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Determination of interfacial tension for H₂-H₂S-water and CH₄-H₂S-water mixtures under different geological conditions for underground hydrogen storage

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Abstract

Hydrogen, a renewable energy source, is expected to see steadily increasing production to meet global net-zero targets. Depleted hydrocarbon reservoirs, with their large storage capacity, offer a promising solution for large-scale underground hydrogen storage (UHS). Stored hydrogen (H₂) and cushion gases (e.g., CH₄) may coexist with residual hydrogen sulfide (H₂S) or H₂S generated locally through geochemical reactions or microbial activity. As gas composition significantly influences the interfacial tension (IFT) between gas and pore water, the distribution and dynamics of H₂ and CH₄ in depleted reservoirs are affected by H₂S under reservoir conditions. This study presents newly determined IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures at 298 K and 343 K with pressures

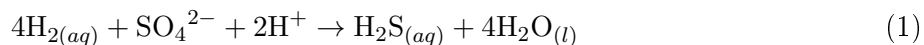
ranging from 10 to 30 MPa using molecular dynamics (MD) simulations. Results reveal that IFT decreases with increasing pressure, temperature, and H_2S concentration, with distinct mechanisms driving these variations. Notably, even small amounts of H_2S (e.g., 10 mol%) significantly reduce IFT, underscoring its critical role in gas-water interactions. With simulated IFT data, two regression models are developed to predict the IFTs of H_2 - H_2S -water and CH_4 - H_2S -water mixtures under geological conditions. This study provides comprehensive IFT expressions for CH_4 - H_2S -water and H_2 - H_2S -water mixtures and offers insights into the mechanisms underlying IFT variations for UHS applications.

1. Introduction

The development and utilization of renewable energy resources are important in the global energy transition and future decarbonization. It is reported that approximately 20–30 % of the world’s energy may come from renewable energy resources around 2040 [1,2]. Green hydrogen, as a renewable energy resource with comparatively low carbon emissions, high energy density, and wide applications in petrochemical feedstocks, will play an important role in the future energy system. As H_2 demand and production increase annually, up to 500–600 Mt. may eventually be required for different applications including transport, refining, industry, and buildings [3]. A challenge arises that such a large demand and production of H_2 would require large-scale storage options as buffer for any mismatch. Underground porous media such as depleted hydrocarbon reservoirs may have sufficient pore space to provide a solution for underground hydrogen storage (UHS) [4]. At almost the same per-unit cost, UHS could provide a larger capacity for H_2 storage than surface storage technologies like cryogenic or high-pressure tanks [5]. For example, in comparison, the storage capacity of depleted hydrocarbon reservoirs could be as high as 1 billion Nm^3 , whereas cryogenic or high-pressure tanks could only reach up to approximately 9 million Nm^3 in maximum [5–7]. In addition to providing such large-scale storage, depleted hydrocarbon reservoirs often have existing infrastructure and proven caprock integrity [4]. Hence, they present attractive options for consideration of UHS [8,9].

When applying UHS in a depleted hydrocarbon reservoir, it may be necessary first to inject a cushion gas (e.g. CH_4) to maintain the reservoir pressure [10,11], before injecting the H_2 working gas. During the storage process, a possible safety and quality issue is hydrogen sulfide (H_2S) which

could be generated locally by geochemical (abiotic) or biological (biogenic) interactions [12,13]. For example, abiotic H_2S could be generated from rocks commonly found in hydrocarbon reservoirs like anhydrite (CaSO_4) and pyrite (FeS_2). Water-rock interactions could produce H_2S directly [14] or a variety of sulfur-based compounds including sulphates (SO_4^{2-}), thiosulfates ($\text{S}_2\text{O}_3^{2-}$), and elemental sulfur (S) [15,16], which in turn can then be biologically reduced to H_2S by microorganisms with the presence of H_2 [17,18], as given by Eq. (1):



Similarly, CH_4 as a cushion gas for UHS, or generated locally by methanogens, could react with CaSO_4 to form H_2S [14]. The generated H_2S could cause unwanted side effects such as souring, corrosion, or stress-cracking of steel. Furthermore, H_2S in local pore spaces can affect the interfacial tension (IFT) between gas mixtures (H_2/CH_4) and residual pore water, and hence their distribution in the reservoir [19,20]. Thus, it is important to determine the IFT between pore water with gas mixtures of H_2 - H_2S and CH_4 - H_2S under geological conditions.

The effect of H_2S as an impurity species on gas-water IFT has been investigated in recent years in the context of both UHS, carbon dioxide capture and sequestration (CCS) and other acid gas geo-storage. For example, Shah et al. [21] used the pendant drop method to determine the IFTs between water with a mixture of CO_2 and H_2S at 77°C with pressures up to 15.6 MPa. Their result shows that 30 mol% H_2S with CO_2 decreases the water- CO_2 IFT and thus capillary failure would be enhanced during CO_2 geological storage if the injected gas is enriched in H_2S . Direct experimental measurement of the IFT involving H_2S species is challenging due to safety, corrosion and toxicity risks. Theoretical models combined with an Equation of State (EoS) have been an alternative method for IFT determination of H_2S systems. However, prior studies have mainly focused on IFT between pure H_2S and water under different pressure and temperature conditions. For instance, Shah and Broseta [22], Khosharary and coworkers [23] applied the gradient theory in conjunction with the PR-EoS and SAFT-EoS respectively to determine the H_2S -water IFT at temperatures up to 398 K and pressures up to 60 MPa.

In addition to theoretical models, computational approaches of molecular simulation such as Monte Carlo (MC) and Molecular Dynamics (MD) have also been used to determine the H_2S -water

and H₂S-brine IFTs at temperatures from 323 to 393 K and pressures up to 30 MPa [24–26]. In a notable study by Ofori et al. [24], molecular behaviors at the H₂S-water interface under different pressure and temperature conditions were investigated using MD simulations. They found that H₂S molecules would adsorb at the interface when below their saturation pressure, while absorbing into the water phase above the threshold pressure. To study the effect of H₂S as an impurity on CO₂-water IFT for CO₂ sequestration in aquifers, Chen et al. determined the IFT between water with a mixture of CO₂ and H₂S at 318 K and 20 MPa using MD simulations [27]. Their results show that 20 mol% H₂S had an outsized impact, reducing the CO₂-water IFT by 65 %. Focusing on IFT variations between water and H₂/CH₄ with H₂S generated from microorganism activity during UHS, Chang et al. [19] used MD simulations to develop IFT expressions of H₂-H₂S-water and CH₄-H₂S-water systems under geological conditions of 343 K and 14.5 MPa. The accumulation of H₂S at the H₂-water and CH₄-water interface was observed based on density distribution profiles, and this led to an IFT reduction between H₂-water and CH₄-water.

It is known that the IFT between gas-pore water in local pore spaces varies with the local pore pressure/temperature and the amount of H₂S generated. Our previous study determined the IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures with different amounts of H₂S for UHS at 343 K and 14.5 MPa. This subsequent study focuses on IFT determination over a wider range of pressure and temperature conditions. The preliminary results we presented at the Society of Petroleum Engineers (SPE) conference [28] validated pressure and temperature effects on the IFT of H₂-H₂S-water and CH₄-H₂S-water mixtures. Therefore, this study focuses on extending IFT estimation of H₂-H₂S-water and CH₄-H₂S-water mixtures to a wider range of geological conditions for UHS. Here, IFTs of H₂-water and CH₄-water with 10–40 mol% H₂S are newly determined under 298 K and 343 K with pressures from 10 to 30 MPa. In addition, the fundamental mechanism behind the pressure/temperature-dependence of IFT is investigated.

The manuscript is organized as follows: Section 2 introduces the methodology and details of the MD simulation. In Section 3, validation cases for the MD simulations are firstly introduced. Then, IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures under different P/T conditions are reported via MD simulations. This is accompanied by a study of the physical mechanisms underpinning their variation. The IFT regression models with limitations are also finalized in this section. Conclusions are summarized in Section 4.

2. Methodology

Molecular dynamics simulation was used in this study for IFT calculations because it has accurately determined the IFTs of gas-water mixtures involving H_2 , CH_4 , H_2S , and water under geological conditions [24,26,29–34]. We used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) for all MD simulations [35]. The gas-water interfacial model we built in our previous paper [19] was also used in this study, where the water phase was sandwiched between two gas mixtures, as shown in Fig. 1. The water phase consisted of 2048 water molecules, while the gas mixture contained 1024 molecules in total. As the composition shown in Table 1, the gas mixture consisted of H_2S with H_2 or CH_4 separately in different H_2S concentrations, from 0 mol% to 40 mol%.

To describe the molecular potential, the F3C and Vrabec single-site force fields were used for H_2O and H_2 respectively. The TraPPE-UA force field was used for CH_4 and Nath’s force field was applied for H_2S [36–39]. The accuracy of these force fields has been validated in the IFT calculation of similar systems [19,26,32,37]. The particle-particle particle-mesh (PPPM) method was employed to calculate Coulombic interactions with a precision of 1×10^{-5} , and the 12–6 Lennard-Jones (LJ) potential was utilized for describing non-bonded interactions. Lorentz-Berthelot combining rules were used to describe the cross LJ parameters between different molecules through Eq. (2) and (3) with force field parameters listed in the Table 2, where ε and σ are the depth of the potential well and finite distance with zero potential, respectively.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (3)$$

To minimize truncation and system-size effects in calculating interfacial properties, the cutoff distances for the LJ potential and Coulombic interactions were set to 15 Å (approximately 4σ), ensuring they remained less than half the minimum dimension of the simulation box [33,40,41]. Periodic boundary conditions (P-P-P) were applied during the simulation.

For $(\text{H}_2\text{S} + \text{H}_2)/\text{water}$ and $(\text{H}_2\text{S} + \text{CH}_4)/\text{water}$ systems with different H_2S concentrations, the initial simulation box was set to be $3.4 \text{ nm} \times 3.4 \text{ nm} \times 10 \text{ nm}$ using the Packmol package [42].

System pressures were simulated in the range of 10 to 30 MPa, corresponding to UHS operating pressure conditions [6]. For temperature conditions, UHS is normally implemented at depths of up to 1000 m [4,43]. With a geothermal gradient of approximately 0.04 K/m, UHS operating temperatures range from 323 to 343 K [4,43], consistent with the temperature range of 298–343 K reported in previous UHS-related studies (listed in Table S1). Furthermore, it has been reported that optimal temperatures for the activity of H₂S-generating bacteria, such as sulfate-reducing bacteria, are typically below 323 K [44–46]. Therefore, considering both the typical UHS operating conditions and the temperature range in which H₂S-generating bacteria are most active, two temperatures, 298 K and 343 K, were simulated.

The system was initialized with a 1-ns run within the NVT ensemble to avoid molecular overlap. Then, a 16-ns run under the NPzT ensemble was applied for the system to reach its equilibrium state. Finally, the IFT (γ) was determined by averaging trajectories from the convergent state of another 20-ns production run under the NP_zT ensemble, through the well-known Gibbs IFT method [47–50]:

$$\gamma = -\frac{1}{2} \left(\frac{P_{xx} + P_{yy}}{2} - P_{zz} \right) L_z \quad (4)$$

where L_z is the length of the simulation box in the Z direction, while P_{xx} , P_{yy} , and P_{zz} are the respective diagonal components of the pressure tensor. The constant factor of $\frac{1}{2}$ comes from the two distinct interfaces within the system as shown in Fig. 1.

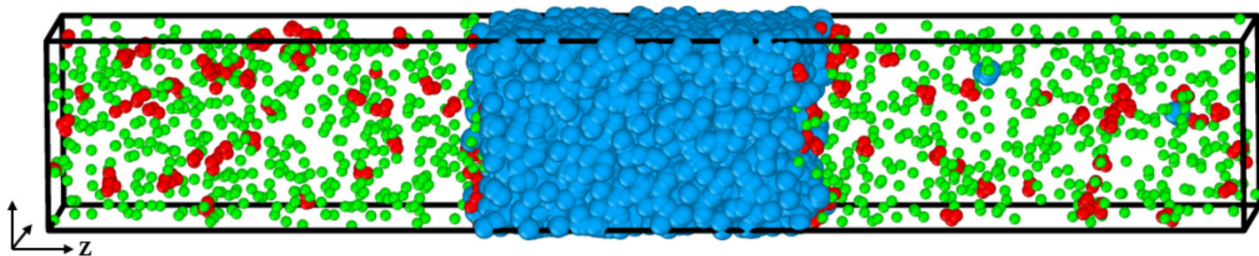


Fig. 1. Gas-water interfacial model, (H₂ + H₂S)/water system with 10 mol% H₂S as an example, red: H₂S molecule, green: H₂ molecule, and blue: water molecule.

Table 1Gas composition in (H₂S + H₂)/water and (H₂S + CH₄)/water systems separately.

H ₂ S mole %	No. of H ₂ S molecules	No. of H ₂ (or CH ₄) molecules
0	0	1024
10	103	921
20	205	819
30	307	717
40	410	614

Table 2

Force field parameters for each species.

Atoms	ε (kcal•mol ⁻¹)	σ (Å)
H (H ₂ O)	0.01	0.82
O (H ₂ O)	0.1848	3.166
H(H ₂ S)	0.0077	0.98
S(H ₂ S)	0.4968	3.72
H ₂	0.0679	2.96
CH ₄	0.2941	3.73

3. Results and discussion

3.1. IFT determination

Before the IFT determination of H₂-H₂S-water and CH₄-H₂S-water mixtures, a series of fundamental calculations were first completed to validate the molecular model, force field, computational method, and interface system used in this study. At 343 K and 14.5 MPa, validations from our previous study [19] including the bulk densities and IFTs of H₂-H₂O, CH₄-H₂O, and H₂S-H₂O agreed well with the experimental data. Here, in addition to our previous validation [19], the bulk densities and IFTs of H₂-H₂O, CH₄-H₂O, and H₂S-H₂O mixtures at 298 K and 343 K with pressures from 10 to 30 MPa were calculated and compared with the experimental data for further validation.

We validated the IFTs of pure gas-water systems involving these species but not their gas mixture-water system directly because no experimental IFT results of such H_2 - H_2S - H_2O and CH_4 - H_2S - H_2O mixtures have yet been reported. In addition, the local density profile of the molecules could be used to study molecular distribution in bulk and interface regions, which is useful for exploring fundamental mechanisms of IFT variation. This is the reason why, besides IFT validation, a series of density checks of related species under the investigated geological conditions were developed.

In detail, the bulk fluid system of H_2 , CH_4 , H_2S , and H_2O was constructed individually as shown in Fig. 2(a) to validate their bulk densities. For the IFT calculation of H_2 - H_2O , CH_4 - H_2O , and H_2S - H_2O , the interfacial model introduced in Sec. 2 was used, consisting of 2048 water molecules and 1024 gas molecules separately, pure H_2 -water interfacial system shown as an example in Fig. 2(b).

Fig. 3 shows good agreement between bulk densities of H_2 , CH_4 , H_2S , and H_2O determined from our MD simulations and values reported from the National Institute of Standards and Technology (NIST) database [51]. The relative deviations of these simulated densities from NIST data range from 0.3 % to 6 %. The IFTs between H_2 - H_2O , CH_4 - H_2O , and H_2S - H_2O were determined and compared with available data in Fig. 4, also showing good consistency. For example, the relative deviations of the simulated IFTs from experimental results are within approximately 7 %, falling within the deviation range of 5 % to 20 % reported before [52]. It is noted that since limited experimental data has been reported for H_2S - H_2O IFTs, only IFTs at 343 K with two geological pressures were used for validation. This exercise gives us confidence in the reliability of the molecular model, force field, computational methodology, and gas-water system to explore different IFT values of H_2 - H_2S -water and CH_4 - H_2S -water mixtures.

With the validated MD simulation, IFTs were determined for H_2 - H_2S -water and CH_4 - H_2S -water mixtures at 298 K and 343 K with pressures of 10 MPa, 14.5 MPa, 22.5 MPa, and 30 MPa (Table 3 and Table 4). In subsequent sections, these IFTs are depicted versus temperature, pressure, and H_2S concentration.

3.2. Temperature effect on IFT

IFTs of H_2 - H_2S -water and CH_4 - H_2S -water mixtures as a function of H_2S concentration (mol%) at 298 K and 343 K are shown in Fig. 5 and Fig. 6, respectively. The results show that IFT

193 between water with H_2 - H_2S and CH_4 - H_2S mixtures decreases with H_2S concentration increases in
 194 all P/T conditions. This is because as the H_2S concentration in the gas mixture increases, more H_2S
 195 accumulates at the gas-water interface, yielding a continuous reduction in IFT [19]. It is notable that
 196 even relatively low concentrations of H_2S affect the IFTs of H_2 -water and CH_4 -water. For example,
 197 under simulated P/T conditions, a 10 mol% H_2S results in an IFT reduction for both H_2 -water and
 198 CH_4 -water, ranging from approximately 7 mN/m to 14 mN/m. While, at a higher concentration,
 199 e.g. 40 mol%, the IFT reduction increases significantly, ranging from 31 mN/m to 49 mN/m. These
 200 results emphasized that in-situ generated H_2S in pore space has an important effect on gas-water
 201 IFT under geological conditions.

202 In addition, the results in Fig. 5 clearly show that under the same pressure condition, the
 203 IFT between H_2 -water with the same amount of H_2S at 298 K is larger than that at 343 K. A
 204 similar temperature effect on the IFT of CH_4 - H_2S -water mixtures was also observed in Fig. 6. Such
 205 temperature effect on IFTs between H_2 -water, CH_4 -water, and H_2S -water was reported by Hosseini
 206 et al., Chow et al., Schmidt et al., and Shah et al. [21,53,56,57]. However, the differences in IFTs for
 207 both H_2 - H_2S -water and CH_4 - H_2S -water mixtures between 298 K and 343 K are not significant, all
 208 of which are within approximately 11 mN/m. Compared to the large impact of H_2S concentration
 209 on gas-water IFT, the effect of temperature is relatively minor.

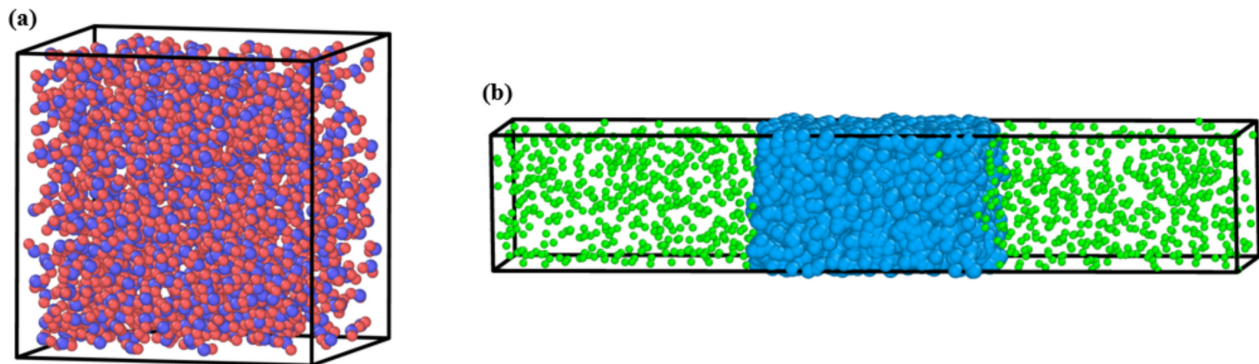


Fig. 2. (a) Bulk water system consists of 1000 water molecules. (b) Pure H_2 -water system consists of 2048
 water and 1024 H_2 molecules.

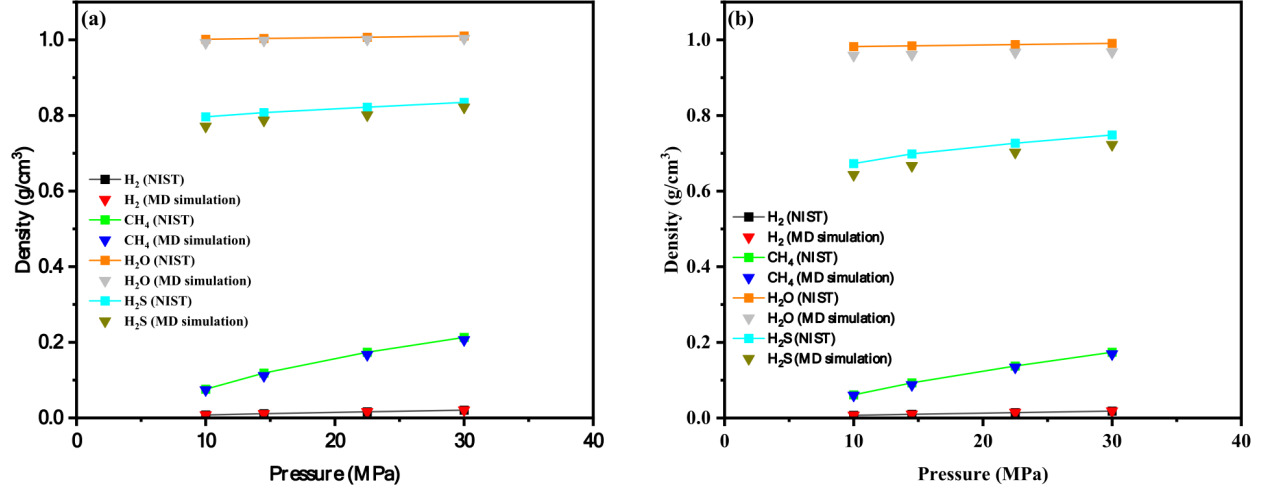


Fig. 3. Bulk densities of H₂, CH₄, H₂S, and H₂O at (a) 298 K and (b) 343 K reported from the NIST database and determined from our MD simulations.

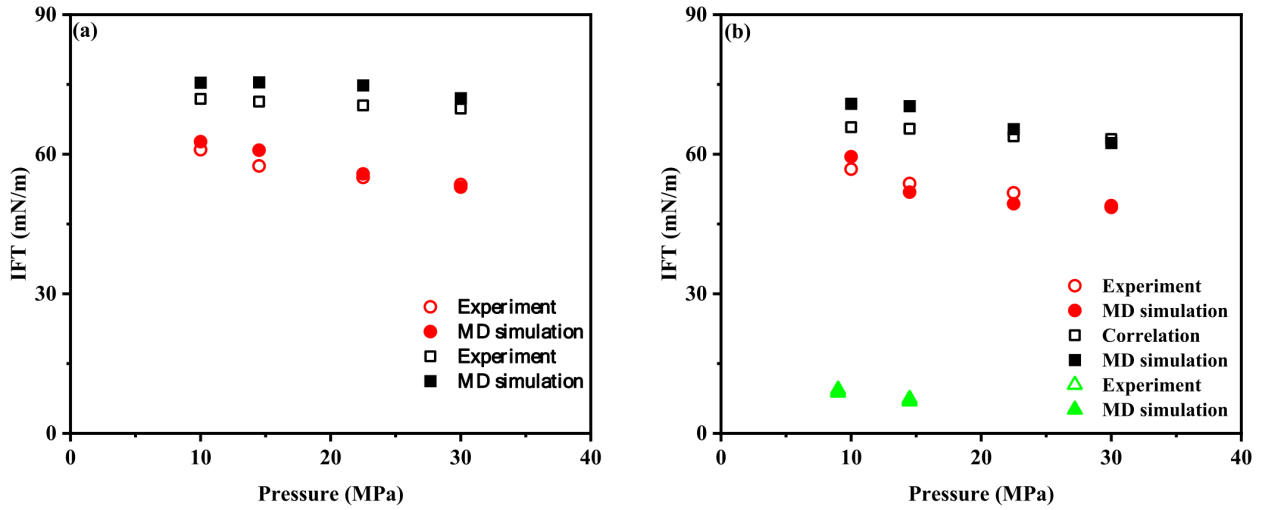


Fig. 4. IFTs of H₂O-H₂ (square), CH₄-H₂O(circle), and H₂S-H₂O(triangle) at (a) 298 K and (b) 343 K with different pressures. Experimental values of H₂O-H₂ at 298 K were directly measured by Chow et al. [53] and we used their empirical correlation for IFT between H₂-H₂O at 343 K. CH₄-H₂O IFTs at 298 K and 353 K (not available at 343 K) are reported by Sachs and Meyn [54] and Ren et al. [55]. Experimental results of H₂S-H₂O IFT at 343 K reported by Shat et al. [21] closely align with the simulated values.

Table 3IFTs and standard deviations (in mN/m) of H₂-H₂S-water mixture under different P/T conditions.

H ₂ -H ₂ S-water at 343 K								
	10 mol% H ₂ S		20 mol% H ₂ S		30 mol% H ₂ S		40 mol% H ₂ S	
P/MPa	IFT	Std	IFT	Std	IFT	Std	IFT	Std
10	64.52	1.08	51.81	1.43	40.93	0.31	28.53	1.09
14.5	58.21	1.67	47.99	0.71	35.63	1.63	26.13	0.13
22.5	54.89	0.60	44.87	0.57	32.25	1.31	23.45	1.07
30	53.85	0.71	42.99	0.32	30.73	0.19	23.36	0.17
H ₂ -H ₂ S-water at 298 K								
	10 mol% H ₂ S		20 mol% H ₂ S		30 mol% H ₂ S		40 mol% H ₂ S	
P/MPa	IFT	Std	IFT	Std	IFT	Std	IFT	Std
10	68.72	0.82	56.73	1.27	43.28	0.28	30.31	0.58
14.5	67.19	1.46	53.59	0.37	40.68	0.33	28.29	1.83
22.5	63.98	0.41	49.53	0.14	39.21	1.33	26.13	0.26
30	61.42	0.76	47.46	1.43	35.69	0.42	25.82	1.71

Table 4IFTs and standard deviations (mN/m) of CH₄-H₂S-water mixture under different P/T conditions.

CH ₄ -H ₂ S-water at 343 K								
	10 mol% H ₂ S		20 mol% H ₂ S		30 mol% H ₂ S		40 mol% H ₂ S	
P/MPa	IFT	Std	IFT	Std	IFT	Std	IFT	Std
10	50.63	0.82	39.13	0.29	30.72	1.24	22.36	0.38
14.5	45.59	1.62	34.33	0.03	26.38	1.91	18.83	0.13
22.5	42.52	1.06	32.84	0.24	24.89	1.00	17.73	0.79
30	42.06	0.53	32.16	0.77	24.07	0.61	17.06	0.63

CH ₄ -H ₂ S-water at 298 K								
	10 mol% H ₂ S		20 mol% H ₂ S		30 mol% H ₂ S		40 mol% H ₂ S	
P/MPa	IFT	Std	IFT	Std	IFT	Std	IFT	Std
10	52.72	1.71	44.45	0.76	32.92	1.14	24.58	0.24
14.5	47.71	1.25	40.09	0.54	30.04	0.89	22.79	1.27
22.5	45.43	1.42	37.09	0.66	28.29	1.76	21.26	0.08
30	44.61	1.18	36.84	1.40	26.99	1.55	21.45	0.37

The cohesive force between water molecules is one of the key factors affecting gas-water IFT at the interface [52,58]. A larger cohesive force results in a stronger ability of water to minimize its surface area at the interface with a higher gas-water IFT. Water cohesive energies of H₂/CH₄-H₂S-water mixtures were computed at 298 K and 343 K. With the method reported by Alshammari et al. [52], water cohesive energy was determined as the water-water intermolecular interaction energy (including electrostatic and van der Waals forces) divided by the number of water molecules. Here, water cohesive energies of H₂-H₂S-water and CH₄-H₂S-water mixture with 20 mol% H₂S are shown as examples in Fig. 7. The results indicate that water cohesive energy decreases as temperature increases, consistent with their IFT variation. In comparison, the impact of pressure on the cohesive energy of water is small (Fig. 7).

We believe that as water cohesive energy decreases, the distance between water molecules would increase, leading to an expansion of gas-water interface. Previous studies have reported that gas-water IFT decreases with an increase in interface width [47,48,58]. Therefore, further analyses of interface width in relation to temperature are discussed in the following paragraphs.

Local density profiles of H₂-H₂S-water and CH₄-H₂S-water mixtures with 20 mol% H₂S shown in Fig. 8 are presented in such a way as to determine the interface width. In detail, the local density profile of each species in the mixture was determined by dissecting the simulation domain into 0.1-Å thick slices along the Z direction, with the mass density of each slice calculated individually. The commonly used Gibbs dividing surface (GDS) was calculated to determine the gas-water interface width, where the width is defined as the distance between the boundaries located at 10 % and 90 % of the bulk water density [47,48,58–60].

For example, the interface width of the H₂-H₂S-water mixture at 343 K and 14.5 MPa was defined as the GDS width in Fig. 8(a), two boundaries represented by black dashed lines. The gas mixture remains in the vapor phase on the left side of the interface region [61], while water presents as the liquid phase on the right. The H₂S density profile indicates that H₂S molecules accumulated at the interface in contact with water because the local densities of H₂S in the interface region are larger than those in the gas mixture and water phases, consistent with the studies by Ofori et al. [24,62] and Dehaghani et al. [26]. Values of GDS widths of H₂-H₂S-water and CH₄-H₂S-water mixtures with 20 mol% H₂S at 298 K and 343 K are listed in Table 5. Consistent with water cohesive energy determined in Fig. 7, as temperature increases, the cohesive force between water molecules decreases [58], yielding the expansion of the GDS width and possibly IFT reduction.

3.3. Pressure effect on IFT

In Fig. 9 and Fig. 10, IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures are shown as a function of pressure at 298 K and 343 K. It is clear that IFTs of both H₂-H₂S-water and CH₄-H₂S-water mixtures decrease as pressures increase. Such pressure effect on IFT was also reported by Chow et al. for H₂-water [53], Ren et al. for CH₄-water [55], and Dehaghani et al. for H₂S-water systems [26]. We determined the maximum differences in IFTs for H₂-H₂S-water and CH₄-H₂S-water mixtures between 10 MPa and 30 MPa, all of which were within 10 mN/m at both 298 K and 343 K. This result indicates that the effect of pressure exists but is not as strong as that of H₂S concentration on gas-water IFT.

Fig. 7 illustrates that under isothermal conditions, the pressure effect on water-water intermolecular interactions is limited. However, previous studies have reported that increasing pressure compresses the gas phase and enhances the intermolecular interactions between the gas and water

253 phases, yielding an IFT reduction [56,63]. In Fig. 11, the intermolecular interaction energies includ-
 254 ing electrostatic and van der Waals forces, for H₂S-water, H₂-water, and CH₄-water in H₂-H₂S-water
 255 and CH₄-H₂S-water mixtures at 343 K under different pressures are determined respectively. Be-
 256 sides, based on their local density profiles, the average gas densities in the interface region (GDS
 257 region) are calculated and also presented in Fig. 11, corresponding to their interaction energies. The
 258 results show that as pressure increases, the intermolecular interactions between water and H₂S/CH₄
 259 increase, while interaction between water with H₂ exhibits a slight change. As the result, more H₂S
 260 and CH₄ molecules accumulate at the gas-water interfaces of H₂-H₂S-water and CH₄-H₂S-water
 261 mixtures as pressure increases. Since the IFT between H₂S and water is significantly smaller than
 262 that between H₂-water and CH₄-water (Fig. 4), the more H₂S accumulated at the interface further
 263 decreases the gas-water IFT as pressure rises.

264 As additional supporting evidence, with the same method described in Sec 3.2, GDS widths of
 265 H₂-H₂S-water and CH₄-H₂S-water mixtures with 20 mol% H₂S were determined and listed in Table
 266 6 under different pressure conditions. Unlike the temperature effect on GDS width, as pressure
 267 increases, GDS width slightly decreases. This slight shrinkage of the interface could be attributed
 268 to the compression caused by increasing pressure. As shown in Table 7, the lengths (L_z) of the
 269 simulation box for H₂-H₂S-water and CH₄-H₂S-water mixtures are determined under different pres-
 270 sures. As pressure increases, the length of the simulation box decreases due to the compression.
 271 Such compression forces the gas mixture and water to merge together, yielding a slight decrease in
 272 GDS width and possibly losing its tension at the interface [58].

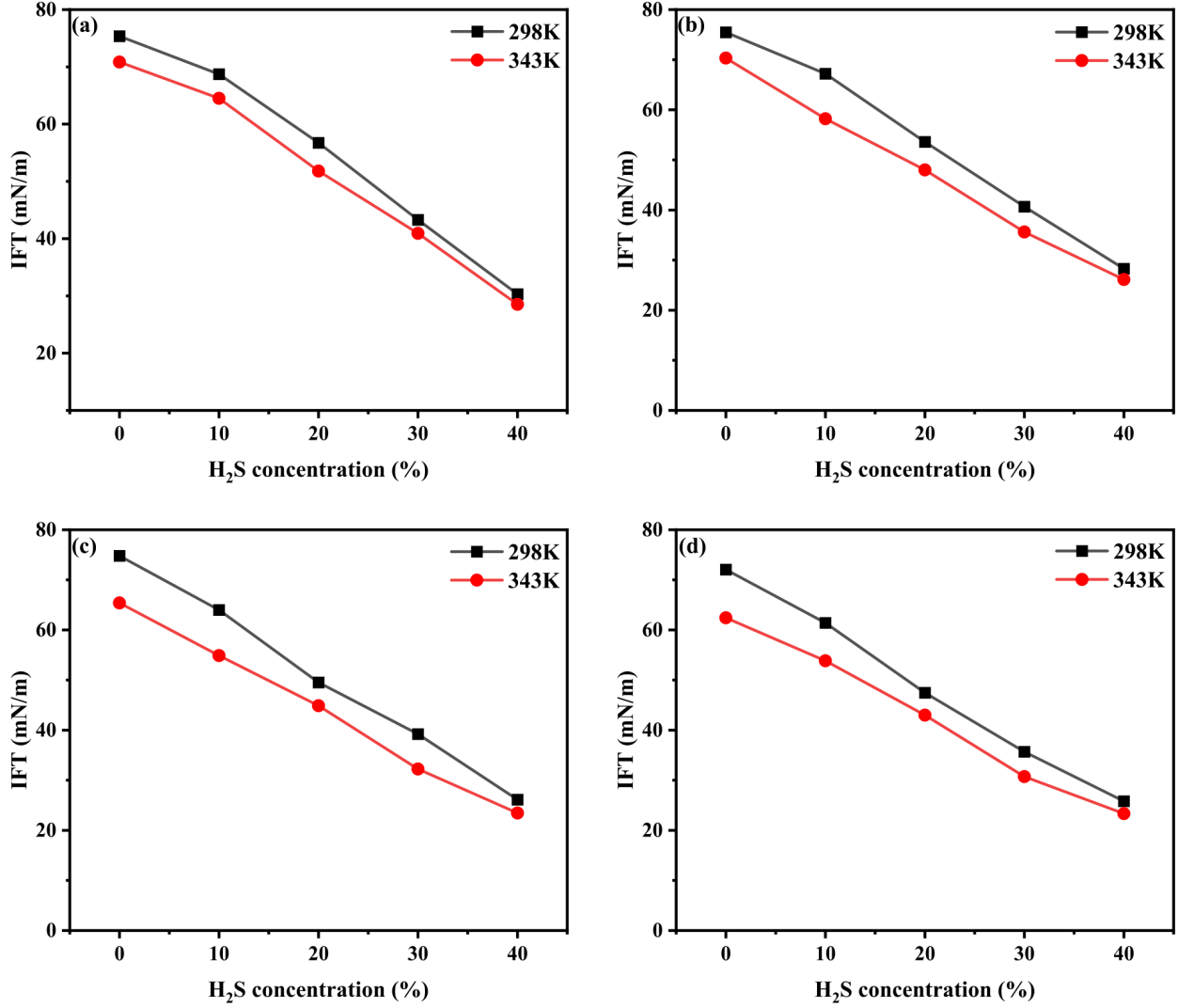


Fig. 5. IFTs of H₂-H₂S-water mixtures as a function of H₂S concentration under different pressure and temperature conditions: (a)10 MPa, (b)14.5 MPa, (c)22.5 MPa, and (d)30 MPa.

3.4. Regression model

In Sec 3.2 and 3.3, the effects of pressure, temperature, and H₂S concentration on gas-water IFT are discussed. Overall, the H₂S concentration in the gas mixture has a significant impact on gas-water IFT, whereas pressure and temperature have only a minor effect. Determining the IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures under geological conditions is crucial for predicting gas/water distribution in the reservoir during UHS. To avoid the high computational costs of using MD simulations, regression models were developed to predict the IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures under geological conditions, valid at 298 K < T < 343 K, 10 MPa < P <

30 MPa, and an H₂S concentration smaller than 40 mol%. Since pressure and temperature have a minor effect on gas-water IFT, and Fig. 5 and Fig. 6 nearly show a linear relationship between H₂S concentration and gas-water IFT, hence a multiple linear regression model was used to fit the IFT data from Table 3 and Table 4.

A total of 80 data points is available for IFTs, with 40 for H₂-H₂S-water and another 40 for CH₄-H₂S-water mixtures, covering H₂S concentrations from 0 to 40 mol% under simulated P/T conditions. For each gas-water mixture, 75 % of the data points (30 out of 40) were randomly selected to fit the regression model, while the remaining 10 data points were used to test the model. The regression model for predicting the IFTs of H₂-H₂S-water and CH₄-H₂S-water mixtures is introduced as:

$$\gamma = A_0 + A_1 \times H_2S\%(mole\ fraction) + A_2 \times P(MPa) + A_3 \times T(K)$$

The corresponding parameters for the regression model of each gas-water mixture are listed in Table 8. In Fig. 12, we evaluate the accuracy of the regression models using 10 data points (T₁ to T₁₀). The average absolute deviations are 1.66 mN/m for H₂-H₂S-water mixture and 1.71 mN/m for CH₄-H₂S-water mixture, both showing a good consistency. Besides, the IFTs of the H₂S-H₂-water and H₂S-CH₄-water systems shown in Fig. 5 and Fig. 6 were reproduced via regression models and compared with the MD simulation results presented in Fig. S1 and Fig. S2 of the Supporting Materials, further validating its reliability.

The fitted temperature coefficients are $-0.118 \text{ mN m}^{-1} \text{ K}^{-1}$ for the H₂-H₂S-water system, and $-0.0896 \text{ mN m}^{-1} \text{ K}^{-1}$ for the CH₄-H₂S-water system, implying average decreases of ~ 5.3 and $\sim 4.0 \text{ mN m}^{-1}$ from 298 to 343 K, respectively. Over the same interval, increasing $x_{(H_2S)}$ by 0.1 lowers IFT by $\sim 11.3 \text{ mN m}^{-1}$ (H₂ case) and $\sim 8.7 \text{ mN m}^{-1}$ (CH₄ case), while raising pressure from 10 to 30 MPa lowers IFT by ~ 7.4 and $\sim 6.1 \text{ mN m}^{-1}$. Thus, within 298–343 K, temperature plays a secondary role relative to composition and pressure. We also note that the correlation is not intended for use outside 298–343 K.

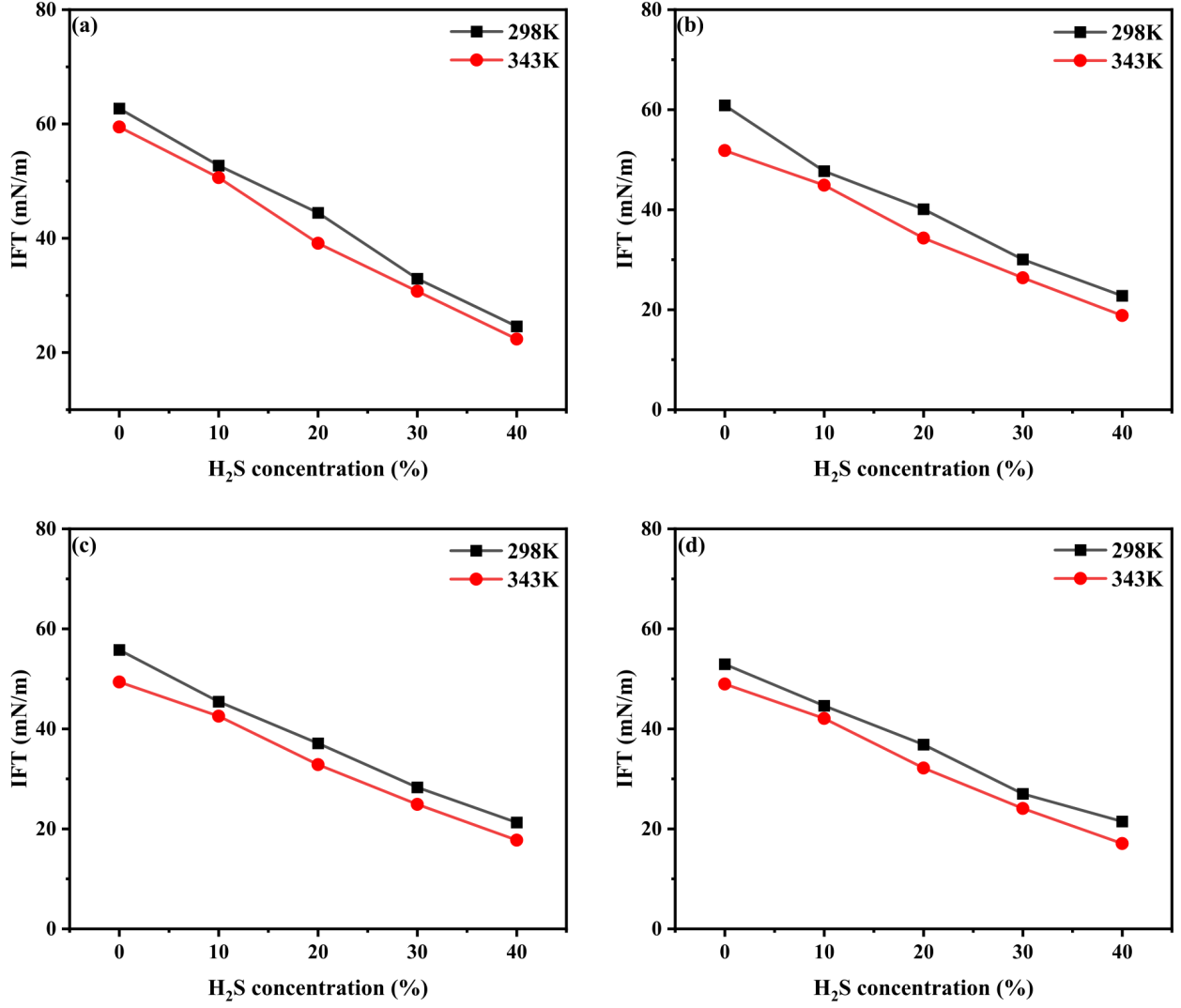


Fig. 6. IFTs of CH₄-H₂S-water mixtures as a function of H₂S concentration under different pressure and temperature conditions: (a) 10 MPa, (b) 14.5 MPa, (c) 22.5 MPa, and (d) 30 MPa.

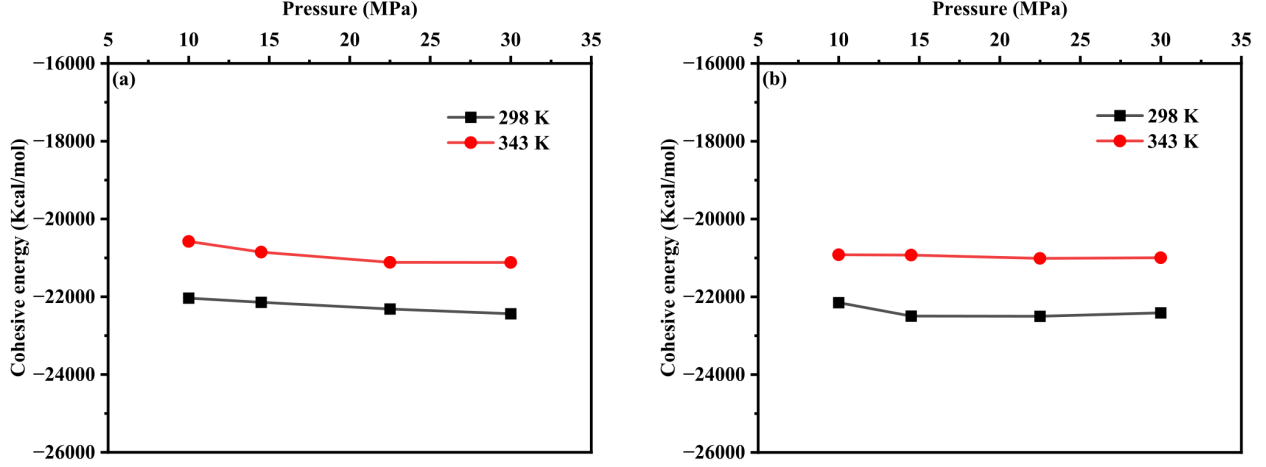


Fig. 7. Water cohesive energies of (a) H_2 - H_2S -water and (b) CH_4 - H_2S -water mixtures with 20 mol% H_2S .

3.5. Limitations and future work

While this study substantially enhances understanding of gas–water interfacial tension relevant to underground hydrogen storage (UHS), several limitations must be acknowledged. **First**, the effects of water salinity and specific ion compositions, which are known to influence gas–water interactions, were not investigated. **Second**, our simulations focused on binary gas mixtures of H_2 - H_2S and CH_4 - H_2S , whereas geological settings can involve multi-component mixtures (e.g., H_2 - CO_2 - H_2S or H_2 - N_2 - H_2S). **Third**, due to handling, safety, and toxicity risks associated with H_2S , direct experimental validation of the simulated IFTs was not performed.

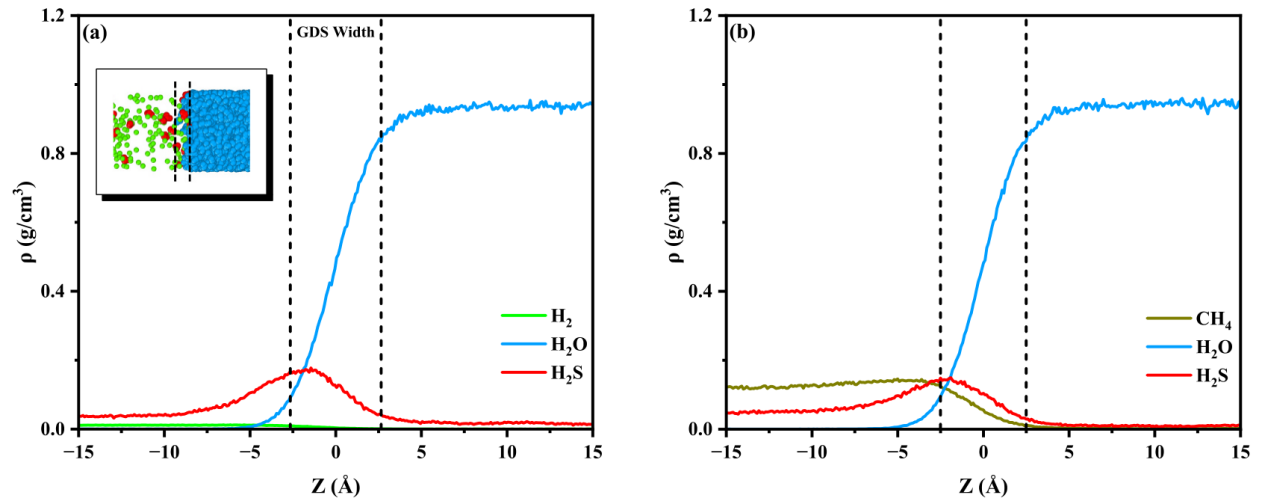


Fig. 8. Local density profiles of (a) H_2 - H_2S -water and (b) CH_4 - H_2S -water mixtures at 343 K and 14.5 MPa.

Table 5

GDS widths of H₂-H₂S-water and CH₄-H₂S-water mixtures with 20 mol% H₂S at 14.5 MPa.

Temperature (K)	H ₂ -H ₂ S-water (Å)	CH ₄ -H ₂ S-water (Å)
298	4.7	4.4
343	5.2	5.1

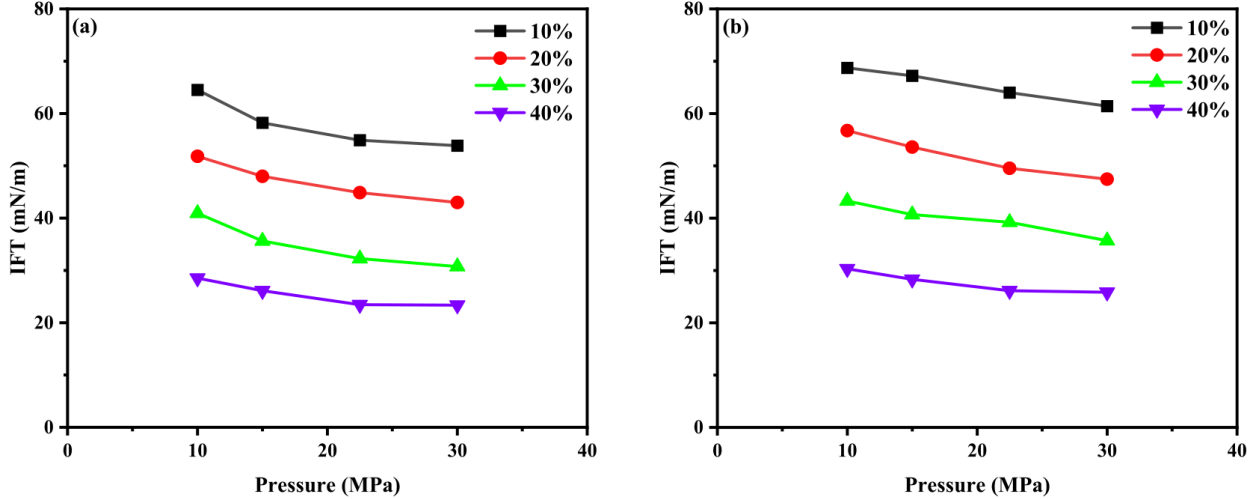


Fig. 9. IFTs of H₂-H₂S-water mixture with different H₂S concentrations at (a) 343 K and (b) 298 K under different pressure conditions.

Only two temperatures of 298 and 343 K were simulated to **bracket the operational window** most relevant to near-term UHS, see also Table S-1 in the SI. Within this narrow interval, we represented temperature with a **first-order term** in the regression and explicitly **restricted the model's domain of validity** to 298–343 K, 10–30 MPa, and H₂S mole fraction ≤ 0.40 . Quantitatively, the fitted temperature coefficients imply average IFT decreases of $\sim 5.3 \text{ mN m}^{-1}$ for H₂-H₂S-water and $\sim 4.0 \text{ mN m}^{-1}$ for CH₄-H₂S-water across 298 to 343 K, which are **smaller than** the corresponding effects of composition (e.g., $\sim 11.3 \text{ mN m}^{-1}$ and $\sim 8.7 \text{ mN m}^{-1}$ decreases for a 0.10 increase in H₂S mole fraction, respectively) and comparable to the pressure effect from 10 to 30 MPa: $\sim 7.4 \text{ mN m}^{-1}$ and $\sim 6.1 \text{ mN m}^{-1}$ decreases, respectively. While the first-order temperature dependence is adequate **within 298–343 K**, the results **should not be extrapolated** to higher-temperature reservoirs without additional calibrations, such as targeted MD at intermediate temperatures or anchoring to measurements/thermodynamic models.

Experimental validation of the simulated IFT values for H_2 - H_2S -water and CH_4 - H_2S -water remains essential to confirm accuracy and reliability. Further studies should quantify the impact of **brine salinity** and **specific ions** on IFT under reservoir conditions and extend simulations to **multi-component gas mixtures** to reflect realistic reservoir compositions. Given the role of IFT in shaping gas-water relative permeability and, consequently, gas distribution and recovery, coupling IFT predictions with **relative permeability and capillary pressure** in the presence of H_2S and other gases would be valuable. Finally, to expand applicability to **higher-temperature reservoirs**, future work should add **more temperature points** spanning and extending beyond 343 K, enabling a higher-order temperature treatment where appropriate.

4. Conclusions

For underground hydrogen storage in depleted hydrocarbon reservoirs, residual hydrogen sulfide or H_2S generated in situ due to geochemical and biological activities can significantly influence gas-water interfacial tension. Accurate determination of the IFT for H_2 - H_2S -water and CH_4 - H_2S -water mixtures under geological conditions is critical for effectively managing underground hydrogen storage (UHS). Given the risks associated with direct experimental measurement involving H_2S , this study employed molecular dynamics simulations to comprehensively evaluate the IFT behavior across a broad range of conditions: H_2S concentrations ranging from 0 to 40 mol%, temperatures of 298 K and 343 K, and pressures between 10 and 30 MPa.

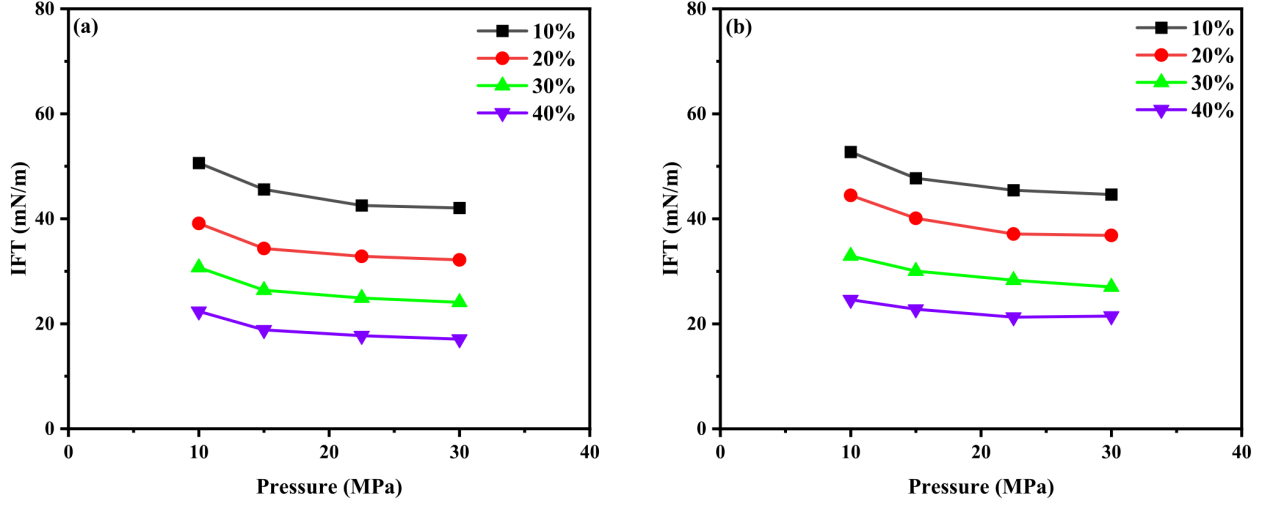


Fig. 10. IFTs of $\text{CH}_4\text{-H}_2\text{S}$ -water mixture with different H_2S concentrations at (a) 343 K and (b) 298 K under different pressure conditions.

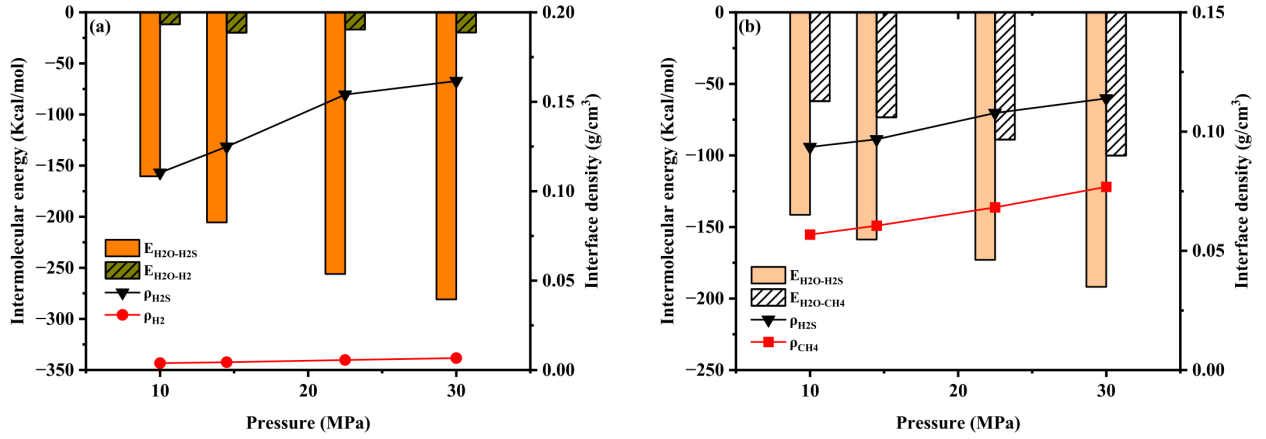


Fig. 11. Intermolecular interaction energies and interface densities of (a) $\text{H}_2\text{-H}_2\text{S}$ -water and (b) $\text{CH}_4\text{-H}_2\text{S}$ -water mixtures with 20 mol% H_2S at 343 K and different pressures.

Table 6

GDS widths of $\text{H}_2\text{-H}_2\text{S}$ -water and $\text{CH}_4\text{-H}_2\text{S}$ -water mixtures at 343 K with different pressures.

Pressure (MPa)	$\text{H}_2\text{-H}_2\text{S}$ -water ($\text{\AA}$)	$\text{CH}_4\text{-H}_2\text{S}$ -water ($\text{\AA}$)
10	5.33	5.15
14.5	5.17	5.10
22.5	5.00	5.10
30	5.00	5.05

Table 7Simulation-box lengths of H₂-H₂S-water and CH₄-H₂S-water mixtures at 343 K with different pressures.

Pressure (MPa)	H ₂ -H ₂ S-water (Å)	CH ₄ -H ₂ S-water (Å)
10	309	218
14.5	256	209
22.5	203	172
30	179	162

Table 8

Parameters of the regression model for each gas-water mixture.

	A ₀	A ₁	A ₂	A ₃
H ₂ -H ₂ S-water	116.84832	-113.49682	-0.37202	-0.11794
CH ₄ -H ₂ S-water	89.44622	-87.21419	-0.3057	-0.08961

The simulation results indicate that IFT consistently decreases with increased H₂S concentration, temperature, and pressure. Even modest amounts of H₂S (e.g., 10 mol%) markedly reduce IFT between both H₂-water and CH₄-water interfaces. Notably, while temperature and pressure influence IFT moderately, the H₂S concentration exhibits a substantially more pronounced effect. Mechanistically, rising temperature reduces the cohesive energy among water molecules, leading to expanded gas-water interfaces and lowering IFT. Pressure increases, on the other hand, intensify intermolecular interactions at the gas-water interface, promoting H₂S accumulation and further diminishing IFT. Additionally, higher pressures compact the gas and water phases, potentially merging them at the interface and contributing to IFT reduction.

The regression models developed in this study offer practical tools for predicting gas-water IFT under realistic geological conditions. These models can be directly integrated into numerical reservoir simulation software, thereby significantly enhancing the accuracy of predictions related to hydrogen storage efficiency, gas recovery, and overall reservoir management. By providing robust predictive capabilities, these models facilitate informed decision-making in reservoir operations, thereby contributing directly to improved safety, operational efficiency, and economic viability of UHS projects. Moreover, the methodological approach—combining molecular dynamics simulations with regression

modeling—demonstrated in this study serves as a versatile framework applicable to other gas-water systems under varied geological storage scenarios. For example, cushion gases such as CH_4 , CO_2 , and N_2 importantly affect H_2 -water IFT under geological conditions [30,52,64–67]. Currently, IFT data for such H_2 -cushion gas-water system remain limited for UHS and can be expanded using the approach introduced in this study.

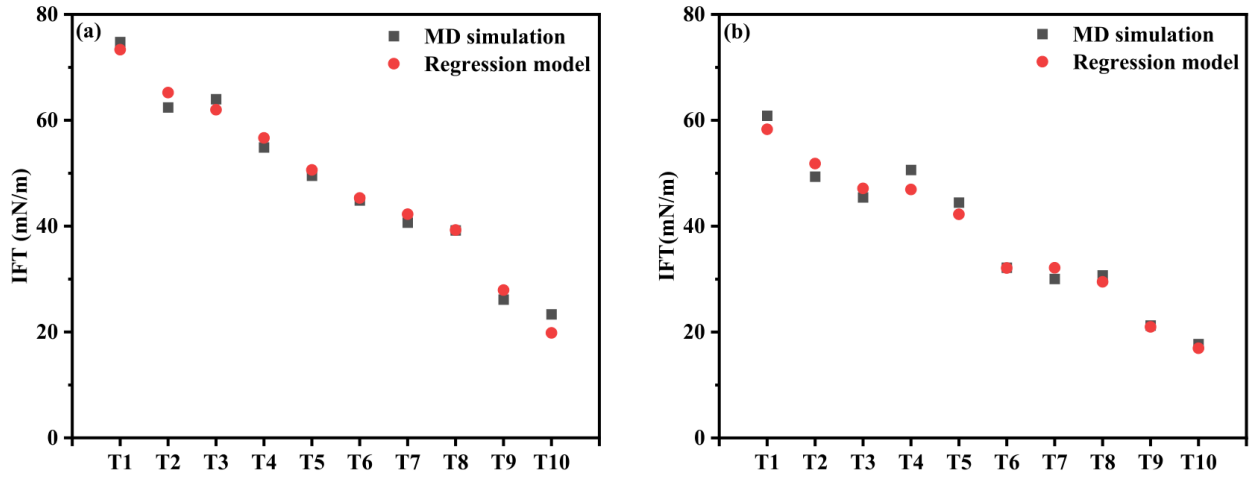


Fig. 12. IFTs determined by MD simulations and the newly developed regression model for (a) H_2 - H_2S -water and (b) CH_4 - H_2S -water mixtures.

Collectively, the findings contribute to a deeper fundamental understanding of the factors governing IFT variations and underscore the critical importance of considering H_2S effects in UHS scenarios. These insights not only enhance the theoretical understanding but also translate directly into practical improvements for reservoir management strategies, promoting safer and more effective implementation of underground hydrogen storage solutions.

CRediT authorship contribution statement

Qiu hao Chang: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **David Dempsey:** Writing – review & editing, Project administration, Methodology, Conceptualization. **Liangliang Huang:** Writing – review & editing, Methodology, Conceptualization.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2025.119683>.

Data availability

Data will be made available on request.

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