

2-15-2022

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[10.1016/j.jcis.2021.10.080](https://doi.org/10.1016/j.jcis.2021.10.080)

Ali, M., Yekeen, N., Pal, N., Keshavarz, A., Iglauer, S., & Hoteit, H. (2022). Influence of organic molecules on wetting characteristics of mica/H<sub>2</sub>/brine systems: Implications for hydrogen structural trapping capacities. *Journal of Colloid and Interface Science*, 608(Part 2), 1739-1749.

<https://doi.org/10.1016/j.jcis.2021.10.080>

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# Influence of organic molecules on wetting characteristics of mica/H<sub>2</sub>/brine systems: Implications for hydrogen structural trapping capacities

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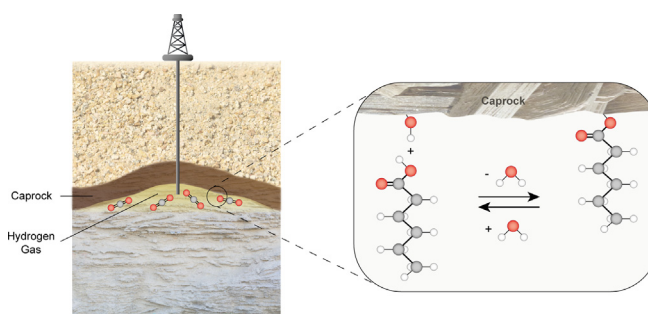
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## HIGHLIGHTS

- Caprock geological formations depict intermediate-wet conditions.
- Increased pressure and reduced temperature inversely affect hydrogen wettability.
- Hydrophilic caprock geological formations become intermediate wet in the presence of organic acids.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 8 September 2021

Revised 8 October 2021

Accepted 14 October 2021

Available online 18 October 2021

### Keywords:

Wettability

Hydrogen geo-storage

Organic acids

Caprock formation

## ABSTRACT

**Hypothesis:** Actualization of the hydrogen (H<sub>2</sub>) economy and decarbonization goals can be achieved with feasible large-scale H<sub>2</sub> geo-storage. Geological formations are heterogeneous, and their wetting characteristics play a crucial role in the presence of H<sub>2</sub>, which controls the pore-scale distribution of the fluids and sealing capacities of caprocks. Organic acids are readily available in geo-storage formations in minute quantities, but they highly tend to increase the hydrophobicity of storage formations. However, there is a paucity of data on the effects of organic acid concentrations and types on the H<sub>2</sub>-wettability of caprock-representative minerals and their attendant structural trapping capacities.

**Experiment:** Geological formations contain organic acids in minute concentrations, with the alkyl chain length ranging from C<sub>4</sub> to C<sub>26</sub>. To fully understand the wetting characteristics of H<sub>2</sub> in a natural geological picture, we aged mica mineral surfaces as a representative of the caprock in varying concentrations of organic molecules (with varying numbers of carbon atoms, lignoceric acid C<sub>24</sub>, lauric acid C<sub>12</sub>, and hexanoic acid C<sub>6</sub>) for 7 days. To comprehend the wettability of the mica/H<sub>2</sub>/brine system, we employed a contact-angle procedure similar to that in natural geo-storage environments (25, 15, and 0.1 MPa and 323 K).

**Findings:** At the highest investigated pressure (25 MPa) and the highest concentration of lignoceric acid (10<sup>-2</sup> mol/L), the mica surface became completely H<sub>2</sub> wet with advancing ( $\theta_a = 106.2^\circ$ ) and receding ( $\theta_r = 97.3^\circ$ ) contact angles. The order of increasing  $\theta_a$  and  $\theta_r$  with increasing organic acid contaminations

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is as follows: lignoceric acid > lauric acid > hexanoic acid. The results suggest that H<sub>2</sub> gas leakage through the caprock is possible in the presence of organic acids at higher physio-thermal conditions. The influence of organic contamination inherent at realistic geo-storage conditions should be considered to avoid the overprediction of structural trapping capacities and H<sub>2</sub> containment security.

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## 1. Introduction

The world economies have been powered by fossil fuels, such as coal, natural gas, and oil, for more than 150 years [1,2]. However, the burning of fossil fuels has resulted in carbon dioxide and other greenhouse gases releasing into the atmosphere, contributing to unfavorable changes in the Earth's climate [3]. The hydrogen (H<sub>2</sub>) economy is an objective, totally replacing fossil fuels with clean and green energy [4–12]. Successfully implementing a H<sub>2</sub> economy entails H<sub>2</sub> production via electrolysis and bi-reforming methane at an industrial scale followed by underground H<sub>2</sub> storage (UHS), which can be retrieved at later stages for use [4,5,12–19,91].

The most suitable geo-storage formations for H<sub>2</sub> are basaltic formations, organic-rich shales, tight gas formations, depleted hydrocarbon reservoirs, deep saline aquifers, and coal seams [6,10,13,14,20–27,92]. The interfacial tension between the rock and fluids and the wettability of the rock in the presence of the respective gas are key parameters in keeping the gas immobilized at the subsurface via containment security [13,15,17,18,28–31]. The gas can be permanently immobilized during UHS via various trapping mechanisms (e.g., capillary, structural, mineral, dissolution, and adsorption trapping) [17,32–35]. However, residual and structural trapping mechanisms have been identified as the main mechanisms of gas storage in geological media, where strong correlations exist between capillary forces and buoyancy [35–38].

The literature reports that organic acids are readily available in geo-storage formations because geological formations are anoxic where reductive conditions succeed [13,35,39–45]. Even though the presence of organics in geo-storage formations and caprock is quite minimal, their minute existence is sufficient to alter the initial hydrophilic condition of the storage medium into hydrophobic conditions (gas wet), which significantly influence the H<sub>2</sub> trapping potential and containment safety [13,35,42–44].

The H<sub>2</sub>-wettability of storage rocks at geo-storage conditions has recently been reported for quartz [13,18], sandstone [15], basaltic rocks [14], and coal seams [17]. However, no literature is available on H<sub>2</sub> wetting characteristics for caprock representative minerals and the associated structural trapping capacities. Structural trapping failure and H<sub>2</sub> leakage through the caprock could occur if the rock becomes H<sub>2</sub> wet due to the upward-directed negative suction force [35,36].

Thus, the influence of organic acid contaminations on the sealing capacities of the caprock must be considered to accurately assess the rock/H<sub>2</sub>/brine wettability at realistic geo-storage conditions. Mica is a good caprock-analogous mineral with ample presence in shale caprock formations and a chemical structure (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub>) equivalent to that of illite [46–49]. Therefore, we measured the advancing ( $\theta_a$ ) and receding contact angles ( $\theta_r$ ) of organic-aged, mica/H<sub>2</sub>/brine systems in geo-storage conditions (323 K and 0.1–25 MPa). The contact angles of mica/H<sub>2</sub>/brine were compared with mica/CO<sub>2</sub>/brine in the presence of organic acids to assess the feasibility of CO<sub>2</sub> as a cushion gas for H<sub>2</sub> retrieval. Thus, the information from this research contributes to the broader-scale implementation of UHS and may assist in the curtailment of project uncertainty.

## 2. Experiment

### 2.1. Materials

The substrate (pristine mica) used as representative caprock was bought from Ward's Natural Science with the following magnitudes (20 × 15 × 3 mm = L × W × H). For measurement of contact angles, the brine concentration was prepared by dissolving 10 wt% of NaCl (purity 99.9%; Rowe Scientific) in deionized water (ultrapure grade; David Gray; with an electrical conductivity of 0.02 mS/cm). Three organic acids (lignoceric, lauric, and hexanoic acids) with varying carbon chain lengths were chosen to age the mica substrates (Sigma Aldrich; > 98 mol% purity). The organic acid details are presented in Table 1.

Nitrogen (gas code 234 from BOC, with 99.999% ultrapure grade) was used for cleaning and removing contaminants from the mica mineral surfaces in pre- and post-aging conditions with organic acids. Moreover, H<sub>2</sub> (gas code 240 from BOC, with 99.999% ultrapure grade) was used to measure the contact angles. The *n*-decane (99.9 mol% pure; Chem-Supply) was used as a base solution to prepare various concentrations of organic acids.

### 2.2. Mica substrate cleaning and aging procedures

The mica substrates were cleaned with deionized water to eliminate surface remains and dust. Then, the substrates were blown with nitrogen (ultrapure) and dried at 80 °C for 120 min to remove the thin film of water after the initial cleaning process. Subsequently, the residual organic impurities were removed from the substrates by treating the samples with air plasma (Diemer Yocto Instrument) for 20 min [50,51]. Ionization of the mica surfaces to simulate caprock conditions [52,53] was ensured by putting the substrate in 2 wt% of NaCl solution for half an hour at room conditions with a ratio of 1:5 (e.g., 1 g of mica mineral was placed in 5 g of pH-calibrated 2 wt% NaCl solution to maintain the uniformity of the ionization aging process). The pH of the brine was maintained at 4 pKa through the addition of aqueous hydrochloric acid (HCl) droplets (5 vol% concentration, purity > 99%; from Sigma Aldrich). This procedure boosts the adsorption of organic acid on the mica surface [42,54–56].

Subsequently, clean ultrapure nitrogen was used to blow off the residual brine from the surface of the ionized mica. For one week, the mica surfaces ionized with HCl/Brine were put in various organic acid/*n*-decane solutions (10<sup>-9</sup> to 10<sup>-2</sup> mol/L) to simulate contact with the formation water for sufficient geological periods [57–59]. This process was conducted by initially preparing a 10<sup>2</sup> mol/L concentration of various organic acids (hexanoic, lauric, and lignoceric acids) by mixing with the *n*-decane solution based on their respective molecular weights at 323 K. The magnetic stirrer and hot plate were used to mix the organic acids with the *n*-decane solution. Afterward, the dilution method was used to prepare lower organic concentrations (i.e., 9 g of *n*-decane solution was mixed with 1 g of 10<sup>-2</sup> mol/L organic concentration solution to prepare a 10<sup>-3</sup> mol/L concentration, etc.). Mica substrates were aged based on a ratio of 1:5 (e.g., 1 g of mica mineral was placed in 5 g of organic solution to maintain the uniformity of the aging process [39,40,60–62]. Organic acids are readily available in geo-

**Table 1**  
Organic acid details for this research.

| Acids      | pH (pKa) | State  | Molar mass (g/mol) | Carbon atom numbers | Molecular formula                              | Molecular structure |
|------------|----------|--------|--------------------|---------------------|--|---------------------|
| Lignoceric | 7.4      | Solid  | 368.63             | 24                  | C <sub>24</sub> H <sub>48</sub> O <sub>2</sub> |                     |
| Lauric     | 5.3      | Solid  | 200.318            | 12                  | C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> |                     |
| Hexanoic   | 4        | Liquid | 116.158            | 6                   | C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>  |                     |

storage formations, and the reaction (chemical bonding) that occurs because of the esterification of organics on the –OH of mica substrates makes the mica surfaces more hydrophobic [32,35,62] (Scheme 1).

### 2.3. Procedure for contact-angle measurements

The procedure for the contact-angle (advancing ( $\theta_a$ ) and receding ( $\theta_r$ )) measurements for the mica/H<sub>2</sub>/brine were conducted at high pressure and temperature (HPHT) through the tilted plate technique [45,62,63]. The HPHT cell comprised a Hastelloy material with the capacity to withstand high temperature and pressure (up to 423 K and 60 MPa), with a sample container tilted at 17° [35]. The HPHT cell was connected to two high-precision ISCO syringe pumps (supplied by Teledyne ISCO D-260), with a pressure accuracy of 0.01%. The first pump supplied the brine, and the second pump supplied the gas (H<sub>2</sub>) during the contact-angle measurement process.

The mica mineral surfaces placed in organic concentrations were positioned at a tilt angle of (17°) in the sample holder. Afterward, the HPHT Hastelloy cell was tightly closed, followed by a steady injection of H<sub>2</sub> pending the attainment of the expected pressure (0.1–25 MPa) and temperature (323 K). Model 900F heating baths (Julabo) controlled the temperature of the fluid in ISCO pumps, whereas the controller and strip heating tape (HTC101-002; Omega Company) controlled the cell temperature [35,41].

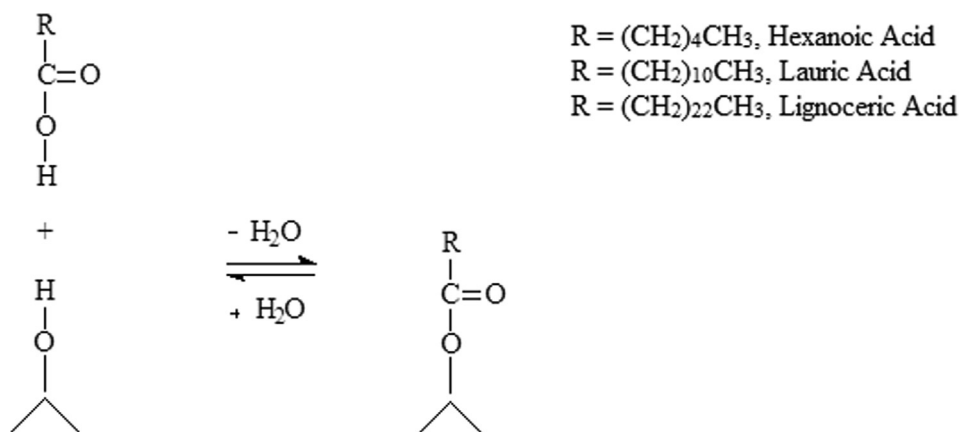
After filling the cell with H<sub>2</sub> at the required geo-storage conditions, the pressure was equilibrated in both pumps and the HPHT cell. A droplet of the equilibrated brine (5.4  $\mu$ L  $\pm$  0.77  $\mu$ L) was presented from the second ISCO pump through a precise needle onto the tilted mica substrate. When the drop of brine touched the surface, the contact angles ( $\theta_a$ , and  $\theta_r$ ) were recorded at the leading

and trailing corners of the brine droplet [46,64–66], using a high-performance video camera (Fujinon CCTV lens: Basler sCA 640–70 fm; HF35HA-1B; frame rate = 71 fps; 1:1.6/35 mm, pixel size = 7.4  $\mu$ m). The images were analyzed, and the contact angles were measured using ImageJ software. Every measurement was repeated three times for the desired experimental situation, followed by computing the contact angles based on the mean values (standard deviation of  $\pm 5^\circ$  for 25 MPa and  $\pm 3^\circ$  for 0.1 and 15 MPa, respectively) [35,41]. The schematic description of the contact-angle system is depicted in Fig. 1.

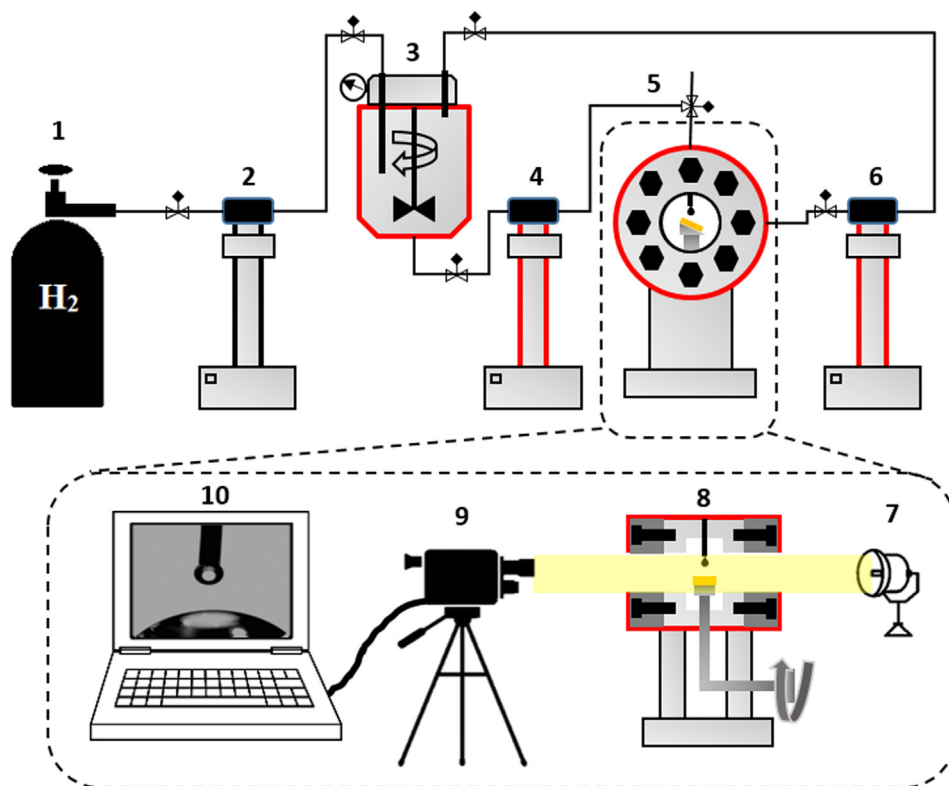
### 3. Results and discussion

The wettability and interfacial phenomena of any geological formation is an important factor that regulates the ability of gas (H<sub>2</sub> in this case) to spread across the formation [67–69]. It controls the rate of gas injection [47,70] and gas withdrawal [13,14,18,71], fluid-flow dynamics [33,70,72], and storage potential [33,34,36] and reduces the uncertainty [41,73–75]. In this context, the caprock formation provides the sealing capacity against the upward flow of H<sub>2</sub> gas for permanent immobilization in the geological formation. When H<sub>2</sub> is injected into the geological formation, it displaces the wetting phase (brine or formation water). This scenario is related to the brine receding contact angle (structural trapping may fail if  $\theta_r > 90^\circ$ ) [76]. Similarly, when cushion gas (CO<sub>2</sub> in this case) is injected to produce H<sub>2</sub> or the wetting phase exerts pressure on the nonwetting phase due to the closure of H<sub>2</sub> injection, this scenario is related to the brine advancing contact angle where the primary drainage does not affect the wettability ( $\theta_a < 50^\circ$ ) [18,48,77,78].

Natural geological formations contain organic acids, which are anoxic and favor reductive conditions [57,58,79]. Therefore, con-



**Scheme 1.** Chemisorption of organic acids on mica surfaces ( $\wedge$  indicates the solid bulk of mica) [35].



**Fig. 1.** Schematic description of the contact-angle system: (1) H<sub>2</sub> gas bottle, (2) HPHT syringe pump to regulate the H<sub>2</sub> flow, (3) HPHT live brine formulation mixing reactor, (4) HPHT syringe pump to regulate the brine flow, (5) IFT cell of Hastelloy material with a tilted plate inside, front view, (6) HPHT syringe pump for H<sub>2</sub> injection into the cell, (7) light projection, (8) IFT cell of Hastelloy material with a tilted plate inside, side view, (9) video camera (high resolution), and (10) interpretation software (ImageJ).

tact angles ( $\theta_a$  and  $\theta_r$ ) were conducted on the mineral surfaces aged in organic acids for mica/H<sub>2</sub>/brine systems. For comparison, advancing and receding contact angles were initially measured on pure mica substrates (this is not the case for natural geological conditions) in the H<sub>2</sub> atmosphere in geological physio-thermal conditions (323 K and 15 and 25 MPa). Pure mica substrates exhibited hydrophilic characteristics with  $\theta_a = 42.9^\circ$  and  $\theta_r = 36.6^\circ$  at 15 MPa and  $\theta_a = 53.4^\circ$  and  $\theta_r = 48.1^\circ$  at 25 MPa.

### 3.1. Effects of organics on hydrogen wettability

It is pivotal to comprehend the wetting characteristics of geological formations and caprock in the H<sub>2</sub> atmosphere to investigate structural and residual trapping capacities for H<sub>2</sub> geo-storage potential [13]. The plots of the organic acid concentrations (lignoceric, lauric, and hexanoic acids) versus the contact angle in a H<sub>2</sub> atmosphere are presented in Figs. 2 to 4. The plotted graphs visibly indicate that higher advancing and receding contact angles were obtained at higher concentrations of organic acids. When the mica substrates were aged in lignoceric acid at 323 K and 15 MPa,  $\theta_a$  increased from 63.2° to 79.6° when lignoceric acid concentration increased from 10<sup>-9</sup> mol/L to 10<sup>-5</sup> mol/L. In contrast, when the lignoceric acid concentration increased to 10<sup>-2</sup> mol/L in the same physio-thermal conditions,  $\theta_a$  attained 91.8°, implying that the mica substrate wetting conditions changed to an intermediate-wet state from the weakly water-wet state. Similarly, at the highest investigated pressure (25 MPa) with the lignoceric acid concentration 10<sup>-2</sup> mol/L, the mica surface became completely H<sub>2</sub> wet with  $\theta_a = 106.2^\circ$  and  $\theta_r = 97.3^\circ$ , respectively.

However, compared with CO<sub>2</sub> at 25 MPa and 323 K with a 10<sup>-2</sup> mol/L lignoceric acid concentration, Fig. 2 further indicates that the  $\theta_a$  and  $\theta_r$  for the mica/CO<sub>2</sub>/brine systems were measured as 133°

and 125°. This results imply that the H<sub>2</sub>-wettability of mica is less than the CO<sub>2</sub>-wettability of mica at similar conditions due to the lower density of H<sub>2</sub> compared to CO<sub>2</sub> and that CO<sub>2</sub> could be used as a cushion gas during H<sub>2</sub> retrieval [13,14].

The aging of the mica substrates in various concentrations of lauric acid confirmed the possibility of H<sub>2</sub> gas leakage through the caprock, but the degree of change is less than that for lignoceric acid contaminations. Moreover, Fig. 3 demonstrates that small concentrations of lauric acid in the caprock could alter the wetting conditions from the weakly water-wet to intermediate-wet state in the H<sub>2</sub> atmosphere. For instance, at 323 K and 25 MPa,  $\theta_a$  increased from 60.4° at 10<sup>-9</sup> mol/L to 74.7° at 10<sup>-5</sup> mol/L and to 89.2° at 10<sup>-2</sup> mol/L, whereas  $\theta_r$  increased from 55.3° at 10<sup>-9</sup> mol/L to 68.3° at 10<sup>-5</sup> mol/L and to 83.8° at 10<sup>-2</sup> mol/L, respectively. Compared with CO<sub>2</sub> at similar physio-thermal conditions, the H<sub>2</sub>-wettability of mica was less than the CO<sub>2</sub>-wettability in the presence of lauric acid. For the mica/CO<sub>2</sub>/brine contact angles at 323 K and 25 MPa with a 10<sup>-2</sup> mol/L lauric acid concentration,  $\theta_a$  was 110.1° and  $\theta_r$  was 102.3°, respectively.

When mica substrates were aged in various hexanoic acid concentrations in the H<sub>2</sub> atmosphere (Fig. 4), the contact-angle change was lower compared to the contact angles for the lauric and lignoceric acids. For example, at 15 MPa and 323 K,  $\theta_a$  increased from 46.1° at 10<sup>-9</sup> mol/L to 56.4° at 10<sup>-5</sup> mol/L and to 67.5° at 10<sup>-2</sup> mol/L. Similarly, at higher pressure (25 MPa) with similar hexanoic acid aging conditions, the degree of change in the contact angle was higher than that for the lower pressure (15 MPa). For example, at 25 MPa and 323 K with a 10<sup>-2</sup> mol/L hexanoic acid concentration,  $\theta_a$  was 80.3° and  $\theta_r$  was 74.7°, respectively. Comparing it with CO<sub>2</sub> in similar physio-thermal conditions, the CO<sub>2</sub>-wettability was higher than the H<sub>2</sub>-wettability in the presence of hexanoic acid. For the mica/CO<sub>2</sub>/brine contact angles at 323 K and 25 MPa with a 10<sup>-2</sup>

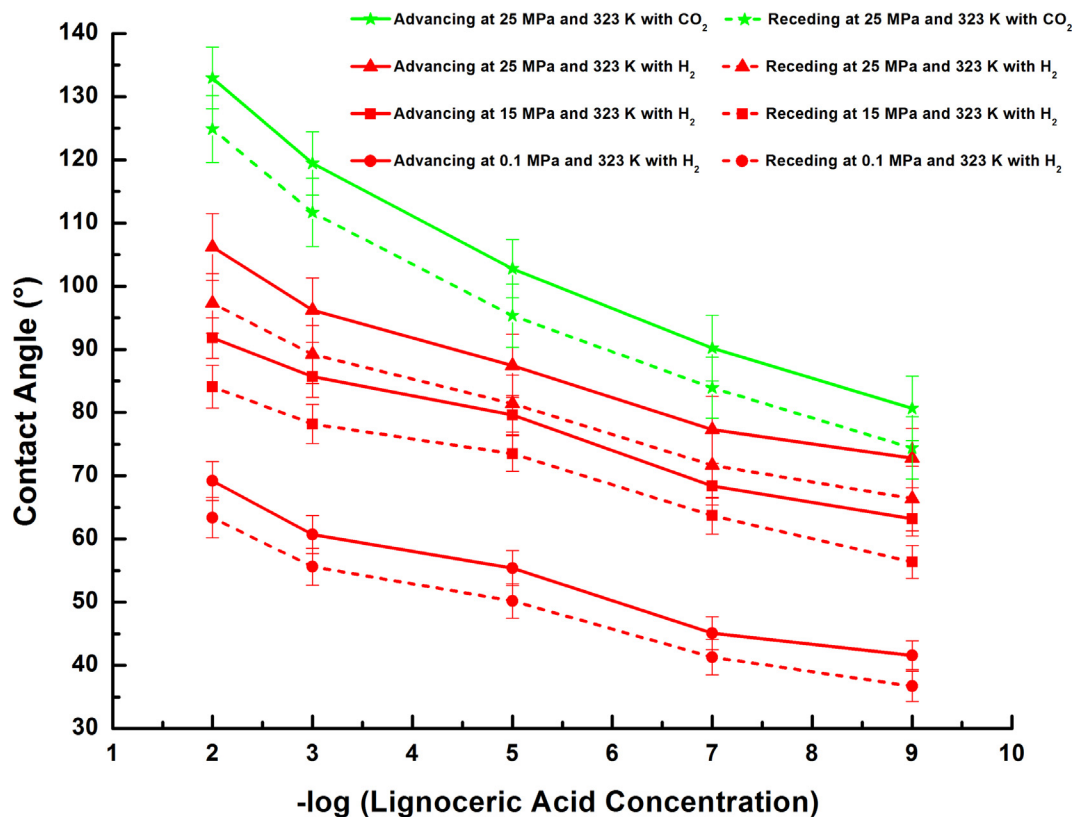


Fig. 2. Effect of the lignoceric acid concentration and pressure on the mica/H<sub>2</sub>/brine and mica/CO<sub>2</sub>/brine contact angles. The CO<sub>2</sub> dataset was acquired from [35].

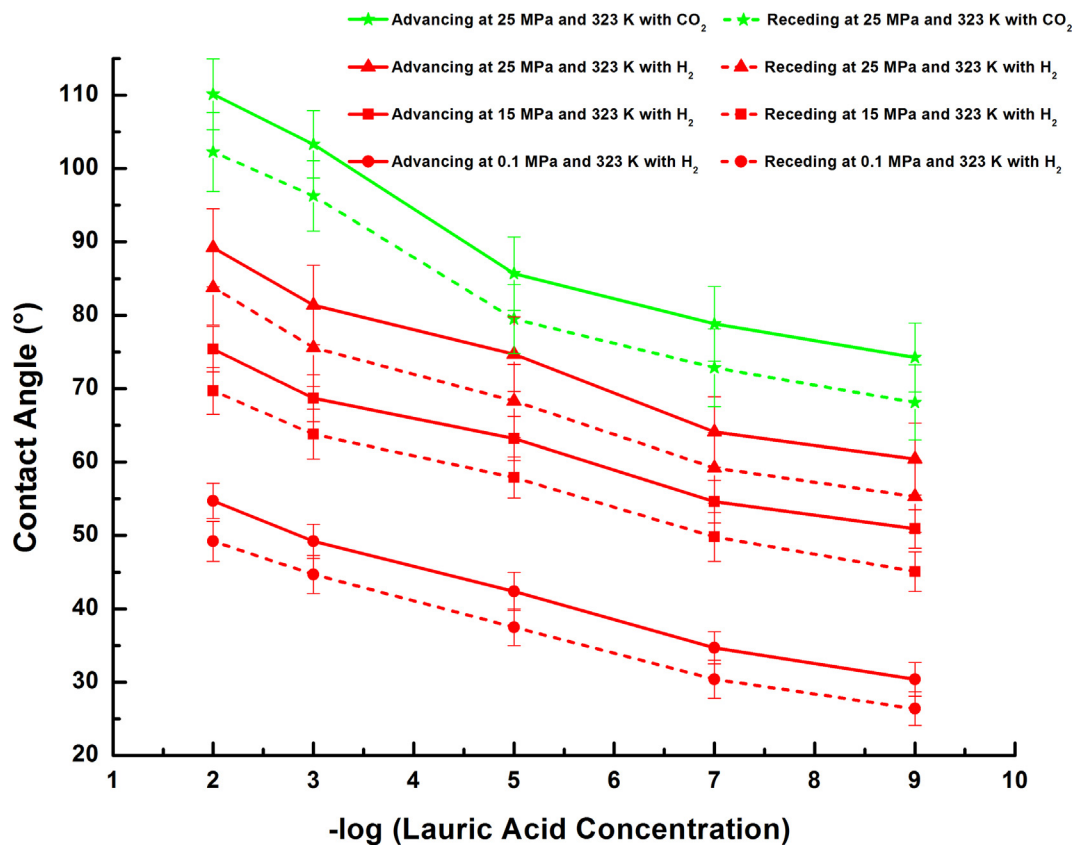


Fig. 3. Effect of the lauric acid concentration and pressure on the mica/H<sub>2</sub>/brine and mica/CO<sub>2</sub>/brine contact angles. The CO<sub>2</sub> dataset was acquired from [35].

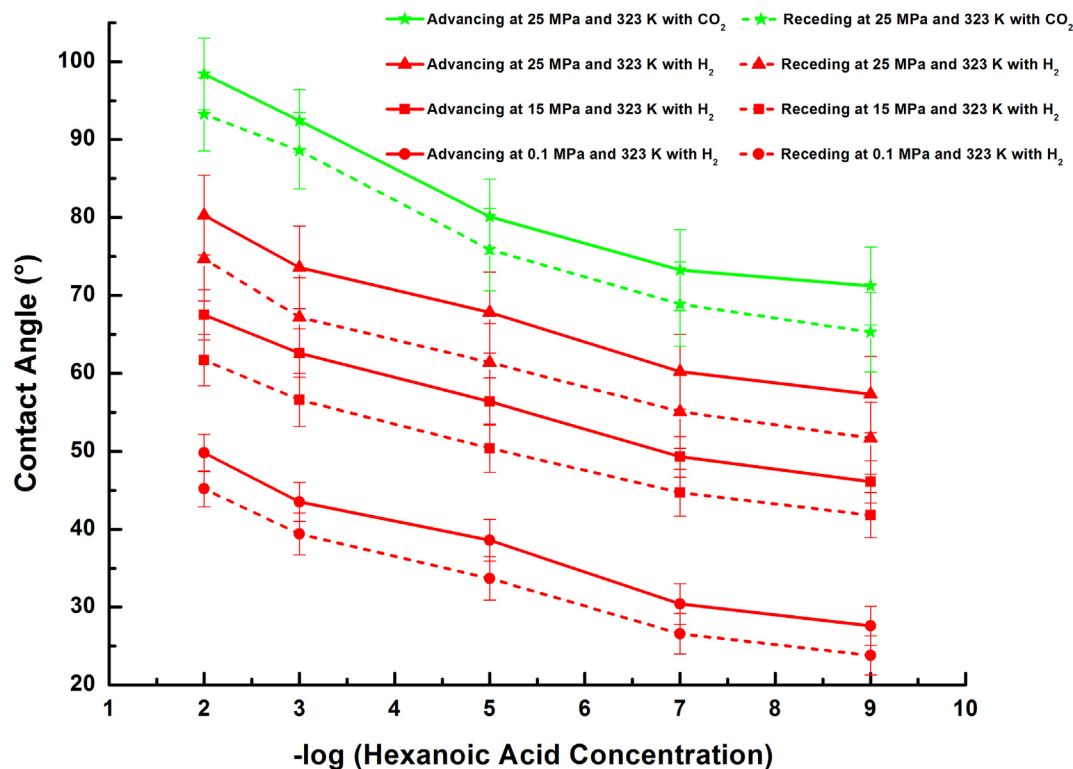


Fig. 4. Effect of the hexanoic acid concentration and pressure on the mica/H<sub>2</sub>/brine and mica/CO<sub>2</sub>/brine contact angles. The CO<sub>2</sub> dataset was acquired from [35].

mol/L hexanoic acid concentration,  $\theta_a$  was 98.4° and  $\theta_r$  was 93.3°, respectively.

These contact-angle datasets suggest that the structural sealing potential of the caprock is bound to reduce in the presence of organic acids and at high pressures, resulting in H<sub>2</sub> gas leakage through the caprock due to the upward negative suction force [13,35,39,42–44,54,80]. The higher hydrophobicity of the mica substrates is attributed to the covalent bonding between the hydroxyl groups of organic acids and the mica surface [42–44]. All the experimental contact angle data in a tabular form in the presence of organic acids for mica/H<sub>2</sub>/brine system is presented in [supplementary information](#) as Table S1.

### 3.2. Effect of pressure and alkyl chain length on hydrogen wettability

Wetting characteristics influence geological formations via direct or indirect involvement of H<sub>2</sub> geo-storage [15,19]. The presence of organic molecules in geological formations is a pertinent factor, and the results reveal that organic acids have substantially altered the wettability in hydrophobic conditions in the presence of H<sub>2</sub>, regardless of the nature of organic acid [35]. However, the molecular structure of organic acids (number of carbon atoms) has a crucial role in determining the degree of change in H<sub>2</sub>-wettability of the caprock formation [39,40,43]. The plots of various organic acids (lignoceric, lauric, and hexanoic acids) versus the contact angles in an H<sub>2</sub> atmosphere at two pressures (15 MPa, and 25 MPa) and a constant temperature of 323 K are combined in Fig. 5. The increasing magnitude of the contact angles is lignoceric acid > lauric acid > hexanoic acid. A higher alkyl chain length results in a higher  $\theta_a$  and  $\theta_r$ .

The results suggest that a significant change in the H<sub>2</sub>-wettability of mica (caprock) is expected with an increasing carbon chain length of the alkyl group in the molecules of organic acids [42–44]. The higher number of carbon atoms modifies the wettability of the mica substrate into more H<sub>2</sub>-wet conditions [42–44].

For example, at a constant pressure of 15 MPa and organic acid concentration of 10<sup>-2</sup> mol/L, the advancing contact angles were 67.5°, 75.4°, and 91.8° for hexanoic, lauric, and lignoceric acid, respectively (the degree of change in the contact angle for the higher pressure of 25 MPa is much higher). For instance, at similar conditions but with a higher pressure of 25 MPa, the advancing contact angles were 80.3°, 89.2°, and 106.2° for the hexanoic, lauric, and lignoceric acids, respectively. This phenomenon has been attributed to the increased gas density at high pressures [66,81–83]. Such increased molecular gas density increases the molecular interaction [33] between the gas (CO<sub>2</sub> or H<sub>2</sub>) and rock surfaces [84].

Inferentially, mica/H<sub>2</sub>/brine contact angles are generally lower than those of the mica/CO<sub>2</sub>/brine contact angles because of the low density of H<sub>2</sub>, resulting in lesser cohesive energy density and lower intermolecular interactions between the H<sub>2</sub> and caprock [13–15,17,18]. However, H<sub>2</sub> could leak (escape) through the caprock with the increased alkyl chain length, organic acid concentration, and H<sub>2</sub> pressure. Thus, it is inappropriate to assume fully water-wet initial conditions for the storage and caprock formations at realistic reservoir conditions. This assumption results in over-predicting and overestimating the structural trapping capacities and containment safety during H<sub>2</sub> geo-storage.

### 3.3. Comparison of organic-aged mica-quartz-hydrogen wettability

In this section, we compare the effects of organic acid contamination on the contact angles of mica/H<sub>2</sub>/brine and quartz/H<sub>2</sub>/brine systems in the presence of various concentrations of organic acids (lignoceric, lauric, and hexanoic acids) at constant temperature (323 K) and two pressure conditions: 15 and 25 MPa (Fig. 6). The results in Fig. 6 indicate that the contact angles of mica/H<sub>2</sub>/brine and quartz/H<sub>2</sub>/brine systems increased with higher pressure, organic acid concentrations, and alkyl chain lengths of the organic acids.



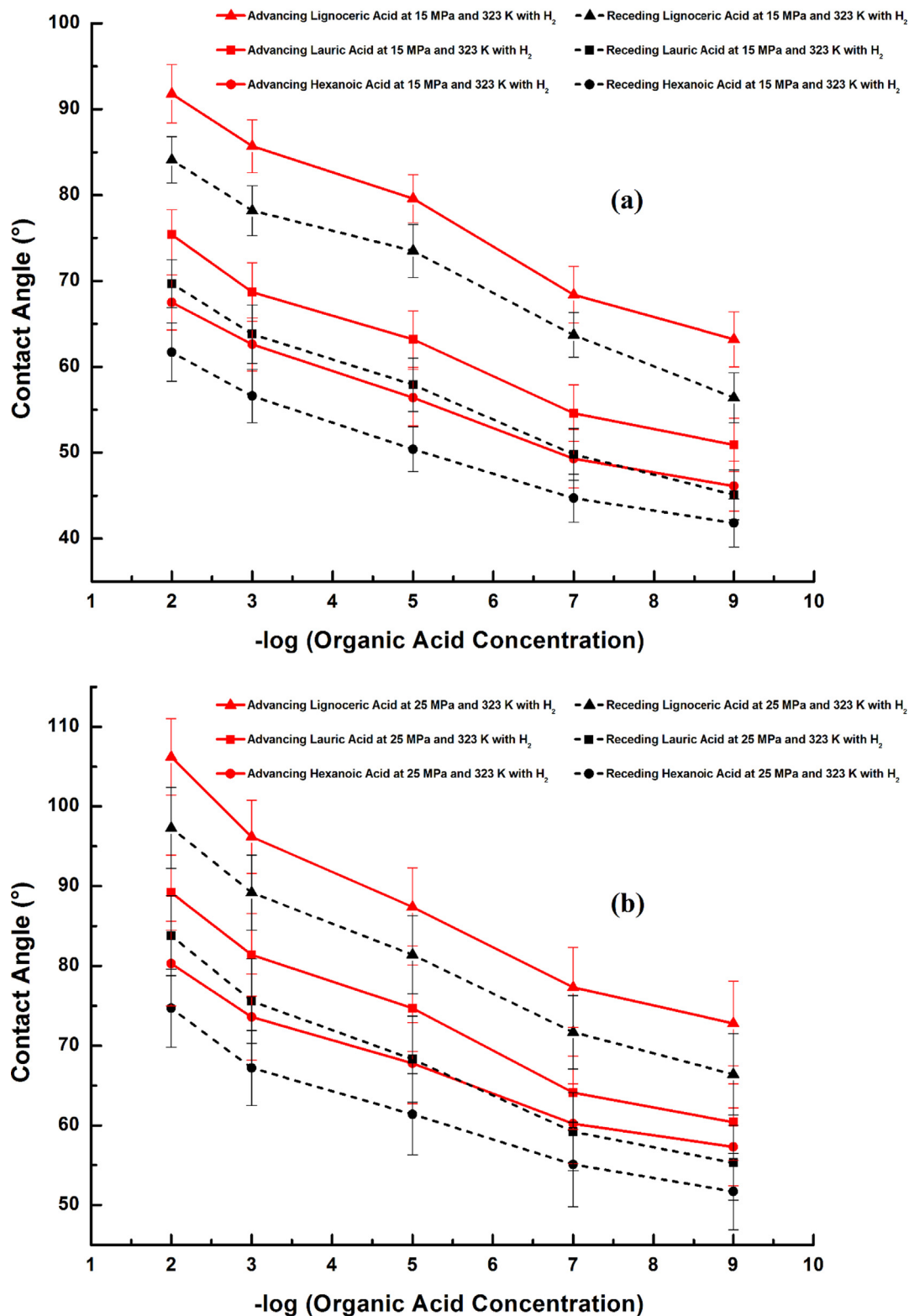


Fig. 5. Effect of the number of carbon atoms present in organic acids and the pressure on the mica/H<sub>2</sub>/brine contact angles: (a) 15 MPa and (b) 25 MPa.

However, in any given condition, the mica/H<sub>2</sub>/brine contact angles were significantly higher than those of the quartz/H<sub>2</sub>/brine systems. For instance, at 323 K and a 10<sup>-3</sup> mol/L lignoceric acid concentration,  $\theta_a$  for mica/H<sub>2</sub>/brine was measured as 60.7° at 0.1 MPa, 85.7° at 15 MPa, and 96.2° at 25 MPa, whereas  $\theta_r$  for mica/H<sub>2</sub>/brine was obtained as 55.6°, 78.2°, and 89.2°, respectively.

At similar conditions,  $\theta_a$  for quartz/H<sub>2</sub>/brine was measured as 51.3°, 69.2°, and 84.6°, whereas  $\theta_r$  for quartz/H<sub>2</sub>/brine was obtained as 44.6°, 62.4°, and 74.3° at 0.1, 15, and 25 MPa, respectively.

The data imply that surfaces with more silanol groups (quartz substrates) have hydrophilic sites covered with the maximum amount of H<sub>2</sub> compared to surfaces with a limited number of sila-

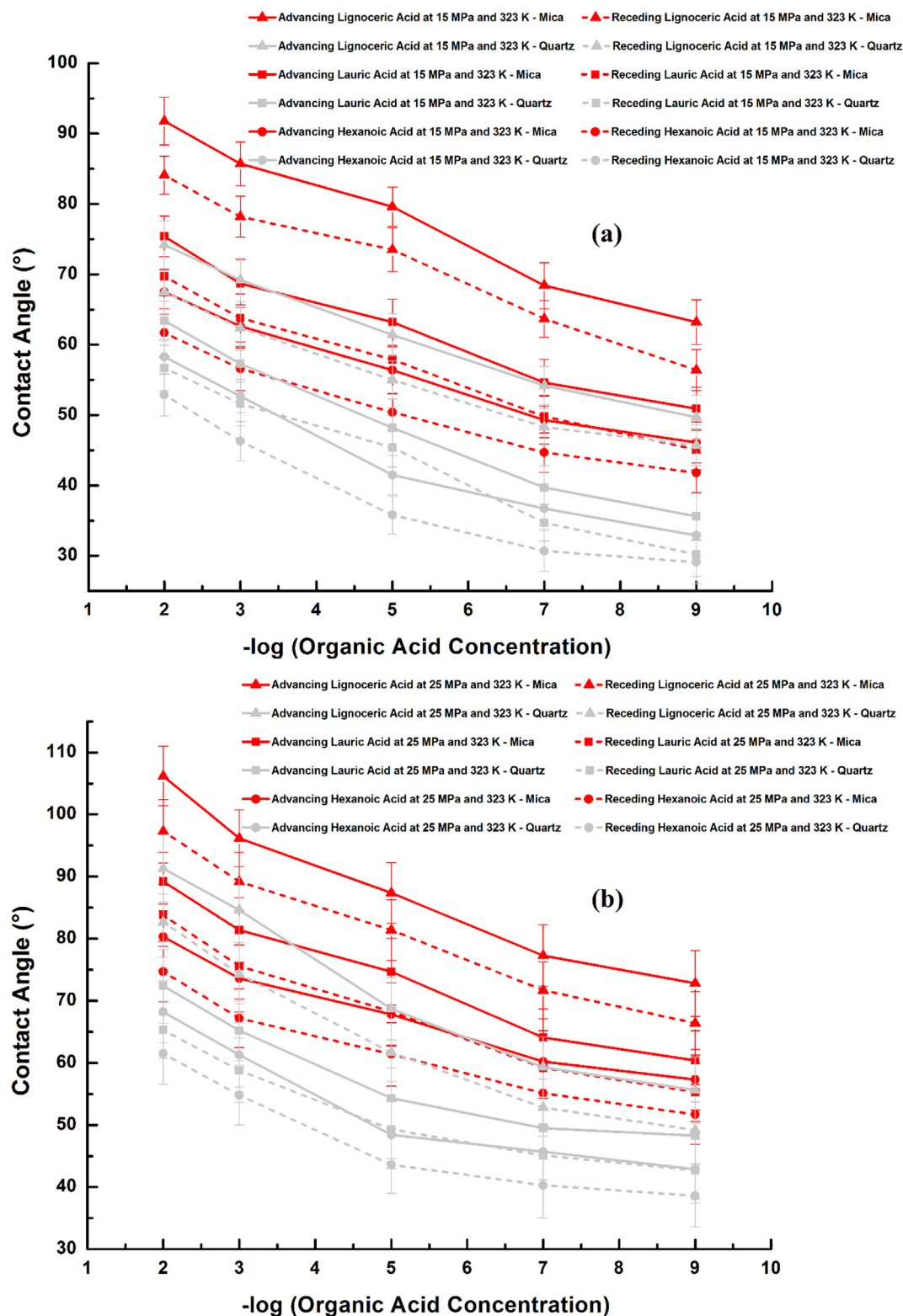


Fig. 6. Comparison of the mica-quartz-hydrogen wettability in various organic acids: (a) 15 MPa and (b) 25 MPa. The quartz/H<sub>2</sub>/brine dataset was acquired from [13].

nol groups (mica substrates). The aged mica substrate surfaces have lower solid/H<sub>2</sub> interfacial energy and, thus, higher contact angles than aged quartz substrates [28,85–88]. The results are relevant for comparing the structural trapping capacities of caprock and the residual trapping potential of the geo-storage formation and assessing the feasibility of large-scale H<sub>2</sub> geological storage projects.

#### 4. Conclusions

The wettability of any geological formation is an important factor that regulates the ability of gas (H<sub>2</sub> in this case) to spread across the formation [67,68]. It controls the rate of gas injection [47,70] and withdrawal [13,14,18,71], fluid-flow dynamics [33,70,72,89], and storage potential [33,34,36] and reduces the uncertainty

[41,73,90]. Organic acids are inherent in H<sub>2</sub> geo-storage and caprock formations in realistic reservoir conditions [13,57–59,79], which significantly influence wetting characteristics and, thus, the H<sub>2</sub> trapping potential [13,14,17,18,71]. However, scarce data exist in the literature regarding the influence of organic acids on the H<sub>2</sub>-wettability of caprock and the associated structural trapping capacities because the assessment of H<sub>2</sub> geo-storage feasibility from the rock-wetting phenomenon is a new research area. Thus, three-phase contact angles ( $\theta_a$  and  $\theta_r$ ) were measured for the mica/H<sub>2</sub>/brine system in the presence of various organic acids (lignoceric, lauric, and hexanoic acids) at geo-storage environments (25 and 15 MPa and 323 K). The results were compared with the contact angles of the mica/CO<sub>2</sub>/brine and quartz/H<sub>2</sub>/brine systems.

The results indicate that mica substrates became H<sub>2</sub> wet in the presence of organic acids at higher pressures, suggesting that the structural sealing potential of the caprock may be lower due to the inherent organic molecules in geo-storage formations. Further, the comparison of the mica/H<sub>2</sub>/brine, mica/CO<sub>2</sub>/brine, and quartz/H<sub>2</sub>/brine systems in the presence of organic acids indicates that the mica/H<sub>2</sub>/brine contact angles are generally less than the mica/CO<sub>2</sub>/brine contact angles due to the gas density difference. However, mica/H<sub>2</sub>/brine contact angles are higher than quartz/H<sub>2</sub>/brine contact angles, indicating that aged mica substrates have lower solid/H<sub>2</sub> interfacial energies than the aged quartz substrates due to the higher number of silanol groups.

This research suggests that inherent organic acids in underground geological formations may substantially affect the caprock sealing capacity. Therefore, it is pertinent for reservoir scheme models to gauge the thresholds of organic contaminations to avoid the failure of H<sub>2</sub> geo-storage projects. Results of this study considerably promote a basic understanding of the auspicious conditions for industrial-scale UHS.

### CRedit authorship contribution statement

**Muhammad Ali:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Nurudeen Yekeen:** Visualization, Writing – review & editing. **Nilanjan Pal:** Data curation, Methodology. **Alireza Keshavarz:** Software, Validation. **Stefan Iglauer:** Validation, Writing – review & editing. **Hussein Hoteit:** Resources, Writing – review & editing, Project administration, Supervision.

### 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.

### Acknowledgments

The authors acknowledge Mr. Antonio García, a scientific illustrator from King Abdullah University of Science and Technology, Saudi Arabia for producing the graphical abstract.

### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2021.10.080>.

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