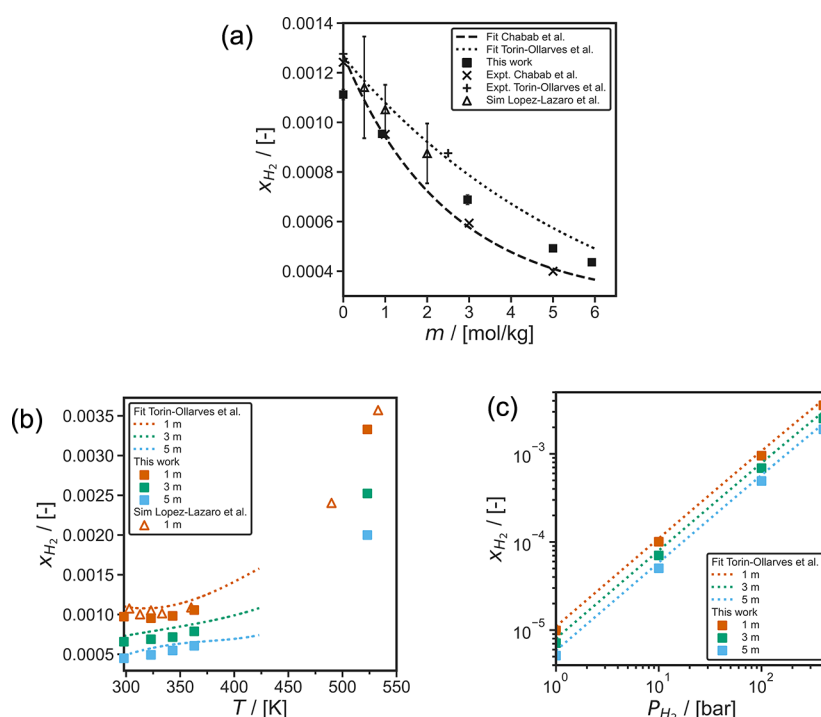
**Table 3. Parameters of eq 14 for Predicting the Computed Finite-Size Corrected Self-Diffusivities  $D$  of  $\text{H}_2$  in Aqueous NaCl Solutions<sup>a</sup>**

$c_1/[\text{m}^2/\text{s}]$	$1.24 \times 10^{-6}$
$c_2/[(\text{mol}_{\text{NaCl}}/\text{kg}_{\text{H}_2\text{O}})^{-1}]$	$-7.29 \times 10^{-2}$
$c_3/[\text{K}]$	$-1.70 \times 10^3$
$c_4/[\text{bar}^{-1}]$	$-1.84 \times 10^{-4}$

<sup>a</sup>Values obtained using the NaCl Madrid-Transport<sup>77,82</sup> force fields, the TIP4P/2005<sup>69</sup>  $\text{H}_2\text{O}$  force field, and the Vrabec<sup>64</sup>  $\text{H}_2$  force field. These parameters are valid for NaCl molalities of (0 to 6) mol NaCl/kg  $\text{H}_2\text{O}$ , temperatures of (298 to 523) K, and pressures of (1 to 1000) bar. Note that eq 14 should only be used at conditions in which water is in the liquid state.

compressible at these conditions. As shown in Figure 4b, the logarithm of the self-diffusivities is also found to decay linearly with respect to variation in the NaCl molalities. Labiberte<sup>136</sup> has shown that the viscosities of aqueous NaCl solutions increase exponentially with respect to NaCl molalities. As the self-diffusivities of gases dissolved in liquids are inversely proportional to the viscosities of the solution,<sup>16,138</sup> the self-diffusivities of  $\text{H}_2$  are expected to decay exponentially with respect to the NaCl molalities. The computed self-diffusivities of  $\text{H}_2$  follow an Arrhenius-type<sup>97</sup> relation with respect to variations in temperature ( $D \propto \exp \left[ \frac{c}{T} \right]$ ) as shown in Figure 4c. This behavior is also observed in literature for gases (e.g.,  $\text{O}_2$ ,  $\text{H}_2$ ) dissolved in aqueous solvents.<sup>60,86,139–141</sup>





**Figure 5.** Computed solubilities of H<sub>2</sub> in aqueous NaCl solutions using the NaCl Madrid-2019 force field,<sup>81</sup> TIP4P/2005<sup>69</sup> H<sub>2</sub>O force field, and Marx<sup>63</sup> H<sub>2</sub> force field as functions of (a) NaCl molality ( $m$ ) in units of mol NaCl/kg H<sub>2</sub>O for a H<sub>2</sub> partial pressure of 100 bar, at 323 K, (b) temperature for a H<sub>2</sub> partial pressure of 100 bar, and (c) H<sub>2</sub> partial pressure at 323 K. The dashed lines represent the experimental correlation provided by Torin-Ollarves and Trusler,<sup>32</sup> and the dotted lines represent the experimental correlation results of Chabab et al.<sup>31</sup> The experimental data of Chabab et al.,<sup>31</sup> and Torin-Ollarves and Trusler,<sup>32</sup> and the simulation results of Lopez-Lazaro et al.<sup>74</sup> (converted from Henry constants) are also shown. The error bars of the simulations of this work are comparable (Figure 5a) or smaller than (Figure 5b and 5c) the symbol size.

**3.4. Solubilities.** In Figure 5, the solubilities of H<sub>2</sub> computed using CFCMC are shown as a function of (a) NaCl molality, (b) temperature, and (c) pressure. The computed solubilities are compared to the experimental measurements of Chabab et al.,<sup>31</sup> Torin-Ollarves and Trusler,<sup>32</sup> and their corresponding experimental correlations (also shown in Figure 5). The correlation of Torin-Ollarves and Trusler<sup>32</sup> is based on the experimental measurements for NaCl molalities of 0 and 2.5 mol NaCl/kg H<sub>2</sub>O, the experimental data by Wiebe and Gaddy,<sup>142</sup> Wiebe et al.,<sup>143</sup> Kling and Maurer,<sup>144</sup> and Choudhary et al.<sup>145</sup> for H<sub>2</sub> solubility in pure H<sub>2</sub>O, and the experiments by Crozier and Yamamoto<sup>37</sup> and Gordon et al.<sup>38</sup> for solubility of H<sub>2</sub> in saline solutions. Chabab et al.<sup>31</sup> provide an extensive experimental data set and a correlation for H<sub>2</sub> solubilities at temperatures of (323 to 373) K, and NaCl molalities in the range of (0 to 5) mol/kg H<sub>2</sub>O. Lopez-Lazaro et al.<sup>74</sup> obtained the Henry constants of H<sub>2</sub> in aqueous NaCl solutions for molalities up to 2 mol NaCl/kg H<sub>2</sub>O using excess chemical potentials computed using the WTPI method.<sup>96,97,120,121</sup> Using the Henry constants reported by Lopez-Lazaro et al.,<sup>74</sup> the solubilities of H<sub>2</sub> at a partial pressure of 100 bar are computed and shown in Figures 5a and 5b. The simulations of Lopez-Lazaro et al.<sup>74</sup> show large error bars (ca. 10–20%). This may be due to the use of the WTPI method,<sup>96,97,120,121</sup> which requires a large number of MC cycles to obtain low standard deviations for excess chemical potentials in the liquid phase.<sup>74,78</sup> The solubilities computed in this work using CFCMC simulations<sup>79,80,112,113</sup> have uncertainties of less than 5%.

Figure 5a shows the decrease of the solubilities of H<sub>2</sub> at increasing molalities of NaCl (i.e., salting-out effect). The

salting-out of nonpolar gases (e.g., H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>) in the presence of salts such as NaCl, KCl, and KOH is a well observed phenomenon.<sup>57,77,135</sup> As shown in Figure 5a, the models by Torin-Ollarves and Trusler<sup>32</sup> and Chabab et al.<sup>31</sup> agree for H<sub>2</sub> solubilities in pure H<sub>2</sub>O and at NaCl molalities below 0.5 mol NaCl/kg H<sub>2</sub>O. For NaCl concentrations higher than 0.5 mol NaCl/kg H<sub>2</sub>O the two models predict different H<sub>2</sub> solubilities. The salting-out effect of H<sub>2</sub> observed in this work using the Madrid-2019<sup>81</sup> Na<sup>+</sup> and Cl<sup>-</sup>, TIP4P/2005<sup>69</sup> H<sub>2</sub>O, and the Marx<sup>63</sup> H<sub>2</sub> force fields shows better agreement to the salting-out effect observed by Torin-Ollarves and Trusler<sup>32</sup> as shown in Figure 5a. The correlation of Torin-Ollarves and Trusler<sup>32</sup> also shows agreement with our simulations at H<sub>2</sub> partial pressures ranging from (1 to 400) bar in the temperature range (298 to 363) K, as shown in Figures 5b and 5c. Our simulation results also agree with the MC simulations by Lopez-Lazaro et al.<sup>74</sup> both for different NaCl molalities, and for different temperatures in the range of (298 to 523) K, even though the choice of the force fields for Na<sup>+</sup>, Cl<sup>-</sup>, and H<sub>2</sub> is different. Lopez-Lazaro et al.<sup>74</sup> have used the OPLS force field<sup>146</sup> for Na<sup>+</sup>, and Cl<sup>-</sup>, combined with the model by Darkim et al.<sup>147</sup> for H<sub>2</sub>.

In Table S13 of the Supporting Information, we provide an extensive database for solubilities of H<sub>2</sub> at temperatures of (298 to 363) K, H<sub>2</sub> partial pressures of (1 to 1000) bar, and at NaCl molalities of (0 to 6) mol/kg H<sub>2</sub>O. The solubilities of H<sub>2</sub> at partial pressures up to 100 bar are computed for a wider temperature range, i.e., (298 to 523) K. These data can be further used to test and train existing machine-learning models<sup>33</sup> or equations of state<sup>148</sup> for predicting H<sub>2</sub> solubilities

in saline solutions at conditions relevant to geological H<sub>2</sub> storage.

#### 4. CONCLUSIONS

Molecular simulations are used to compute (a) interfacial tensions of H<sub>2</sub> and aqueous NaCl solutions for temperatures, pressures, and molalities of (298 to 523) K, (1 to 600) bar, and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively, (b) self-diffusivities of H<sub>2</sub> in aqueous NaCl solutions for temperatures, pressures, and molalities of (298 to 723) K, (1 to 1000) bar and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively, and (c) solubilities of H<sub>2</sub> in aqueous NaCl solutions for temperatures, pressures, and molalities of (298 to 363) K, (1 to 1000) bar, and (0 to 6) mol NaCl/kg H<sub>2</sub>O, respectively. The simulations for computing H<sub>2</sub> self-diffusivities are also used to yield predictions for densities and viscosities of the NaCl solutions. The interfacial tensions and self-diffusivities are computed using MD simulations, and the solubilities are computed using CFCMC simulations. The H<sub>2</sub>O TIP4P/2005<sup>69</sup> force field, the NaCl Madrid-2019<sup>81</sup> force fields, and H<sub>2</sub> Vrabec<sup>64</sup> and Marx<sup>63</sup> force fields are used. In addition, a modified version of the Madrid-2019 force field (i.e., the Madrid-Transport<sup>77,82</sup> force field) is used, which is optimized for transport properties of aqueous solutions. Our results are validated against the available experimental data, models, and simulations. Excellent agreement between the results and experimental data is found with deviations smaller than 10% for the vast majority of the data points. The results of the NaCl Madrid-Transport force field were in better agreement with experimental data for transport properties, while the Madrid-2019 force field was sufficiently accurate for interfacial tensions and solubilities. The new data are used to develop engineering equations for interfacial tension and self-diffusion capturing the effect of pressure, temperature, and solution molality.

#### ■ ASSOCIATED CONTENT

##### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.2c00707>.

Solubilities of H<sub>2</sub> in pure water; force field parameters; additional info MD and CFCMC simulations; raw data MD simulations for interfacial tensions; density and viscosity data; raw data MD simulations for self-diffusivities; raw data CFCMC simulations; solubilities of H<sub>2</sub> in pure water; density profile of Na<sup>+</sup> and Cl<sup>-</sup> of a MD simulation to calculate interfacial tensions; solubilities of H<sub>2</sub> in aqueous NaCl solution at H<sub>2</sub> partial pressures of 1–100 bar; densities of NaCl solutions; viscosities of NaCl solutions (PDF)

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#### Notes

The authors declare no competing financial interest.

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