

Research papers

Influence of hydrogen sulfide on gas-water interface in underground hydrogen storage: A molecular dynamics study

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ABSTRACT

In this study, we investigate the dynamics of interfacial tension (IFT) between residual pore water and gas mixtures containing H₂, CH₄, and H₂S within subsurface porous media, essential for underground hydrogen storage (UHS) systems. Utilizing molecular dynamics simulations, we established specific IFT correlations across a spectrum of H₂S concentrations, ranging from 5 % to 80 %, under the conditions of 14.5 MPa and 343 K. Our results demonstrate a marked decrease in IFT, with a notable 12 % reduction observed even at a minimal H₂S concentration of 5 % for H₂S-H₂ mixtures, contrasting with a 6 % reduction in H₂S-CH₄ mixtures, and reaching a saturation point at concentrations exceeding 80 %. The presence of CH₄ at the interface mitigates the reduction in IFT caused by H₂S, underscoring the complexity of gas interactions in subsurface storage. These insights into the molecular dynamics at the gas-water interface carry significant implications for the optimization of UHS operations, informed by the substantial variations in IFT with different H₂S concentrations.

1. Introduction

Hydrogen, lauded for its multifaceted applications, is vital to the future landscape of zero-emissions energy systems [1–4]. Projections suggest that achieving global net-zero emissions by 2050 will necessitate the production of an estimated 660 million tons of hydrogen [5]. A pressing obstacle in scaling hydrogen production is the inadequate storage capacity to manage such a voluminous output [6–8]. The potential of subterranean structures, including caverns, aquifers, and particularly depleted hydrocarbon reservoirs, has been recognized for their expansive storage capabilities and cost-effectiveness [6,9–12]. Depleted hydrocarbon reservoirs are especially promising for underground hydrogen storage due to their established storage efficacy, clearly defined geological formations, verified caprock integrity, and pre-existing facility infrastructure [6,9,12].

One of the primary issues facing UHS is the generation and contamination of the stored H₂ with hydrogen sulfide (H₂S). The presence of H₂S in a hydrocarbon reservoir is known to cause unwanted side effects such as souring, corrosion, and stress-cracking of steel [13,14].

H₂S production can occur geochemically (abiotic), biologically via microbial interaction with their environment (biogenic) or from a mixture of geochemical and biological interactions. Abiotic H₂S can arise from rocks commonly found in hydrocarbon reservoirs such as anhydrite (CaSO₄) and pyrite (FeS₂). Water-rock interactions can generate H₂S directly [15] or produce a variety of sulfur-based compounds including sulphates (SO₄^{2−}), thiosulfates (S₂O₃^{2−}), elemental sulfur (S) [16,17] which in turn can then be biologically reduced to H₂S by microorganisms. For example, at elevated temperatures (> 770 K), pyrite (FeS₂) can react with brines to form iron oxides and sulfate species [16,17]. Similarly, methane (CH₄) introduced into a UHS reservoir as a cushion gas (Fig. 1) or generated by methanogens (CH₄-generating prokaryotes from the domain *Archaea*) can react with CaSO₄ to form H₂S [15]. While the abiotic generation of H₂S generally occurs at elevated temperatures, biogenic H₂S occurs at temperatures (< 395 K) by a taxonomically diverse group of microorganisms (*Archaea* and *Bacteria*) that utilize sulfur-containing compounds as electron acceptors for dissimilatory sulfur reduction [18]. Within an UHS scenario, H₂ is presumed to be the primary source of reducing power (Eq. (1)) for dissimilatory sulfur-

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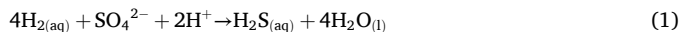
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reducing microorganisms such as *Desulfovibrio vulgaris* and *Desulfotomaculum salinum* [19], although other electron donors for this reaction can also include lactate, acetate, glucose, sucrose, ethanol, and propionate [20].



Other forms of sulfate reduction include assimilatory sulfate reduction, which describes the assimilation of sulfur into cellular biomass via H_2S reduction to O-acetyl serine and finally to sulfur-containing amino acids and compounds such as cysteine [21]. Desulfurization reduces organic sulfur, and during disproportionation, $\text{S}_2\text{O}_3^{2-}$ can be used as either an electron donor or an electron acceptor [22], as shown in Fig. 1. Sulfur/sulfate-reducing prokaryotes are found in a variety of extreme environments such as hydrothermal vents, marine trenches, and hydrocarbon reservoirs [23–30]. In these hot temperatures and high-pressure environments, microorganisms reduce sulfate to H_2S . Indeed, a number of reports show that the rate of dissimilatory sulfate reduction increases with elevated temperatures and pressures, as high as 368 K and over 50 MPa, respectively [24,29]. Whilst not demonstrated within a reservoir system, it is understood the sulfate-reducing prokaryotes will inhabit the gas-water interface in a similar way that methanotrophs and methanogens will inhabit the oxic/anoxic interface of water tables, with methanotrophs utilizing the methane that methanogens are producing [31,32].

In the context of underground hydrogen storage, the activities of these organisms are of particular interest due to their ability to utilize hydrogen as an electron donor in the reduction of sulfate to sulfide. This biological conversion is a thermodynamically favorable process under the high-pressure and high-temperature conditions typical of subsurface reservoirs. The resultant H_2S poses, due to its corrosive nature and toxicity, challenges. It influences the physicochemical properties of the storage environment, including the interfacial tension between gas and water phases. Interfacial tension (IFT) is a critical factor influencing the segregation of gas mixtures and water within the pore spaces of

underground storage systems and dictating the distribution and stability of stored gases [33–35]. The advent of H_2S , generated through the metabolic pathways of microorganisms, presents an additional complexity in this process. H_2S tends to integrate with hydrogen and cushion gases such as CH_4 , altering the gas-water interfacial characteristics through preferential adsorption or dissolution mechanisms into the pore water, thus impacting the storage process [36]. Direct experimental characterization of IFT in the presence of H_2S , particularly under geological storage conditions, remains limited. Shah and coworkers employed the pendant drop method to gauge the IFTs in H_2S -water systems, observing a decline in IFT concurrent with increasing pressures, up to 393 K and 15 MPa [37]. Their research also extended to mixtures containing CO_2 and H_2S , noting that the inclusion of H_2S reduced the IFT when compared to pure CO_2 and water interactions. Such insights underscore the need for in-depth analysis and simulation to understand the effects of H_2S within subsurface hydrogen storage contexts, where experimental approaches face constraints.

Investigating interfacial tension under high-pressure and high-temperature conditions, particularly involving hydrogen sulfide, poses significant safety risks due to its toxicity and corrosiveness [38]. As a result, theoretical models, complemented by Equations of State (EoS) and molecular simulations, have emerged as alternatives for investigating the properties of H_2S interfacial systems. For instance, Shah and Broseta [39] utilized gradient theory alongside the Peng-Robinson EoS to simulate the water- H_2S IFT at 298 K, noting a linear decrease in IFT with increasing pressure up to a threshold of 2 MPa. In another notable study, Khosharay and coworkers [40] applied the gradient theory in conjunction with the statistical associating fluid theory (SAFT) EoS to evaluate surface tensions between H_2S and H_2O over a range of temperatures and pressures extending to 398 K and 60 MPa, with findings indicating a decrease in surface tension in response to rising pressures up to a plateau beyond 12.5 MPa. Similarly, Biscay et al. [41] adopted Monte Carlo simulations to determine the pressure dependency of water- H_2S IFT at 383 K, confirming that the impact of pressure on IFT diminishes once a critical pressure point is surpassed.

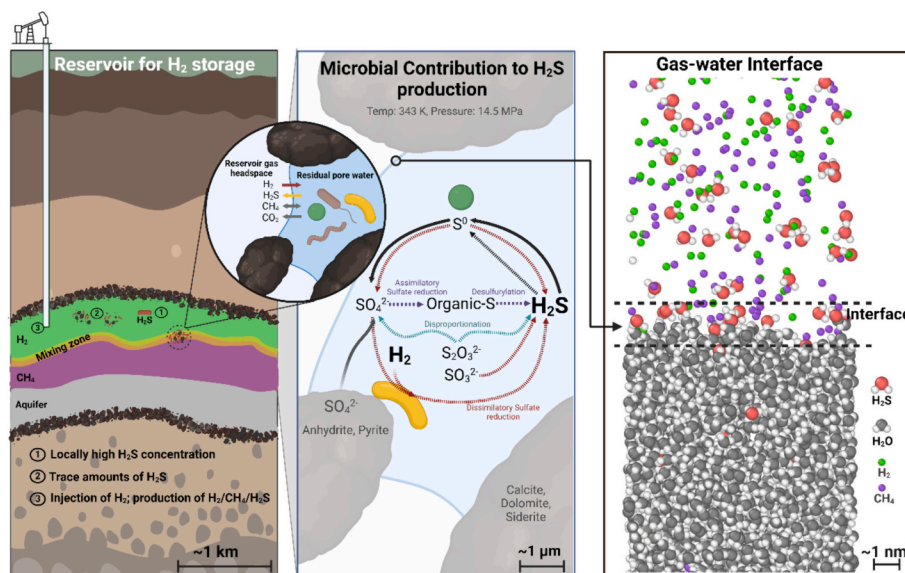


Fig. 1. Schematic for hydrogen sulfide (H_2S) generation and mixing in underground hydrogen storage at the kilometer (left panel), micrometer (center panel), and nanometer (right panel) scales. At the kilometer scale, hydrogen gas (H_2) is placed at the top of the reservoir, sitting on a cushion gas layer of methane (CH_4), which in turn sits on any reservoir aquifer. As illustrated in the microbial sulfur cycle (center), sulfur can act as an energy source and is found in the residual water as SO_4^{2-} or in the surrounding rocks in the form of anhydrite or pyrite. Sulfate can be reduced to H_2S via assimilatory or dissimilatory reduction; assimilatory reduces sulfate to H_2S and then further to amino acids (no H_2S is released from the cell). Dissimilatory sulfate reduction is the reduction of SO_4^{2-} to H_2S which is excreted from the cell. Other sulfur reduction pathways include disproportionation (oxidation or reduction of $\text{S}_2\text{O}_3^{2-}$) and desulfurization (reduction of organic-S). Red lines indicate the aerobic oxidation pathway. At the gas-water interface (right panel), molecular behaviors such as adsorption, absorption, and orientation affect the gas-water interfacial properties like IFT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The impact of H₂S as an impurity on the interfacial tension of CO₂-water systems was also analyzed by Chen et al. [42] through molecular dynamics (MD) simulations at conditions of 20 MPa and 318 K. Their research revealed that a 20 mol% concentration of H₂S can significantly reduce the CO₂-water IFT by 65 %. Another study by Ofori et al. [36] investigated the properties at the H₂S-water interface across varying pressure and temperature conditions. Their simulations indicated that H₂S molecules predominantly adsorb at the interface below their saturation pressure, while at pressures above the threshold, the H₂S molecules were absorbed into the water phase. Building upon these insights, Dehaghani et al. [43] employed MD simulations to explore the IFT between H₂S and brine, extending temperature and pressure ranges from 323 K to 393 K and up to 30 MPa. Their findings suggest a marked increase in IFT when NaCl and CaCl₂ are present in brine, deviating from the properties exhibited by pure water. Additionally, their results highlighted a direct correlation between rising temperatures and increased H₂S-brine IFT, providing critical information for the optimization of subsurface storage environments where both temperature and salinity can significantly influence interfacial behaviors.

These studies provide insights into the behaviors of H₂S-related interfacial systems under conditions important to geological storage. On the other hand, research on the interfacial properties critical to underground hydrogen storage, particularly in water and gas mixtures involving hydrogen sulfide, methane as a cushion gas, and hydrogen as a working gas, remains sparse. Addressing this knowledge gap, our study employs MD simulations to investigate the intricate interfacial properties in varying gas mixtures, including interfacial tension, absorption, and molecular orientation. Specifically, we inspect the interfacial dynamics of H₂S-H₂, H₂S-CH₄, and H₂S-CH₄-H₂ mixtures under 343 K and 14.5 MPa, typical subsurface storage conditions [44]. The manuscript is organized to facilitate a comprehensive understanding of our research: Section 2 delineates the gas-water models and details of the MD simulations; Section 3 introduces the foundational concepts of interfacial properties and the methodologies for their computation; Section 4 is dedicated to presenting the simulation results and providing an in-depth discussion of their implications; and Section 5 synthesizes our findings into conclusive insights that contribute to the field of underground hydrogen storage.

2. Models and simulation details

For all MD simulations, we employed the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), a software package renowned for its accuracy and computational efficiency. We explored the interfacial properties of two distinct system configurations—binary gas-water and ternary gas-water systems—at a consistent pressure of 14.5 MPa and temperature of 343 K. The binary systems, specifically the (H₂S + H₂)/H₂O and (H₂S + CH₄)/H₂O configurations, were initiated with 2048 water molecules centrally placed within a simulation box, bordered by approximately 1024 gas molecules. These gases, H₂S and H₂, or H₂S and CH₄, were introduced in varying concentration ratios, creating a realistic representation of subsurface conditions. The simulation box dimensions were set to 3.4 nm × 3.4 nm × 10 nm, providing ample space for molecular interactions to occur uninhibited. A series of six H₂S concentrations, ranging from a minor 5 % to a substantial 80 %, were systematically analyzed to assess their impact on the system. While unlikely at the macro-scale, such high concentrations of H₂S may arise locally under vigorous microbial activity, hence our inclusion of them here. Four parallel calculations were conducted on binary systems, employing identical H₂S concentration ratios to ensure comparative integrity. The precise gas compositions used in each simulation scenario are summarized in Table S1.

For the system studied, we initially conducted a 1-ns run within the canonical ensemble (NVT) to alleviate any potential molecular overlap. This was succeeded by a 15-ns equilibrium run in the specialized isothermal-isobaric (NPzT) ensemble, where the pressure in the Z

direction is fixed, ensuring the system reaches an equilibrium state. Throughout the NVT and NPzT ensembles, we utilized the Nose-Hoover thermostat and barostat to control the temperature and pressure of the system. In line with the recommendations of Muller et al. [45], we designed the production phase for IFT calculation to extend sufficiently to achieve convergence of the interfacial tension values. An additional 10-ns production run was performed following the equilibrium state within the NPzT ensemble. We extracted the data from the final 2 ns of this run to determine the gas-water IFT, ensuring that our results reflect a system at equilibrium.

As evidenced in Fig. S1, the convergence of IFT relative to production time illustrates that a 10-ns simulation run was sufficient to ascertain accurate IFT values for our systems. This indication of convergence is important as it validates the stability and reliability of the calculated IFT. The ternary system, comprising H₂S, H₂, and CH₄ within the water, underwent identical simulation protocols to ensure consistency in our approach. Notably, within this ternary mixture of (H₂S + H₂ + CH₄)/H₂O, the H₂S concentration varied between 5 % to 80 %, whereas the molar ratio between H₂ and CH₄, excluding H₂S, was maintained at a fixed 1:1 ratio. Table S2 lists the composition of the ternary system, outlining the specific ratios and concentrations employed within our MD simulations.

Periodic boundary conditions were implemented in all three spatial dimensions of our simulations. We adopted the leapfrog algorithm for integrating the equations of motion with a timestep set at 1 femtosecond (fs). The choice of force field models is critical for capturing the nature of molecular interactions with high fidelity. In this study, F3C model for H₂O [46], Vrabec single-site model for H₂ [47], TraPPE-UA for CH₄ [48], and Nath's three-point potential model for H₂S [43,49], were selected due to their demonstrated reliability on interfacial simulation of vapor-liquid or liquid-liquid systems involving these species [43,47,50,51]. Coulombic interactions were computed using the particle-particle-particle mesh (PPPM) method, while the non-bonded interactions were described by the 12–6 Lennard-Jones (LJ) potential. A cutoff distance of 15 Å was used for the LJ potential and Coulombic interactions. The equilibrium states of the binary and ternary systems are illustrated in Fig. 2.

3. Interfacial tension, density profile, and molecular orientation properties

Interfacial tension, a critical property defining the stability of gas-water interfaces, was quantified using the established Gibbs IFT formulation [52]:

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

where L_z denotes the length of the simulation box in the Z direction, and P_{xx} , P_{yy} , and P_{zz} are the respective normal stress components of the pressure tensor. The factor of $\frac{1}{2}$ accounts for two distinct interfaces within the system, as illustrated in Fig. 2. We constructed density profiles to map the spatial distribution of molecules, therefore determining absorption and dissolution behaviors. The simulation domain was dissected into 1-Å thick slices along the Z direction, with the mass density of each slice calculated individually, providing a granular view of molecular distribution within the system. We note that the influence of the molecular orientation of water molecules on gas-water and liquid-water interfacial properties like IFT is well-documented at the molecular level [51,53–55]. In this work, the molecular orientation at the interface was analyzed by computing the orientational order parameter (S). This parameter quantifies the preferential alignment of molecules relative to the interface as a function of their z-directional positioning [56]:

$$S = \frac{1}{2} \langle 3\cos^2(\theta) - 1 \rangle \quad (3)$$

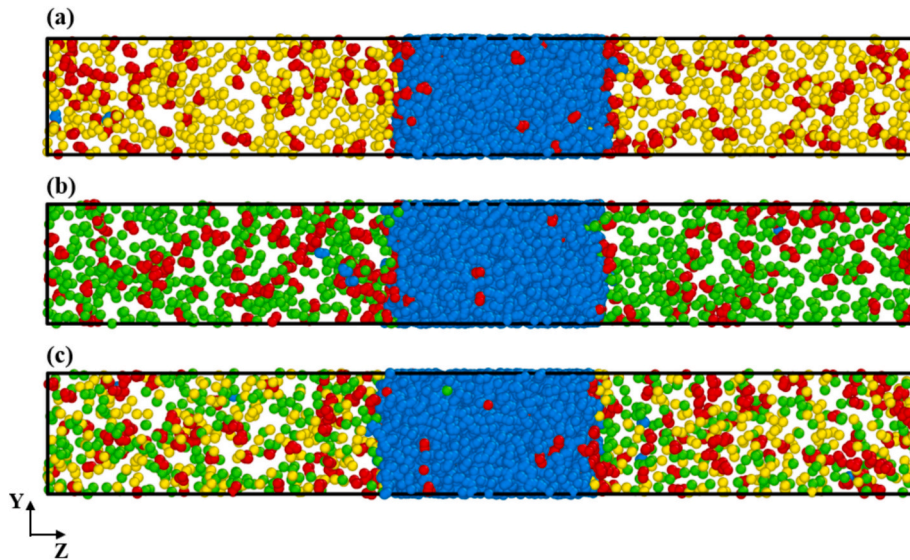


Fig. 2. The equilibrium states at 343 K and 14.5 MPa: (a) $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$; (b) $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$; (c) $(\text{H}_2\text{S} + \text{H}_2 + \text{CH}_4)/\text{H}_2\text{O}$. The colour codes are: red— H_2S , yellow— H_2 , blue— H_2O , green— CH_4 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where θ is the angle between the dipole vector of H_2O and the z-axis. Here, S values approaching -0.5 denote a parallel alignment to the interface, S values near 1.0 indicate a perpendicular orientation and values around zero are indicative of a random orientation distribution.

4. Results and discussions

4.1. Validation

Before delving into the simulation outcomes, we validated molecular models, force field parameters, and computational methods. This preliminary step is indispensable for ensuring our simulation results stand up to scrutiny. Therefore, we conducted simulations to ascertain the bulk densities of H_2 , CH_4 , H_2S , and H_2O at 343 K and 14.5 MPa. Supplementary Figs. S2 and S3 depict the configurations of these bulk systems. The calculated densities from these simulations are summarized, with references from the National Institute of Standards and Technology (NIST) database. The comparison, as presented in Table 1, demonstrates remarkable agreement between our simulated data and the established NIST values, reinforcing the credibility of the simulation framework.

Subsequent to the bulk density simulations, we also constructed and calculated the IFTs of three gas-water systems: H_2 - H_2O , CH_4 - H_2O , and H_2S - H_2O . The spatial arrangements for each simulated system are exhibited in Supplementary Fig. S4, offering a snapshot of the molecular configurations attained at equilibrium. The same controlled conditions of 343 K and 14.5 MPa were applied, and the calculated IFTs are summarized in Table 2. The coherence between our simulated IFT values and experimental data not only reaffirms the reliability of our simulation methods but also enhances confidence in the predictive power of our models for subsurface interfacial phenomena. The coherence between our simulated IFT values and experimental data indicates the simulation methods are reliable. This gives us confidence in their predictive power for subsurface interfacial phenomena. Finally, the

Table 1
Bulk fluid densities at 343 K and 14.5 MPa.

Fluid	This study (g/cm^3)	NIST database (g/cm^3)
H_2	0.0095	0.0095
CH_4	0.088	0.089
H_2S	0.67	0.70
H_2O	0.99	0.98

Table 2

Comparison of calculated IFTs and experimental results.

Systems	IFT-MD (mN/m)	IFT-Exp(mN/m)
H_2 -Water	70.3 ± 1.7	~ 65.0 [57]
CH_4 -Water	52.4 ± 2.5	$53.7\text{--}55.9$ [58]
H_2S -Water	6.9 ± 0.7	7.4 ± 0.4 [37]

combination of 2048 water with 1024 gas molecules for system size was validated by sensitivity analyses shown in Table S4 to Table S6.

As shown in Fig. 3 and Fig. 4, detailed density profiles identify gas-water interface regions within the H_2 - H_2O , CH_4 - H_2O , and H_2S - H_2O systems. These profiles were instrumental in demarcating the interface region, a zone characterized by notable decreases in the densities of both gases and water. Employing the established “10–90” theoretical framework [43,59–62], we identified the boundaries of the interface region. The left boundary was defined where the local density of water falls to 10 % of the bulk water density, signaling the onset of the gas phase. Conversely, the right boundary was established at the point where water density reaches 90 % of the bulk density, indicating the transition back to the aqueous phase. These demarcations are visually delineated by black dashed lines in the figures, providing clear and objective criteria for interface identification based on molecular density distributions.

The density profiles we observed show notable variations among the different gases at the interface. Consistent with the findings of Rooijen et al. [50], H_2 exhibited a pronounced reduction in density near the interface, suggesting minimal presence of H_2 molecules within this region. In contrast, the density of CH_4 peaked at the interface, indicative of CH_4 adsorption at the interface, highlighting the affinity of CH_4 molecules for this boundary and echoing the observations of several prior studies [63–65]. The H_2S profile was particularly distinct, revealing a significant concentration of H_2S molecules within the interface region. This can be interpreted as a result of H_2S absorption into the water phase, which is in line with the insights provided by previous research [36,43]. Such an accumulation markedly influences the structure of the gas-water interface, leading to a reformation of its characteristics, a phenomenon graphically illustrated in Supplementary Fig. S4(c). The consistency of our results with observations reported before reinforces the reliability of our force field parameters and the computational approaches employed in this study.

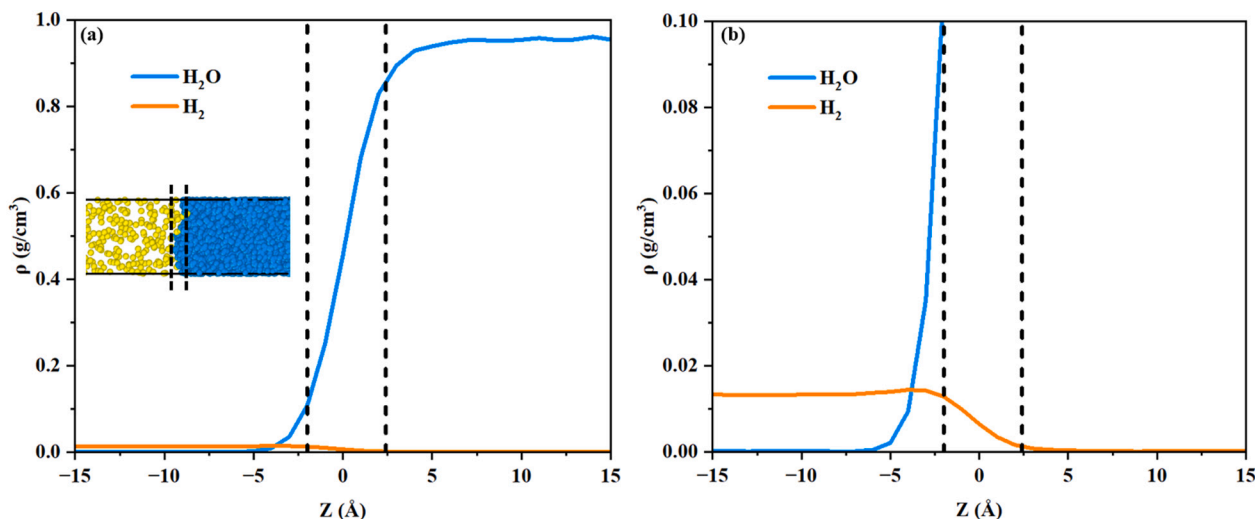


Fig. 3. (a) Density profiles of H_2 - H_2O system at 343 K and 14.5 MPa. (b) The y-axis has been rescaled to highlight the density profile of H_2 . The left and right dashed lines denote 10 % and 90 % density of the bulk water, respectively.

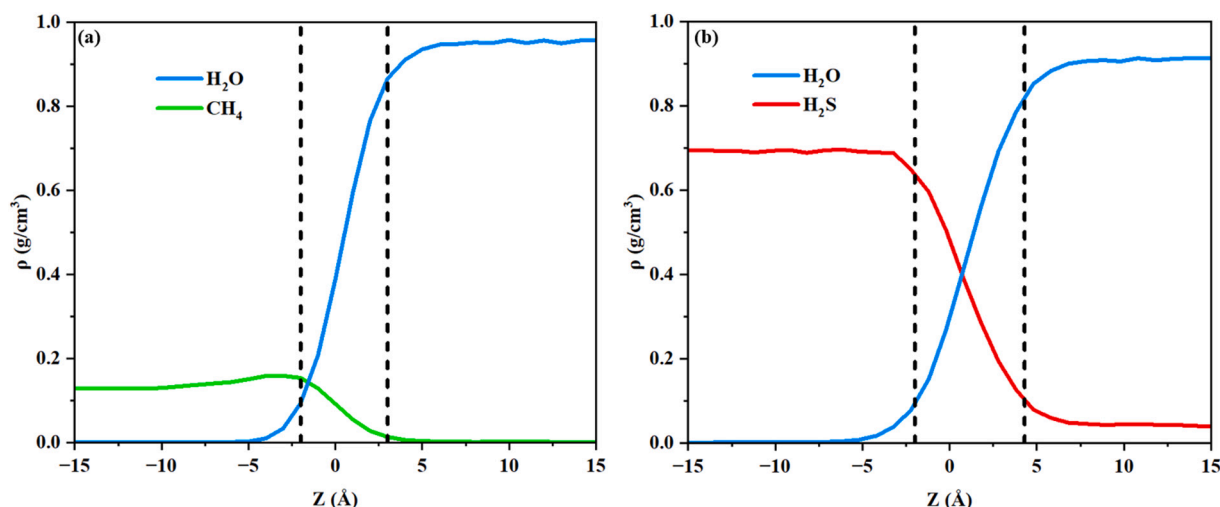


Fig. 4. Density profiles at 343 K and 14.5 MPa: (a) CH_4 - H_2O ; (b) H_2S - H_2O .

4.2. Binary gas-water system

4.2.1. Interfacial tension (IFT) dynamics

Fig. 5 illustrates the relationship between IFT and H_2S concentration for binary systems of $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ and $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ at 343 K and 14.5 MPa. Our findings demonstrate a trend where IFT diminishes with escalating concentrations of H_2S . Notably, at a minimal H_2S concentration of 5 %, the IFT reduction is pronounced, registering at approximately 12 % for the $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ system. In stark contrast, the $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ system exhibits only a 6 % reduction in IFT under the same concentration. This comparative analysis suggests that H_2S exerts a more substantial influence on IFT when interacting with H_2 than CH_4 in an aqueous environment. It is also worth noting that the diminution of IFT becomes more pronounced as H_2S concentration increases beyond the 10 % threshold, indicative of a significant influence of H_2S on the gas-water IFT across both binary systems studied. Yet, it is important to note that such an effect plateaus when the H_2S concentration surpasses 80 %, beyond which any further increase in H_2S concentration yields minimal additional impact on IFT.

4.2.2. Local density profiles

Local density profiles offer useful perspectives on the molecular

distribution at the gas-water interface. Fig. 6 illustrates these profiles for $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ and $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ systems at a nominal H_2S concentration of 5 %. Despite the low concentration, we observe a distinct accumulation of H_2S within the interface region for both systems, which contributes to the observed reduction in IFT. In the H_2S - H_2 - H_2O system, the interface is characterized by a higher local density of H_2S molecules compared to H_2 , underscoring the dominant role of H_2S in affecting interfacial properties. By contrast, in the H_2S - CH_4 - H_2O system, CH_4 molecules demonstrate a greater affinity for the interface, resulting in a higher local density of CH_4 relative to H_2S in this region. This disparity in local density distributions is postulated to explain why H_2S has a more pronounced effect on reducing IFT in the presence of H_2 than with CH_4 , particularly at lower H_2S concentrations.

Fig. 7 reveals changes within the local density profiles of H_2S and H_2 in the $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ system across a spectrum of H_2S concentrations. In parallel, Supplementary Fig. S5 assesses the corresponding local density profiles for H_2S and CH_4 in the $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ system. A clear trend emerges from these analyses: an incremental increase in H_2S concentration within the gas mixture leads to a corresponding rise in H_2S local density at the interface, simultaneously reducing H_2 and CH_4 densities in this region. This inverse relationship is instrumental in the observed IFT reduction as H_2S concentrations climb. Furthermore, a

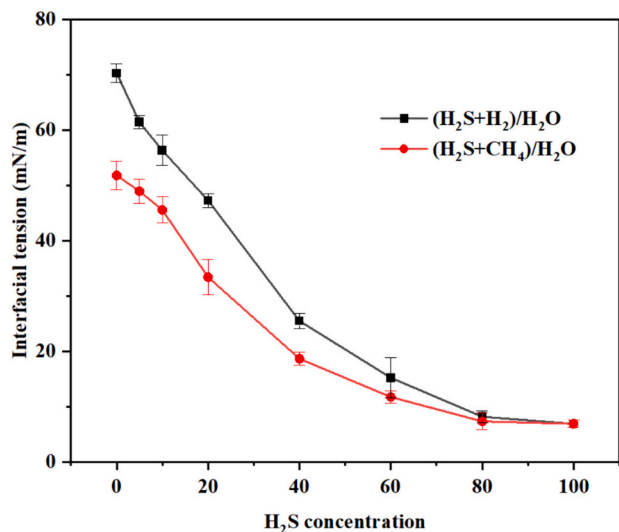


Fig. 5. IFTs at 14.5 MPa and 343 K as a function of H₂S concentration for (H₂S + H₂)/H₂O and (H₂S + CH₄)/H₂O systems.

comparison between Fig. 7(a) and Fig. S5(a) highlights an intriguing dynamic. The presence of CH₄ at the interface results in a relatively lower accumulation of H₂S in the (H₂S + CH₄)/H₂O system compared to the (H₂S + H₂)/H₂O system, given the same H₂S concentration. This phenomenon suggests that CH₄'s interfacial adsorption moderates the impact of H₂S on IFT, providing a partial buffering effect against the IFT reductions driven by H₂S.

4.2.3. Gibbs dividing surface analysis

We determined the Gibbs Dividing Surface (GDS) location to explain the molecular distribution within the interface region. The GDS is identified as the plane where the surplus of water molecules on the gas side is balanced by the shortfall on the water side, as per established methods in the literature [43,59–61,66]. In Supplementary Fig. S6(a), the GDS within the H₂S-H₂O interface is illustrate the concept.

Subsequently, Fig. S6(b) defines the first contact region between H₂S and water, Region II, stretching from the GDS to the right boundary. This demarcation is critical since gas molecules in Region II are in immediate proximity to water molecules, influencing the latter's orientation through direct intermolecular forces. It is accepted that the interactions between H₂S and water molecules within Region II predominantly dictate the IFT, given their direct contact and consequent interaction dynamics. As visualized in Fig. 8, the local H₂S densities within Region II for both (H₂S + H₂)/H₂O and (H₂S + CH₄)/H₂O systems were analyzed to reveal a consistent increase in local H₂S densities. After surpassing an 80 % H₂S concentration, the densities plateau, suggesting a saturation threshold within Region II. This saturation underpins the minimal IFT variations observed beyond the 80 % concentration threshold. The average H₂S densities in Region II, as depicted in Fig. 9, further substantiate this finding. The curve plateaus post the 80 % concentration mark, indicating a saturation point for H₂S in the interface region. Such saturation effects are important in understanding the limits of IFT reduction in response to increased H₂S concentrations within subsurface storage environments.

4.2.4. Molecular orientation

Fig. 10 shows the molecular orientation profiles for water in H₂-H₂O, CH₄-H₂O, and H₂S-H₂O systems, illustrating the spatial orientation of water molecules across the Z direction. These profiles leverage the local

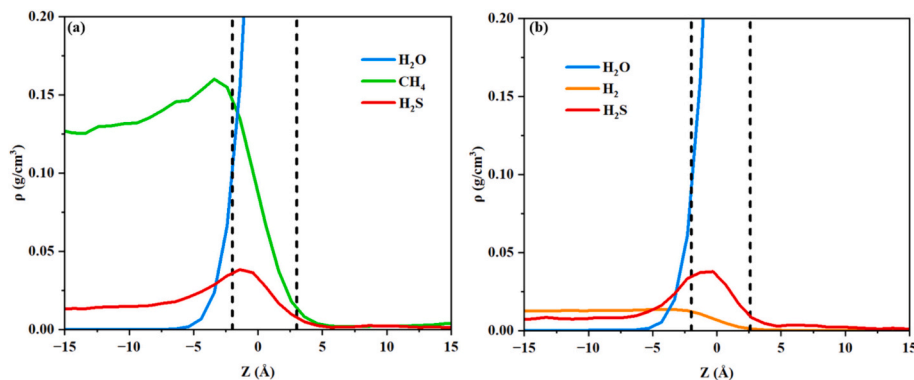


Fig. 6. The local density profiles with 5 % H₂S concentration at 14.5 MPa and 343 K: (a) (H₂S + CH₄)/H₂O; (b) (H₂S + H₂)/H₂O.

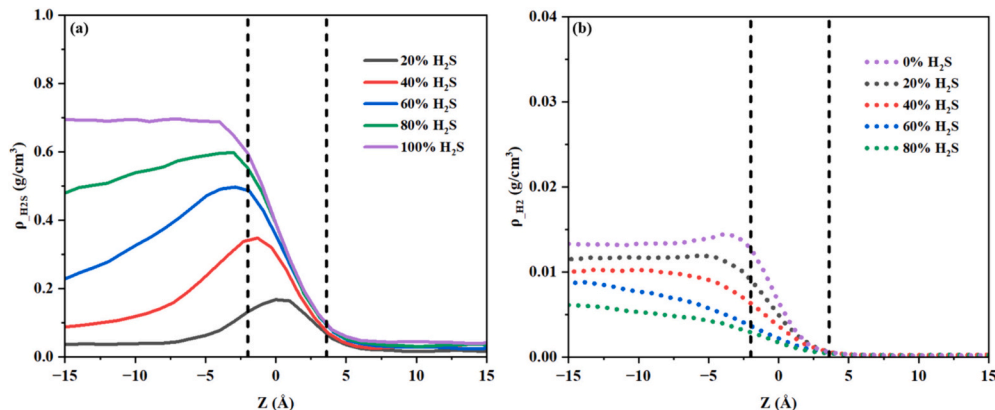


Fig. 7. Local density profiles for the (H₂S + H₂)/H₂O system at different H₂S concentrations: (a) H₂S; (b) H₂.

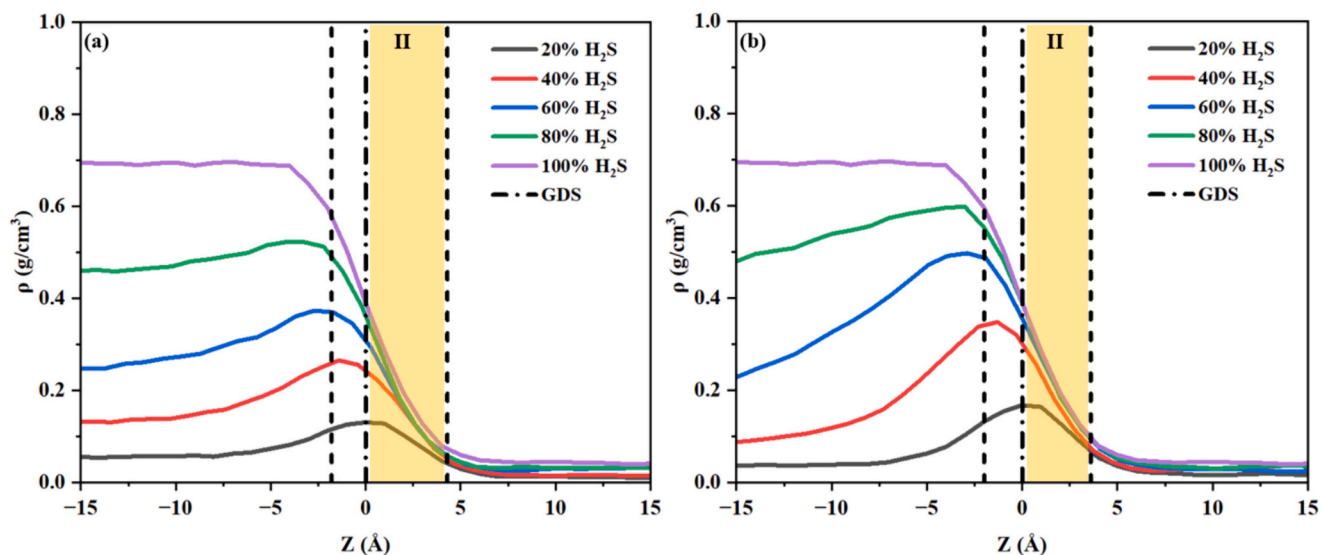


Fig. 8. The local densities of H_2S in Region II are highlighted for (a). $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ and (b). $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ systems with different H_2S concentrations.

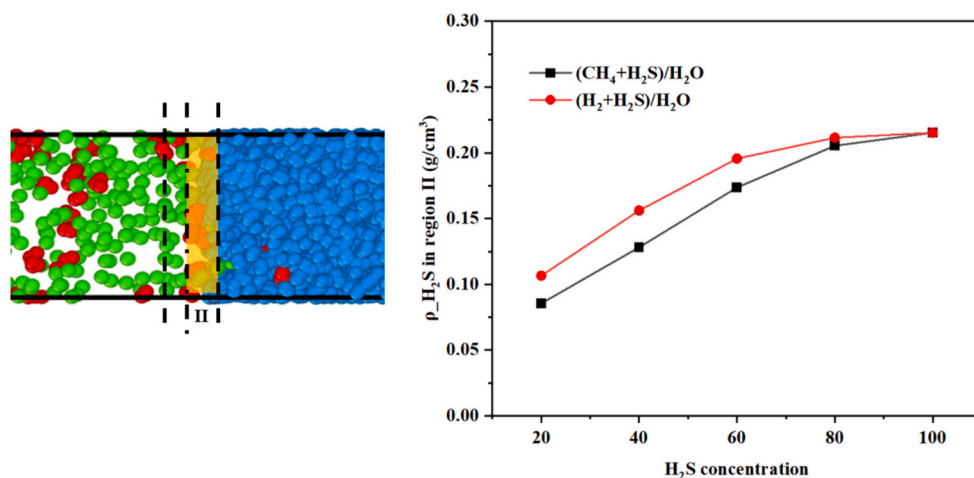


Fig. 9. The local densities of H_2S in region II are averaged for $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ and $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ systems with different H_2S concentrations.

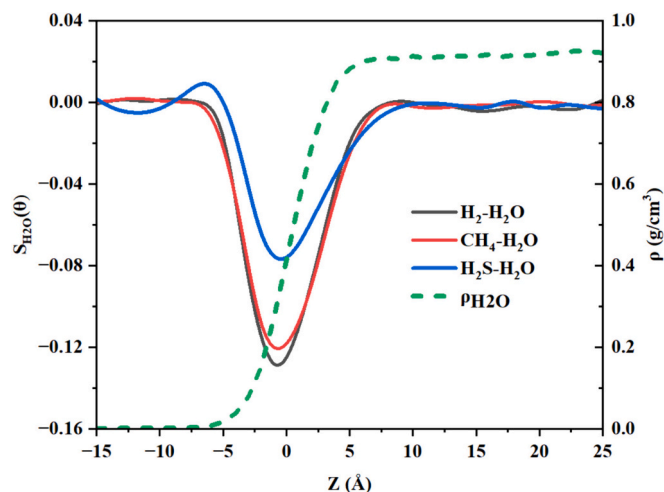


Fig. 10. Orientation profiles of H_2O molecules along the Z direction in three binary gas-water systems. The water density profile is used to locate the gas-water interface region.

density profile of H_2O to demarcate the gas-water interface. In the bulk water phase, the orientation order parameter (S) values approximate zero, reflecting a lack of preferential orientation and a random distribution of molecular dipoles. Conversely, negative S values within the interface region reveal a distinct trend in which water molecules prefer to align parallel to the interface. This observed behavior aligns with findings reported in existing literature for similar gas-water interfaces [53,54].

Notably, the S values for water in the H_2 - H_2O and CH_4 - H_2O systems are more negative than those in the H_2S - H_2O systems. This suggests that in the absence of H_2S , water molecules at the interface exhibit a stronger preferential parallel orientation. The incorporation of H_2S into the water matrix attenuates the sharpness of the phase boundary, potentially transitioning the interface from a distinctly immiscible to a more partially miscible state. This interaction may explain the more randomized orientation of water molecules observed at the H_2S -enriched interface, indicative of the modulating effect of H_2S on the structural characteristics of the interfacial region.

Fig. 11 further demonstrates the orientation order parameter (S) values of water molecules within $(\text{H}_2\text{S} + \text{H}_2)/\text{H}_2\text{O}$ and $(\text{H}_2\text{S} + \text{CH}_4)/\text{H}_2\text{O}$ systems across varying H_2S concentrations. A clear trend emerges from the data: as the H_2S concentration within the gas mixture increases, so

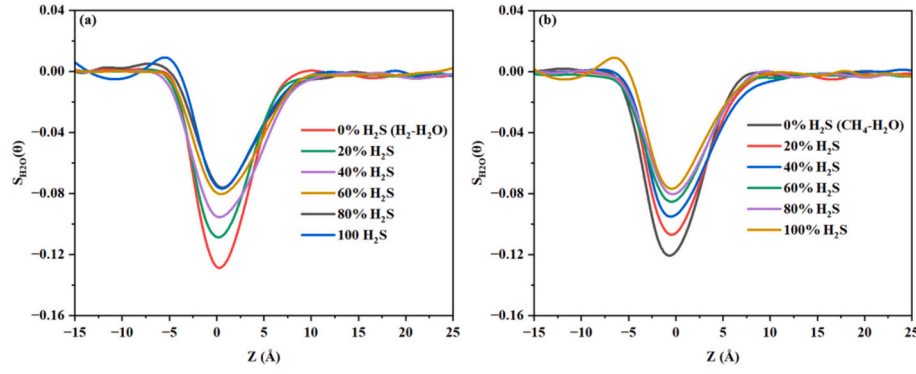


Fig. 11. H₂O orientation profiles with different H₂S concentrations: (a) (H₂S + H₂)/H₂O; (b) (H₂S + CH₄)/H₂O.

does its accumulation at the interface, influencing the preferential orientation of water molecules in this region. Specifically, the S values for water tend to rise with increasing H₂S concentration, indicating a shift towards a less pronounced preferential orientation parallel to the interface.

Yet, beyond a certain saturation point, identified here as an 80 % H₂S concentration, additional increases in H₂S concentration do not significantly alter the S values. This saturation echoes the trends observed in IFT and local density profiles, where a saturation of H₂S in the first contact region leads to minimal further changes in both gas-water IFT and water molecular orientation. Such observations suggest that at H₂S concentrations above 80 %, the interface region's capacity to accommodate more H₂S molecules is maximized, resulting in only marginal subsequent impacts on the interfacial properties.

4.3. Ternary gas-water system

In the context of UHS, where methane may act as a cushion gas during the initial stages [67–71], understanding the interfacial behavior of a ternary (H₂S + H₂ + CH₄)/H₂O system is critical. Fig. 12 illustrates the IFT of the ternary system across a range of H₂S concentrations at 343 K and 14.5 MPa. Notably, in the absence of H₂S (0 % concentration), the IFT of the equimolar (50 % H₂ + 50 % CH₄)/H₂O mixture logically situates itself between the IFTs of the binary H₂-H₂O and CH₄-H₂O systems.

The introduction of H₂S into the ternary system causes a progressive decrease in gas-water IFT. At a modest H₂S concentration of 5 %, a decrease in IFT by approximately 9 % was observed, a reduction that is

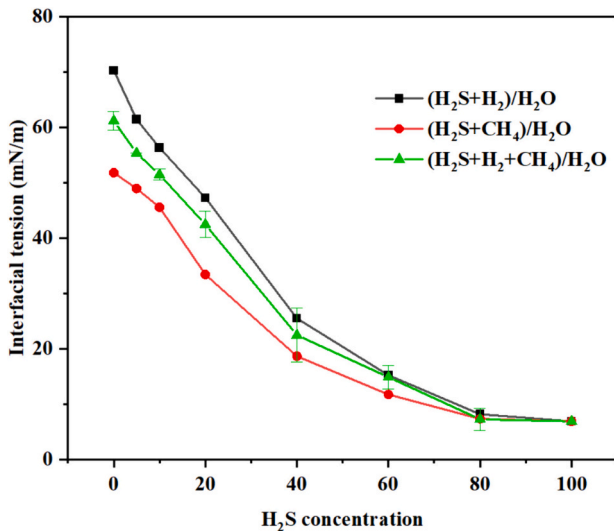


Fig. 12. IFTs of (H₂S + H₂ + CH₄)/H₂O are compared with binary gas-water systems at 14.5 MPa and 343 K with different H₂S concentrations.

more substantial than that seen in the (H₂S + CH₄)/H₂O system but less so compared to the (H₂S + H₂)/H₂O system with the same H₂S concentration. This subtle behavior underscores the influence of H₂S on gas-water IFT, even at lower concentrations, which is particularly relevant in UHS scenarios where only limited volumes of cushion gas are introduced.

Furthermore, consistent with observations from binary systems, an increase in H₂S concentration beyond 80 % does not significantly impact the IFT, indicating a saturation effect similar to that seen in the binary counterparts. This trend reaffirms the importance of considering H₂S presence when evaluating UHS interface properties, even when CH₄ is present as a cushion gas.

Fig. 13(a) presents density profile analyses of the (H₂S + H₂ + CH₄)/H₂O system at a 40 % H₂S concentration. These analyses reveal a significant presence of both H₂S and CH₄ in the interface region. This is attributed to the adsorption of H₂S and the adsorption of CH₄, which collectively surpass the presence of H₂ in this critical zone. Fig. 13(b) expands on this by illustrating how varying concentrations of H₂S affect its density within the interface region, particularly highlighting the first contact region, Region II. The data indicate that an increase in H₂S concentration leads to a corresponding increase in its local density at the interface, which in turn contributes to the decrease in IFT. Notably, the profiles for H₂S at 80 % and 100 % molar concentrations are nearly indistinguishable within Region II, signifying a saturation point for H₂S at around the 80 % concentration level, consistent with their average densities in Region II shown in Fig. 14(a). Beyond this saturation point, further increases in H₂S concentration do not yield significant changes in IFT, implying a limit to the interface's capacity to accommodate additional H₂S molecules.

Furthermore, the molecular orientation of water in the interface region, as depicted in Fig. 14(b), aligns with the variations in IFT related to H₂S concentration. The consistency of orientational behavior past the 80 % H₂S concentration mirrors the saturation effect, confirming that water molecules' interfacial tension and molecular orientation experience minimal changes once the saturation threshold is reached.

5. Conclusions

This study elucidates the critical role of H₂S generated from microbial activity in shaping gas-water interactions during underground hydrogen storage. Using molecular dynamics simulations, we have demonstrated that the presence of H₂S significantly influences interfacial tension between pore water and gas mixtures, notably those containing hydrogen and methane.

Our models establish a clear trend of decreasing IFT with increasing H₂S concentration under subsurface storage conditions of 14.5 MPa and 343 K. Remarkably, even a modest H₂S molar concentration (e.g., 5 %) can lead to a substantial IFT reduction, with a 12 % decrease in H₂S-H₂-H₂O mixtures compared to a 6 % decrease in H₂S-CH₄-H₂O mixtures. We

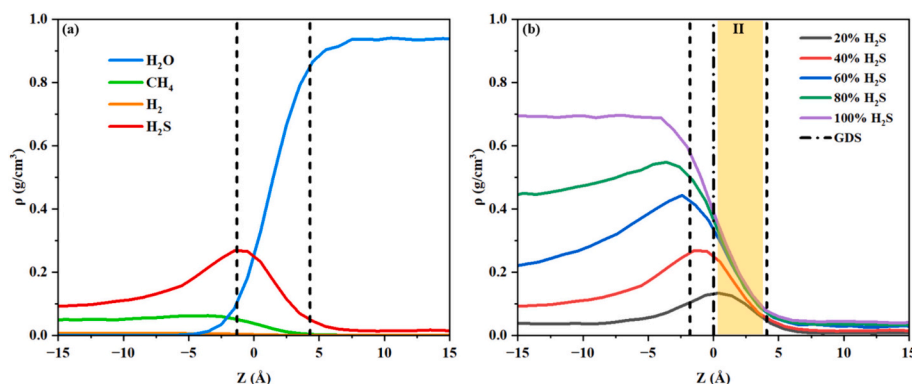


Fig. 13. Local density profiles at 343 K and 14.5 MPa: (a) (H₂S + H₂ + CH₄)/H₂O system with 40 % H₂S concentration; (b) H₂S of (H₂S + H₂ + CH₄)/H₂O systems.

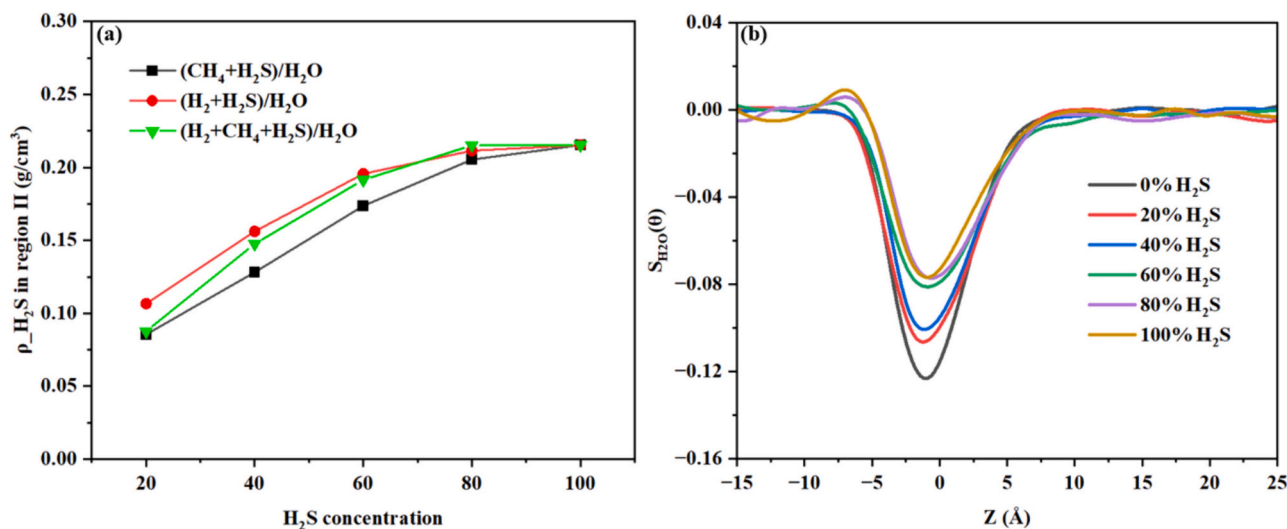


Fig. 14. (a) Average densities of H₂S in region II and (b) H₂O orientation profiles in (H₂S + H₂ + CH₄)/H₂O system with different H₂S concentrations.

observed a saturation effect beyond an 80 % H₂S concentration, with only marginal further reductions in IFT.

In-depth analyses of local density distributions and water molecule orientations have illuminated the mechanisms behind these IFT changes. The accumulation of H₂S at the interface, resulting from its absorption into the water, consistently contributed to IFT reduction across all mixtures. Additionally, CH₄ adsorption at the interfaces partially counteracts the IFT decrease caused by H₂S, particularly noticeable at lower H₂S concentrations where CH₄'s influence is more pronounced. In contrast, no significant adsorption or absorption of H₂ at the interface was detected.

The molecular orientation of water molecules at the interface corroborates the IFT and density distribution trends. From 0 % to 80 % H₂S concentration, changes in water orientation play a considerable role in lowering IFT. At concentrations above 80 %, the near saturation of H₂S in the first contact region results in minimal further orientation shifts and IFT reduction.

These findings advance our understanding of the molecular-level phenomena governing H₂S's impact on gas-water IFT, thereby informing the management and optimization strategies for UHS in depleted hydrocarbon reservoirs. Future work should focus on the experimental validation of these simulations to corroborate the observed trends and to refine the molecular models used. Further, it may be useful to assess the effects of other impurities commonly found in hydrogen storage environments, such as carbon dioxide and nitrogen. Changes in pressure and temperature during reservoirs operations may also have an effect on IFT and could be explored in further analysis. Finally, the macro-scale effect

of mixture-dependent IFT should be considered in upscaled pore and continuum scale models, particularly in its relation to relative permeability, sweep efficiency and mixing mechanisms.

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CRediT authorship contribution statement

Qiuhaio Chang: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Liangliang Huang:** Writing – review & editing, Software, Formal analysis. **Kelsey McKenzie:** Writing – original draft, Visualization, Conceptualization. **Carlo Carere:** Writing – review & editing, Visualization, Conceptualization. **Matthew Stott:** Writing – review & editing, Conceptualization. **Andy Nicol:** Project administration, Funding acquisition, Conceptualization. **David Dempsey:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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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.2024.112766>.

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