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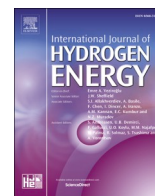
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A prediction of interfacial tension by using molecular dynamics simulation: A study on effects of cushion gas (CO₂, N₂ and CH₄) for Underground Hydrogen Storage

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ABSTRACT

Carbon Dioxide (CO₂) emissions from fossil fuel consumption have caused global warming and remain challenging problems for mitigation. Underground Hydrogen Storage (UHS) provides clean fuel and replaces traditional fossil fuels to reduce emissions of CO₂. Geological formations such as depleted oil/gas reservoirs, deep saline aquifers and shale formations have been recognized as potential targets to inject and store H₂ into the subsurface formations for large-scale implementation of CCS and UHS. However, the presence of H₂ with cushion gas at different fractions under different geo-storage conditions, which can influence Hydrogen's flow properties, was not investigated widely. Until now, studies of interfacial properties between water and a mixture of cushion gas (CO₂, N₂ or CH₄) in the presence of H₂ are very limited or unavailable data in experiments and simulations. In this study, many predictions by using molecular dynamics simulation were conducted to predict the interfacial tension (γ) for the systems of H₂/CO₂/H₂O, H₂/N₂/H₂O and H₂/CH₄/H₂O at different pressures, temperatures, and fractions of cushion gases. A comparison between the predicted γ results from the simulation and previous research were also made. The findings of this study indicated that γ of H₂/CO₂/H₂O, H₂/CH₄/H₂O, and H₂/N₂/H₂O, as a function of pressure, temperature, and fraction of H₂, decreased with increasing pressures and temperatures and increased with increasing H₂% in the mixture. Additionally, an extending or new γ data in simulation for the CO₂/H₂/H₂O, N₂/H₂/H₂O and CH₄/H₂/H₂O systems from this study were reported and support evaluating the stability and storage capacity of H₂ combined with the cushion gas in geological formations. Furthermore, it can contribute to de-risking and proceeding safely and efficiently for the large-scale implementation of Underground Hydrogen Storage.

1. Introduction

Global warming due to Carbon Dioxide (CO₂) emissions from consuming fossil fuels remains a complicated challenge in reaching the Paris Agreement's goals [1]. Several technological solutions are offered for this problem, including Carbon Capture and Storage (CCS) and Underground Hydrogen Storage (UHS) [2,3]. The CCS solution reduces CO₂ emissions from fossil fuel power plants and carbon-intensive industries [4,5]. To cut carbon dioxide emissions, the solution of UHS supplies clean fuel and replaces conventional fossil products [6,7]. Geological formations such as depleted oil/gas reservoirs, deep saline aquifers and

shale formations have been recognized as potential targets to inject and store H₂ into the subsurface formations for large-scale implementation of CCS and UHS by storage capacity and geological stability [8–10]. Specifically, in the porous media, the injected H₂ will replace the in-situ pore fluids (water or residual hydrocarbon) at the subsurface formations and be distributed under an impermeable layer or cap rock by a lower density of Hydrogen [8]. Currently, the UHS in depleted hydrocarbon reservoirs has assessed the best selection for large-scale implementation for significant reasons. First of all, geological structures and reservoir characterization data were gathered and analyzed carefully in the exploration and operation phases. Next, surface and subsurface

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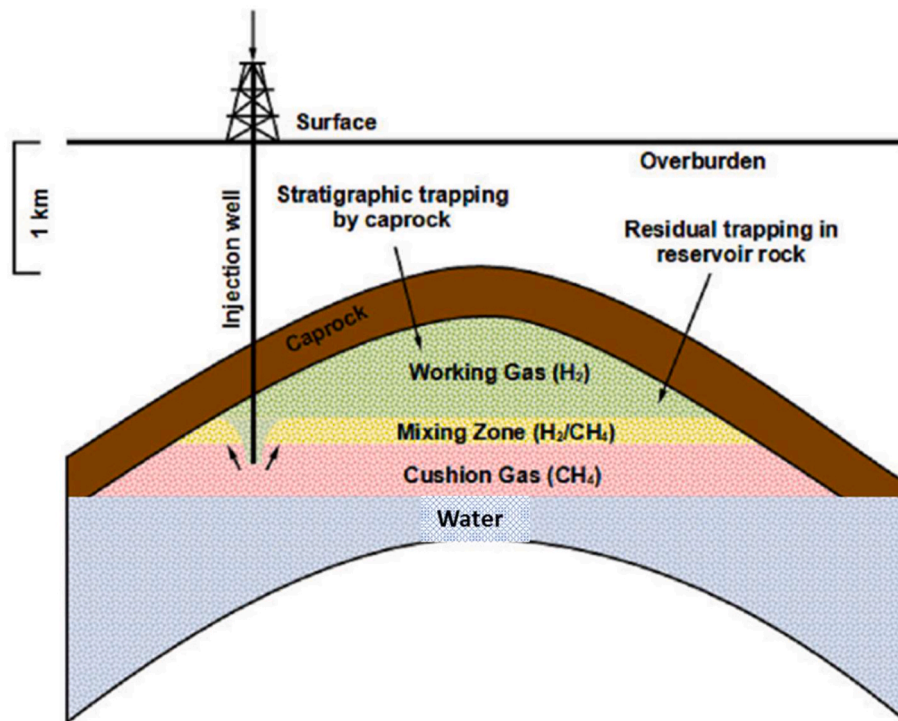


Fig. 1. A conceptual model of Underground Hydrogen Storage in depleted hydrocarbon reservoirs between Hydrogen and cushion gas (CH₄) [16].

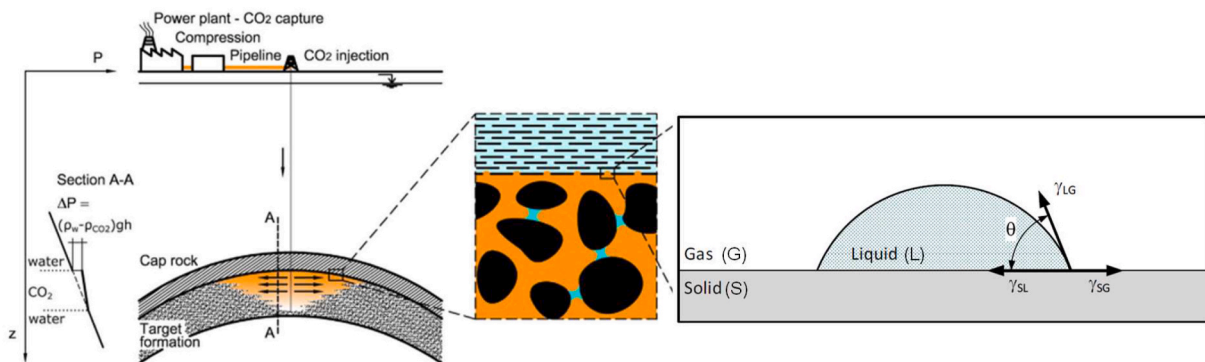


Fig. 2. A simple description of interfacial properties that influence CCS and UHS projects' reliability and storage capacity [11,24,25].

equipment of H₂ storage projects can be inherited from depleted oil/gas projects with minimal or without modification. Furthermore, many best practices and lessons learnt from gas injection for enhancing hydrocarbon recovery in the oil and gas industry are still valid and applicable to the UHS projects [11,12].

The UHS is considered in common concepts with Underground Gas Storage (UGS) [13]. In practice, a storage process at underground formations requires a cushion gas (CO₂, N₂ or CH₄) to maintain high sufficient pressure in reservoirs as working gas (or H₂) is being withdrawn and also prevent water production [10,14,15], as shown in Fig. 1. Specifically, the process requires the cushion gas to be injected into the subsurface formation before implementing the H₂ injection. It leads to forming a mixing zone that includes cushion gas and H₂ during injection [12,16]. However, the level of blending of the cushion gas and injected H₂, interactions between the gas and liquid and influences of hydrodynamics at underground formations are unclear for the UHS [12]. To date, there has been minimal study on the effects of cushion gas for implementing Hydrogen underground storage. Hence, the presence of H₂ and different fractions of cushion gas under different geo-storage conditions [8] can influence the flow characteristics of H₂ via the

injection and production cycle conditions [17], which needs attention for investigation.

Accurate storage capacity assessment requires estimating the volume of H₂ that can be safely stored in subsurface formations is complicated. Because injected gas in the subsurface formations possibly escapes via caprock when the breakthrough pressure of injected gas is higher than the capillary entry pressure. So, the reliability and storage capacity for a subsurface formation is controlled significantly by capillary pressure [18–21], which is described as a function of contact angles and interfacial tensions and pore radius, as described by the equation of Young-Laplace (1)

$$P_c = P_g - P_w = \frac{2\gamma \cos\theta}{r} \quad (1)$$

where P_c is the capillary entry pressure, P_g and P_w are the pressure of the gas and water phase; γ is the interfacial tension between water and gas, θ is contact angle, and r is effective radius of the pore, as displayed in Fig. 2. The equation (1) shows that γ is a critical parameter revealing an amount of Hydrogen can be injected for storage and how the gas plume spreads in the underground formations [22,23]. Besides, the estimation

Table 1A summary of previous studies for interfacial tension between H₂O and gas mixture in the presence of H₂.

Authors	Year	Method	Systems	Pressure, MPa	Temperature, K	Cushion Gas %
Hosseini et al.	2022	Experiment	H ₂ /Brine ^a	1–35	298–423	
Chow et al.	2018	Experiment	H ₂ /H ₂ O	0.5–45	298–448	
Massoudi et al.	1974	Experiment	H ₂ /H ₂ O	7.6	298.15	
Yang et al.	2022	Simulation	H ₂ /H ₂ O	1–160	298–523	
Doan et al.	2023	Simulation	H ₂ /H ₂ O	1–70	298–323	
Georgiadis et al.	2010	Experiment	CO ₂ /H ₂ O	1–60	298–374	
Kvamme et al.	2007	Experiment	CO ₂ /H ₂ O	0.1–20	278–335	
Silvestri et al.	2019	Simulation	CO ₂ /H ₂ O	1–50	308, 323 and 383	
Yan et al.	2001	Experiment	CO ₂ /N ₂ /H ₂ O	1–30	298–373	
Chow et al.	2016	Experiment	CO ₂ /N ₂ /H ₂ O	2–40	298–448	
Ren et al.	2000	Experiment	CH ₄ /H ₂ O	1–30	298–373	
Naeiji et al.	2020	Simulation	CH ₄ /H ₂ O	1.4–10	275–323	
Chow et al.	2018	Experiment	H ₂ –CO ₂ –Water	0.5–45	298 to 448	CO ₂ (30 %)
Isfehiani et al.	2023	Experiment	H ₂ –CO ₂ –Water	3–20	323	CO ₂ (30%–70 %)
Mirchi et al.	2022	Experiment	H ₂ –CH ₄ –Brine ^a	6.9	295, 313 and 333	CH ₄ (20%–80 %)
Alanazi et al.	2023	Experiment	H ₂ –CH ₄ –Brine ^a	0–11	323	CH ₄ (50 %)
Doan et al.	2023	Simulation	H ₂ –CH ₄ –Water	1.0–70	300	CH ₄ (40 %)

^a Brine is from NaCl.

of the interfacial tensions of H₂ in the presence of subsurface fluids aims to understand the fluid behaviour at reservoir conditions for assessing the gas storage efficiency and designing the proper schemes of injection and withdrawal [12].

To date, a few studies have reported the γ between Hydrogen and pure water (or brine) at subsurface conditions. The reported data in experiments and simulations for water and a mixture of cushion gas such as CO₂, N₂ or CH₄ in the presence of H₂ is very limited or unavailable. Table 1 summarizes previous γ studies in the presence of H₂ with different thermo-physical conditions and percentage of cushion gas. Most previous studies from Table 1 have been focused on the binary system of Hydrogen and pure water (or brine) and performed at temperatures from 275.15 to 423 K and pressures up to 70 MPa in experiments [26–31] and in simulations ([11],[32]). However, for the H₂–CH₄–H₂O system, two experimental studies [16,33] were conducted by varying percentages of cushion gas (or CH₄) from 20 % to 80 % by Ref. [33] and at 50 % CH₄ by Ref. [16], only a simulation study [11] was performed a portion at 40 % of CH₄ in the mixture. Furthermore, for the H₂–CO₂–H₂O system, only two experiments with changing the proportion of CO₂ in the mixture from 30% to 70 % were reported [17,28], but no simulation data was reported. However, until now, no data has been available in experiments and simulations for the system of H₂–N₂–H₂O. Previous studies of the system of H₂–CH₄–H₂O and H₂–CO₂–H₂O reported that the interfacial tension of the system declined by increasing the percentage of cushion gas (CO₂ or CH₄) in the mixture to compare with the binary system of pure H₂/H₂O so that it could raise a concern for H₂ diffusion through the cap rock or increasing risk for storing H₂ in depleted oil/gas reservoirs [16,33]. Therefore, studying the effects of the interfacial tension under different thermal dynamics conditions and varying the percentage of cushion gas (CO₂, N₂ and CH₄) in the mixture in the presence of H₂ at the subsurface formations is crucial for implications for UHS operations and stability.

In this work, therefore, many predictions of the interfacial tension (γ)

Table 2

The values of parameters for Lennard Jones and Coulombic interactions.

Models	Atom	σ (nm)	ϵ (kJ/mol)	q (e)
H ₂ (IFF)	H	0.2918	0.064	0.000
N ₂ (IFF)	N	0.3670	0.279	0.000
CO ₂ (EPM2)	C	0.2757	0.234	0.651
	O	0.3033	0.668	–0.326
CH ₄ (OPLS)	C	0.3500	0.276	–0.240
	H	0.2500	0.126	0.060
H ₂ O (TIP4P/2005)	H	0.0000	0.000	0.524
	O	0.3159	0.775	–1.048

for the systems of H₂/CO₂/H₂O, H₂/CH₄/H₂O, and H₂/N₂/H₂O at different pressure, temperature, and fraction of cushion gases (CO₂, N₂ and CH₄) from 10 % to 90 % were conducted by using molecular dynamics simulation. Comparisons between the predicted γ results and experimental and simulation data from previous research were made. The achieved results deliver extending or new γ data in simulation for the systems of H₂/CO₂/H₂O, H₂/CH₄/H₂O, and H₂/N₂/H₂O. The findings of this study support assessing the stability and long-term practicality of several primary Underground Hydrogen Storage (UHS) in de-risking and proceeding safely and efficiently for large-scale implementation of UHS.

This research is organized into sections: Section 2 explains the simulation setup and model and the methods used for MD simulation. In Section 3, the results of simulations are found and discussed, and Section 4 provides a summary and conclusion.

2. Methodology

All molecular dynamics simulations were conducted in this study using the open-source LAMMPS program [34] to predict interfacial tension at temperatures of 300 K, 323 K–343 K and pressure from 1.0 to 70 MPa. Initial configurations for simulation boxes were built with Packmol [35]. And the OVITO software [36] is used for data visualization.

2.1. Force field selection

The intermolecular potential forces employed in this study are divided into van der Waals and electrostatic interactions. The Lennard-Jones (L-J) 12–6 potential [37] was used to describe the van der Waals intermolecular potential force (nonbonded) as in equation (2).

$$U_{vdw} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

where ϵ_{ij} is the depth of potential well between atoms *i* and *j* at the distance between atoms r_{ij} , and σ_{ij} is the effective distance of atoms.

The Lorentz-Berthelot mixing rule [38] was applied to define the parameters of van der Waals interaction between unlike atoms, as shown in equation (3)

$$\sigma_{ij} = (\sigma_{ij} + \sigma_{ij}) / 2 \text{ and } \epsilon_{ij} = \sqrt{\epsilon_{ij}\epsilon_{ij}} \quad (3)$$

Coulomb's law [39] was used to calculate electrostatic interactions according to the equation (4):

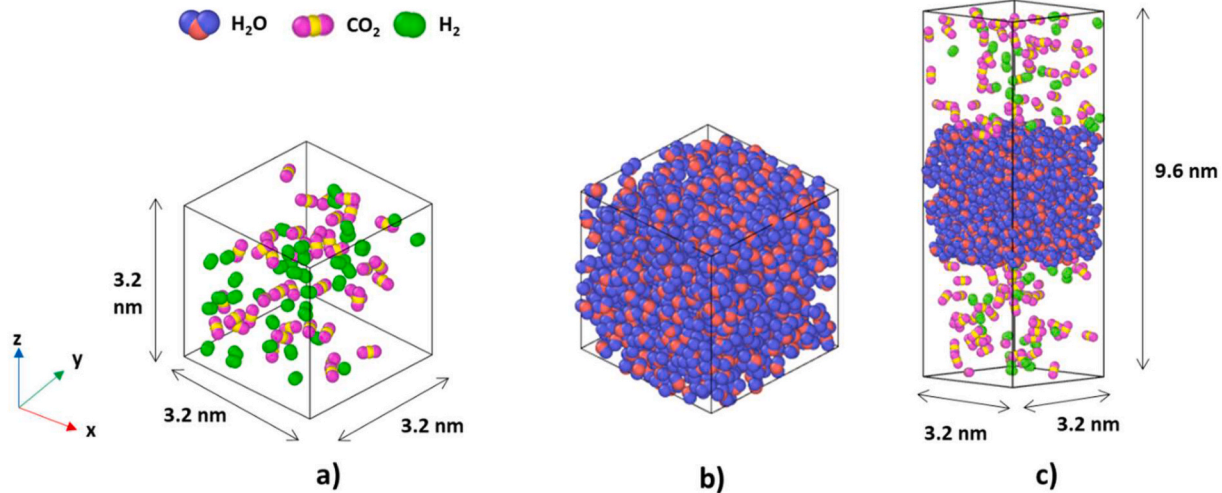


Fig. 3. A snapshot of initial arrangements of H₂O, CO₂ and H₂ in simulation boxes: a) a mixed gas of CO₂ and H₂, b) bulk water, and c) a gas mixture of H₂-CO₂-H₂O system.

$$U_{coul} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}^2} \quad (4)$$

where q_i and q_j are the partial charges on atoms i and j , ϵ_0 is the vacuum permittivity.

For modelling water molecules, the force field of rigid TIP4P/2005 [40] was applied, while CO₂ is represented by the EPM2 force field [41]. Methane (or CH₄) is modelled by the OPLS force field [42]. And the Interface force field or IFF [43] was applied to both N₂ and H₂ molecules. Table 2 summarizes the L-J potential parameters and charges used for simulations in this study.

2.2. Simulation details

The simulation approach was followed from previous studies [44,45] by equilibrating simulation boxes independently prior to merging the simulation boxes, as in Fig. 3. At the beginning step, the simulation box with a size of 3.2 nm × 3.2 nm × 3.2 nm are made and to generate the initial structures and three dimensions were applied the periodic boundary conditions [46]. A number of cushion gas molecules (CO₂, N₂, or CH₄) and H₂ molecules were initialized in the simulation box based on different conditions of temperature, pressure and fraction, which vary from 8 to 515 molecules. Another simulation box was also set up by placing 1088 H₂O molecules. After the initialization of molecules in the simulation boxes, a required energy minimization was also carried out before running the simulations [44,46]. The Maxwell-Boltzmann distribution [46] was used to create the initial velocity distribution of the molecules. For the Lennard-Jones and long-range nonbonded electrostatic interactions, 10 Å was defined as the cut-off radius to ensure less than half the smallest size in the three dimensions of the simulation box. The simulation was handled with the method of Ewald [47] with a relative error of 10⁻⁶ for the long-range electrostatic interactions. Using the SHAKE [48,49] algorithm, the simulation was constrained to the bond length and angle of H₂O molecules. The timestep was assigned to be 0.5 fs to calculate the nonbonded interactions. The Nose-Hoover thermostat and barostat with a relaxation time of 1 ps were also applied to control temperature and pressure while running the simulation. The simulations were run initially under NVT for a 0.5 ns ensemble before switching to an NP_zT ensemble with a 5 ns to ensure the obtained density values from the simulation near the value of the experimental data's NIST database [50]. Specifically, the NP_zT ensemble was used to modify the length of the simulated box in the z-direction only, and the x-length and the y-length were kept unchanged [45,46]. In the second step for predicting interfacial tension, a rectangular simulation box

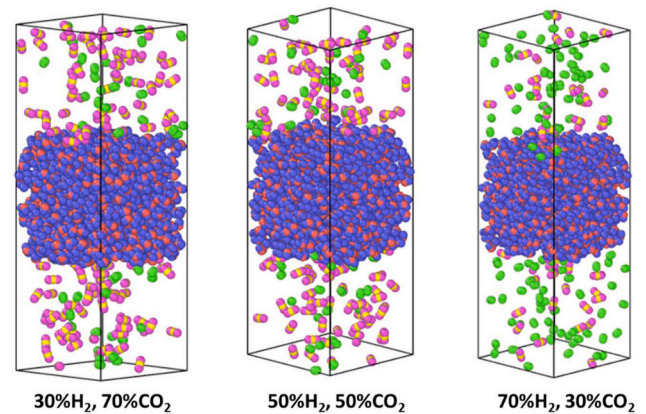


Fig. 4. An illustration of varying mole fractions of H₂ and cushion gas (CO₂).

merged with water in the middle and a mixture of cushions gas (CO₂ N₂ or CH₄) and H₂ gas on both sides, as displayed in Fig. 4. The system equilibrated at the desired pressure and temperature for 5.5 ns under the NVT ensemble. Data was collected at the remaining 5 ns of simulation as a production stage for interfacial tension prediction.

2.3. Interfacial tension

The interfacial tension (γ) can be obtained for the H₂O and mixture of cushion gas in the presence of H₂ as in equation (5).

$$\gamma = \gamma_{sim} + \gamma_{tc} \quad (5)$$

where γ_{sim} is the interfacial tension calculated from simulation by employing Kirkwood's mechanical method [51], as described in equation (6)

$$\gamma_{sim} = \frac{L_z}{2} \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) \quad (6)$$

where L_z is the length of the simulated system along the z-axis, and the three components of tensor pressure along the x-direction, y-direction and z-direction were defined as P_{xx} , P_{yy} and P_{zz} .

γ_{tc} is the tail correction applied by following the Sun's approach [52] to calculate the impacts of truncating intermolecular potentials.

Table 3

Predicted $\gamma(\text{H}_2\text{-CO}_2\text{-H}_2\text{O})$, $\gamma(\text{H}_2\text{-N}_2\text{-H}_2\text{O})$ and $\gamma(\text{H}_2\text{-CH}_4\text{-H}_2\text{O})$ at different pressure and temperature. The standard error is displayed in parentheses.

Temperature (K)	Pressure (MPa)	Interfacial tension, γ (mN/m)		
		$\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$	$\text{H}_2\text{-CH}_4\text{-H}_2\text{O}$	$\text{H}_2\text{-N}_2\text{-H}_2\text{O}$
300	1	62.9 (0.6)	64.4 (0.5)	64.0 (0.5)
	5	61.8 (1.0)	63.0 (0.5)	62.2 (0.4)
	10	59.5 (0.5)	62.6 (0.8)	62.4 (0.7)
	20	57.5 (1.0)	60.6 (0.9)	61.1 (0.9)
	30	53.1 (0.8)	60.2 (1.2)	60.5 (0.4)
	50	49.8 (1.0)	59.9 (1.1)	59.3 (0.7)
323	70	45.9 (1.1)	59.4 (1.0)	59.5 (0.6)
	1	59.1 (0.7)	60.5 (0.9)	60.3 (0.4)
	5	56.5 (1.0)	60.2 (0.7)	59.7 (0.5)
	10	55.6 (0.5)	59.2 (0.6)	59.9 (0.6)
	20	54.4 (1.0)	56.9 (0.8)	58.9 (1.1)
	30	52.1 (0.7)	56.6 (0.9)	58.4 (0.7)
343	50	45.6 (1.0)	57.0 (0.3)	57.9 (0.5)
	70	45.8 (0.7)	57.1 (0.6)	56.5 (0.5)
	1	58.6 (1.0)	56.8 (0.3)	57.3 (0.4)
	5	54.5 (0.2)	56.6 (0.3)	57.2 (0.3)
	10	53.4 (0.6)	57.0 (0.2)	56.4 (1.0)
	20	52.0 (1.1)	56.8 (0.2)	55.8 (1.0)
343	30	49.8 (1.1)	54.6 (0.6)	55.5 (0.6)
	50	46.7 (0.8)	55.2 (0.5)	54.6 (1.1)
	70	42.2 (1.1)	54.2 (0.8)	55.4 (0.6)

3. Results and discussion

3.1. Interfacial tension as a function of pressure and temperature

The interfacial tension of $\text{H}_2\text{-CO}_2\text{-H}_2\text{O}$, $\text{H}_2\text{-N}_2\text{-H}_2\text{O}$, and $\text{H}_2\text{-CH}_4\text{-H}_2\text{O}$ in different conditions of temperatures from 300 K to 343 K and pressure from 1.0 MPa to 70 MPa are reported in Table 3. The mole fracture of mixture gas was decided to select a ratio of 70:30 mol for $\text{H}_2\text{:CO}_2$, $\text{H}_2\text{:N}_2$ and $\text{H}_2\text{:CH}_4$, because this ratio is similar to that

performed in previous experimental studies ([28], Isfehiani et al., 2023). However, there is unavailable experiment data for comparing with the results of the $\text{H}_2\text{-N}_2\text{-H}_2\text{O}$ system, so the experimental values from $\text{H}_2\text{/H}_2\text{O}$ [11,28] and $\text{CO}_2\text{/N}_2\text{/H}_2\text{O}$ [53,54] were used for comparison purposes.

$\gamma(\text{H}_2\text{-CO}_2\text{-water})$, as a function of pressure and temperature, is displayed in Fig. 5. Simulated outcomes indicated a similar trend to the experimental data ([28]; Isfehiani et al., 2023). The γ at temperatures 300 K and 323 K are lower than the experimental data by around 12 % when the pressure is below the critical pressure of CO_2 (or less than 7.6 MPa). In contrast, the degree of agreement was improved as increasing pressure was higher at 7.6 MPa. The γ data at elevated pressure (over 50 MPa) are likely constant or altered very slightly, revealing no or minor dependence on temperature.

$\gamma(\text{H}_2\text{-N}_2\text{-water})$ was found to generally decrease with increasing pressure and temperature, as displayed in Fig. 6, demonstrating agreement with experimental values of the $\text{H}_2\text{/water}$ [28] and the $\text{CO}_2\text{/N}_2\text{/water}$ system [53,54]. Specifically, the simulated results are less than $\text{H}_2\text{/water}$ caused by presenting N_2 molecules and higher than the $\text{CO}_2\text{/N}_2\text{/water}$ due to the presence of H_2 in the system. However, at fixed temperatures (300 K, 323 K and 343 K), the reduction rate of the γ ($\text{N}_2\text{-H}_2\text{-water}$) is lower than the $\text{H}_2\text{-CO}_2\text{-water}$ system, which can be explained due to the density of CO_2 being heavier than the density of N_2 . Furthermore, when pressure increases above 30 MPa, the γ data tends to be unchanged or constant.

$\gamma(\text{H}_2\text{-CH}_4\text{-water})$ reported that it decreased with increasing both temperature and pressure, Fig. 7. The γ is an analogous trend in comparison to the experiment and simulation data of $\gamma(\text{CH}_4\text{-H}_2\text{O})$ and $\gamma(\text{H}_2\text{-H}_2\text{O})$. However, the γ values are lower than the system of $\text{H}_2\text{/H}_2\text{O}$ [11,28] at a fixed temperature or pressure. The lower γ values are caused by the presence of CH_4 molecules in the mixture gas, which increases the density of CH_4 molecules at the interface. In contrast, when pressure is over 10 MPa, the simulation values of the $\text{H}_2\text{-CH}_4\text{-water}$ system are higher than the $\text{CH}_4\text{-water}$ system in presenting H_2 molecules in the

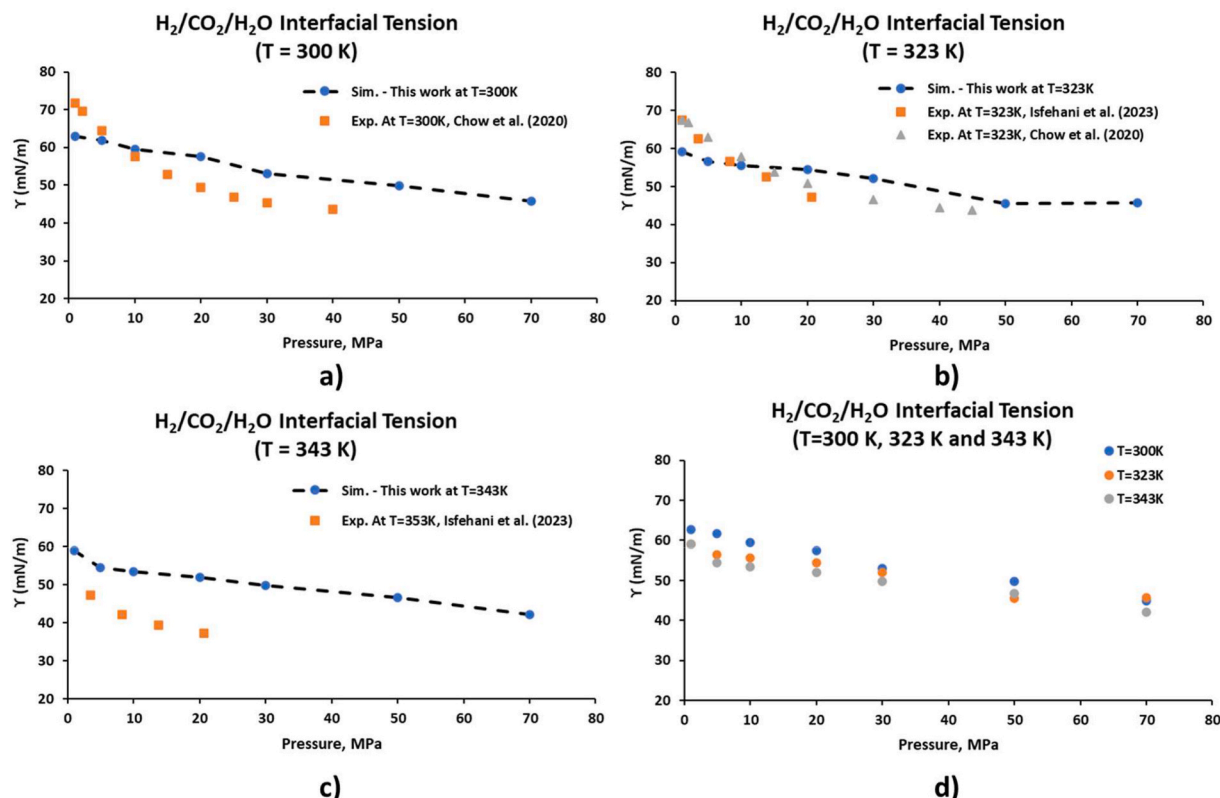


Fig. 5. Pressure dependence of $\gamma(\text{H}_2\text{-CO}_2\text{-H}_2\text{O})$: (a) at $T = 300$ K, (b) at $T = 323$ K, (c) at $T = 343$ K and (d) Comparison at different temperature conditions.

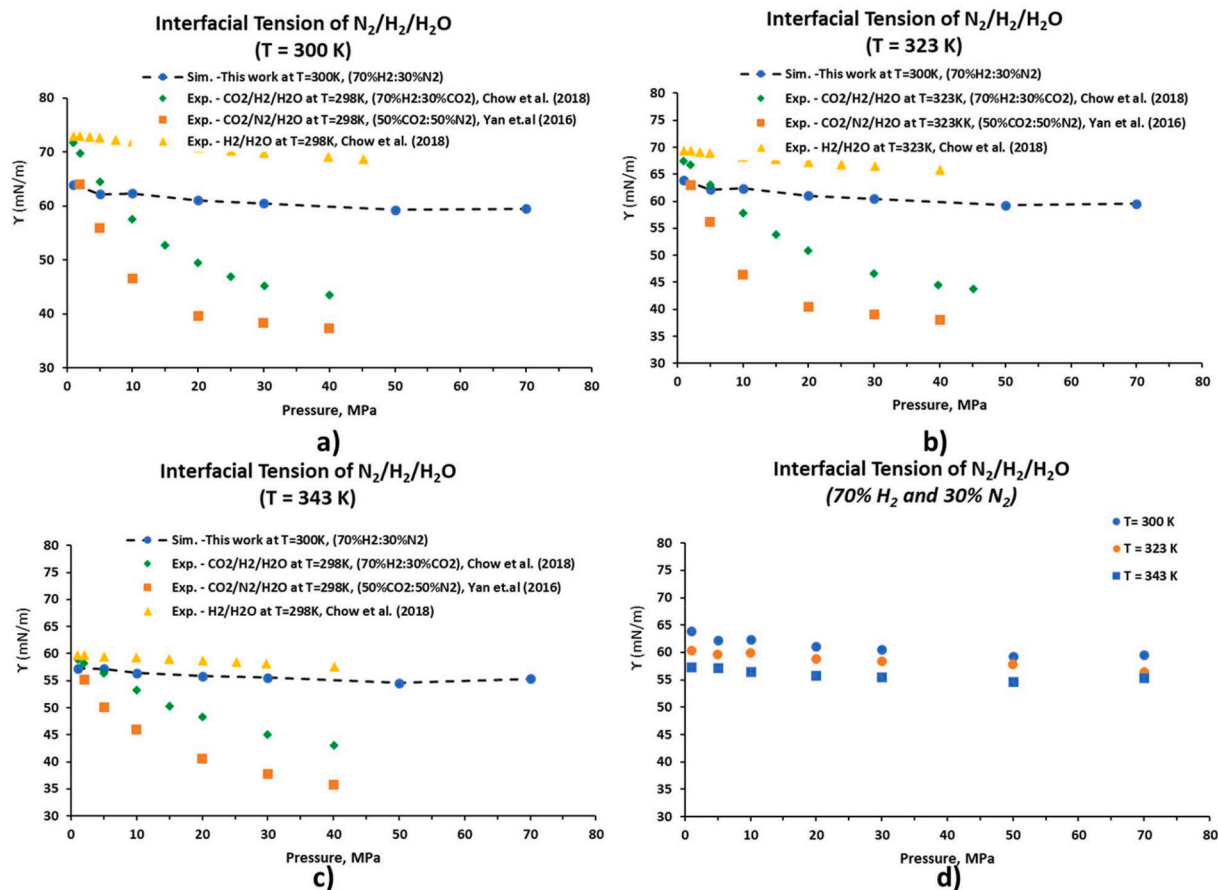


Fig. 6. Pressure dependence of $\gamma(H_2-N_2-H_2O)$: (a) at $T = 300$ K, (b) at $T = 323$ K, (c) at $T = 343$ K and (d) Comparison at different temperatures.

mixture gas. The cause is that the intermolecular interaction of CH_4 molecules with H_2O at the interface [55] is more substantial than H_2 with H_2O . In addition, the γ data tends to be changed slightly or unchanged when pressure increases above 30 MPa.

3.2. Interfacial tension as a function of the fraction of cushion gases (CO_2 , N_2 and CH_4)

The interfacial tension of $H_2-CO_2-H_2O$, $H_2-N_2-H_2O$, and $H_2-CH_4-H_2O$ in varying fractions at t conditions of 300 K and 10 MPa are reported in Table 4. The mole fraction of H_2 changed from 10 % to 90 % in the mixture gas, including CO_2 or N_2 or CH_4 . While only the H_2-CO_2 -water system is available experimental data [17,28] for comparison, both the $H_2-N_2-H_2O$ and $H_2-CH_4-H_2O$ are unavailable literature in the experiment and simulation. So, the γ experiment data of the CO_2/H_2O [56], N_2/H_2O [54], CH_4/H_2O [57] and H_2/H_2O [28] systems were used as compared data.

Fig. 8 indicates the γ of the ternary systems of H_2/CO_2 /water, H_2/CH_4 /water, and H_2/N_2 /water increase with increasing the fraction of H_2 in the mixture gas. The simulated γ ($H_2/CO_2/H_2O$) is a similar trend in comparison with earlier reports 16,17,28. Specifically, the simulated γ ($H_2/CO_2/H_2O$) with 70 % H_2 showed excellent agreement with experimental data [28] by about 3 %. For the $N_2-H_2-H_2O$, the γ values are lower than the H_2/H_2O [28] and higher than the N_2/H_2O [54]. In contrast, the γ values ($CH_4-H_2-H_2O$) are lower than the H_2/H_2O [28] and higher than the CH_4/H_2O [57]. Furthermore, the simulated results indicated that the $\gamma(H_2/CO_2/H_2O)$ increase rate is higher than the $H_2-N_2-H_2O$ and $H_2-CH_4-H_2O$ systems. At the fixed fraction of H_2 , the simulated values of CO_2 are the lowest to compare with the other systems. This outcome can be caused by decreasing the amount of CO_2 molecules at the interface when increasing the presence of Hydrogen in

the mixture. Furthermore, the outcomes from investigating the effects of increasing the percentage of cushion gas indicated that the interfacial tension at a low concentration of H_2 in the earlier injection stage is low (especially in the case of cushion gas is CO_2), which likely causes the injected H_2 at depleted reservoirs to escape through the caprock. The findings from simulation works validated and confirmed previous experimental studies [12,16,28]. Hence, the injection scheme for UHS suggests attention to selecting a proper ratio of cushion gas and H_2 to be safe and more efficient for large-scale implementation of Underground Hydrogen Storage.

The γ of ternary systems of $H_2/CO_2/H_2O$, $H_2/CH_4/H_2O$, and $H_2/N_2/H_2O$ decrease with increasing pressure and temperatures and increase with increasing $H_2\%$ in the mixture. At constant pressure, the $H_2/N_2/H_2O$ system showed the highest γ value, while the $H_2/CO_2/H_2O$ system received the lowest γ value. This outcome is explained by increasing the quantity of molecules adsorbed (or intermolecular forces) at the interface [55]. At a fixed temperature, the γ value of $H_2/CO_2/H_2O$ needs lower pressure to reach an unchanged or plateau for comparison to the γ value of $H_2/CH_4/H_2O$ and $H_2/N_2/H_2O$ due to the number of adsorptions of CO_2 molecules increase at the surface, higher when compared with N_2 or CH_4 [55]. Hence, the simulated result recommends that N_2 offers an appropriate selection for cushion gas with higher interfacial tension than CO_2 and CH_4 . This also aligns with the research by Ref. [58] to improve reservoir support and efficiency for implementing UHS.

Here, the extended and new γ ($H_2/CO_2/H_2O$, $H_2/CH_4/H_2O$, and $H_2/N_2/H_2O$) results from this work were carried out at a pressure from 1.0 MPa to 70 MPa and at different temperatures of 300 K, 323 K and 343 K and under various $H_2\%$ or cushion. The outcomes indicated the same trend in comparison with earlier experiments. However, there is a lack of data available on the systems of $CO_2-H_2-H_2O$ and $CH_4-H_2-H_2O$ and no data on $N_2-H_2-H_2O$ to validate the predicted outcomes and

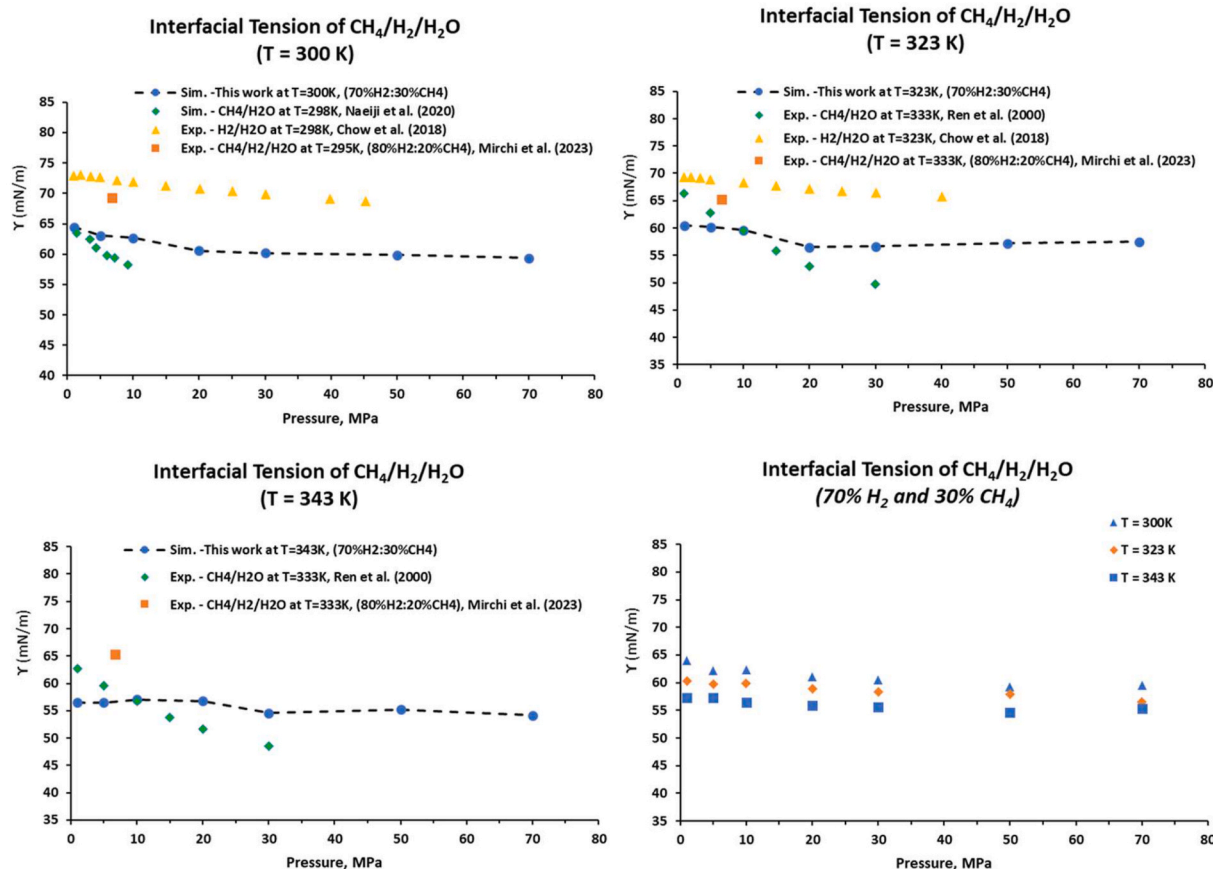


Fig. 7. Pressure dependence of γ ($\text{H}_2\text{-CH}_4\text{-H}_2\text{O}$): (a) at $T = 300\text{ K}$, (b) at $T = 323\text{ K}$, (c) at $T = 343\text{ K}$ and (d) Comparison at different temperature conditions.

Table 4

Predicted γ ($\text{H}_2\text{-CO}_2\text{-water}$), γ ($\text{H}_2\text{-N}_2\text{-water}$) and γ ($\text{H}_2\text{-CH}_4\text{-water}$) as a function of the fraction of cushion gases (CO_2 , N_2 and CH_4). The standard error is displayed in parentheses.

H_2 Mol, %	γ , mN/m ($P = 10\text{ MPa}$ and $T = 300\text{ K}$)		
	$\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$	$\text{CH}_4/\text{H}_2/\text{H}_2\text{O}$	$\text{N}_2/\text{H}_2/\text{H}_2\text{O}$
10	51.0 (0.9)	60.2 (0.3)	61.7 (0.7)
30	55.0 (1.0)	61.2 (1.1)	61.9 (0.4)
50	57.7 (0.6)	61.4 (0.8)	62.0 (0.9)
70	59.5 (0.5)	62.6 (0.8)	62.5 (0.7)
90	63.0 (0.3)	63.5 (0.7)	64.4 (1.0)

significant alterations between this work's simulation data and former experimental data. Furthermore, the difference in the γ values from simulation and experiment data can be caused by choosing forefield models [59], employing a combining rule from the Lorentz-Berthelot [60] and the size of the simulation box (Li et al., 2013). In addition, results indicated a gap difference between the predicted γ and experiment data can be caused by finite size effects when pressure is low (or a small number of H_2 molecules in the system).

4. Summary and conclusions

The interfacial tension (γ) of water and a mixture of cushion gas such as CO_2 , N_2 , or CH_4 in the presence of H_2 under different geo-storage conditions is vital for evaluating the storage capacity and containment security of H_2 in geo-storages. This study was conducted to fill gaps of very limited or unavailable data in experiments and simulations to investigate Hydrogen's effects when exposed to cushion gas.

1. Molecular dynamics simulations were conducted to predict interfacial tension (γ) for various ternary ($\text{CO}_2\text{-H}_2\text{-H}_2\text{O}$, $\text{N}_2\text{-H}_2\text{-H}_2\text{O}$, and $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$) systems at different temperatures (300 K, 323K, and 343 K) and a range of pressure from 1.0 to 70 MPa and varying concentration of cushion gas from 10 % to 90 %.
2. The γ values of $\text{CO}_2\text{-H}_2\text{-H}_2\text{O}$, $\text{N}_2\text{-H}_2\text{-H}_2\text{O}$, and $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ systems, as a function of pressure and temperature, decreased as increasing pressure and temperature. At fixed temperatures (300K, 323K, and 343K), the reduction rate of the γ ($\text{N}_2\text{-H}_2\text{-water}$ and $\text{CH}_4\text{-H}_2\text{-water}$) is lower than the $\text{CO}_2\text{-H}_2\text{-water}$ system. At the fixed pressure, the γ ($\text{CO}_2\text{-H}_2\text{-water}$ system) is the lowest compared to the other systems. In addition, at high pressure (above 30 MPa), the γ data tends to be changed slightly or unchanged.
3. The γ values, as a function of H_2 fraction, increased with increasing the fraction of H_2 in the mixture gas. At the fixed fraction of H_2 , the γ ($\text{N}_2\text{-H}_2\text{-water}$ and $\text{CH}_4\text{-water}$) is higher than the $\text{CO}_2\text{-H}_2\text{-water}$ system.
4. The findings noted that selecting a fraction of cushion gas (in the case of CO_2) with H_2 at the initial injection period is vital to avoid the risk of the injected H_2 escaping via the caprock. Furthermore, the cushion gas with N_2 is a reasonable selection to compare with CO_2 and CH_4 to improve reservoir support and minimize risk for implementing UHS.
5. It suggests further study on different force fields and simulation box sizes to select a proper setup or configuration (especially at low pressure) to improve the difference γ between simulation and experiment data. Furthermore, further research and development should investigate which ratio of cushion gas and the injected H_2 during the injection and withdrawal process are suitable, efficient, and safe for large-scale implementation of UHS.

This study's results deliver extending or new γ data in simulation for

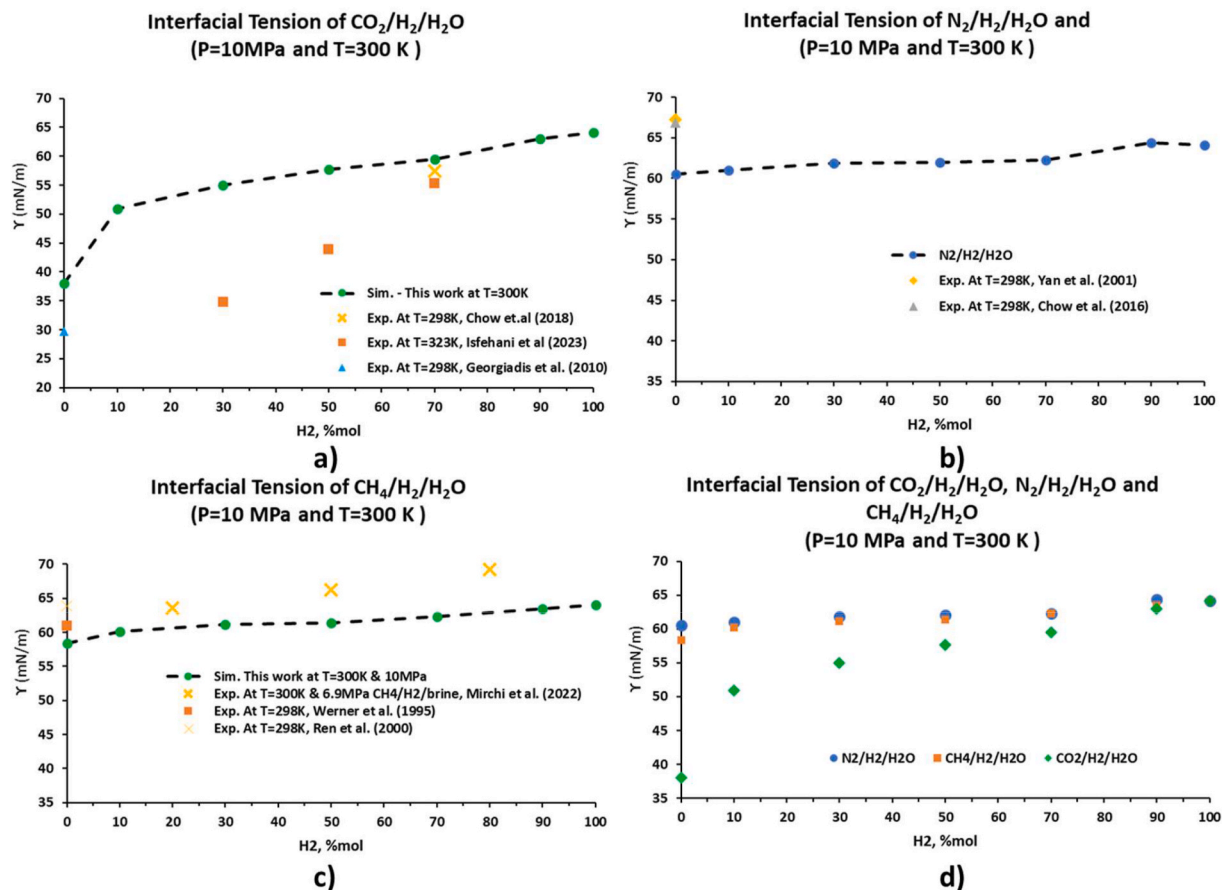


Fig. 8. γ as a function of the fraction of cushion gases (CO₂, N₂ and CH₄) at T = 300 K for (a) H₂-CO₂-H₂O system, (b) H₂-N₂-H₂O, (c) H₂-CH₄-H₂O and (d) Comparison at different temperature conditions.

the CO₂/H₂/H₂O, N₂/H₂/H₂O and CH₄/H₂/H₂O systems under different geo-storage conditions. This research contributes to understanding the flow characterization and fluid behaviour in the presence of H₂ and cushion gas at reservoir conditions for selecting and designing the proper schemes of injection and withdrawal. Furthermore, it can strongly contribute to de-risking and proceeding safely and efficiently at depleted hydrocarbon reservoirs for the large-scale implementation of Underground Hydrogen Storage.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Stefan Iglauer reports financial support was provided by Australia Research Council's Discovery Projects funding scheme (project DP220102907). Quoc Truc Doan reports financial support was provided by Bear and Brook Consulting.

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Nomenclature

CCS Carbon Capture and Storage
EPM2 Elementary Physical Models

LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
MD Molecular Dynamics
NVT Canonical Ensemble
NPT Isothermal-isobaric Ensemble
NIST National Institute of Standard and Technology
IFF Interface Force Field
OPLS Optimised Potentials for Liquid Simulations
OVITO Open Visualization Tool
P Pressure
P_c Capillary Pressure
T Temperature, Absolute
TIP4P/2005 Transferable Intermolecular Potential with Four Points for Water
UGS Underground Gas Storage
UHS Underground Hydrogen Storage

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