Effect of organic acids on CO$_2$-rock and water-rock interfacial tension: Implications for CO$_2$ geo-storage

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A R T I C L E   I N F O

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A B S T R A C T

A small concentration of organic acid in carbon dioxide (CO$_2$) storage formations and caprocks could significantly alter the wettability of such formations into less water-wet conditions, decreasing the CO$_2$-storage potential and containment security. Recent studies have attempted to infer the influence of the organic acid concentration on the wettability of rock-CO$_2$-brine systems by measuring advancing and receding contact angles. However, no studies have investigated the influence of organic acid contamination on CO$_2$-storage capacities from rock-fluid interfacial tension (IFT) data because solid-brine and solid-CO$_2$ IFT values cannot be experimentally measured. Equilibrium contact angles and rock-fluid IFT datasets were used to evaluate the viability of CO$_2$ storage in storage rocks and caprocks. First, the contact angles of rock in brine-CO$_2$ systems were measured to compute Young’s equilibrium contact angles. Thereby, rock-brine and rock-gas IFT values at CO$_2$ geo-storage conditions were computed via a modified form of Neumann’s equation of state. For two storage-rock minerals (quartz and calcite) and one caprock mineral (mica), the results demonstrated high CO$_2$-brine equilibrium contact angles at high pressure (0.1–25 MPa) and increasing concentrations of stearic acid ($10^{-5}$ to $10^{-2}$ mol/L). Rock-brine IFT increased with the increased stearic acid concentration but remained constant with increased pressure. In all conditions, the order of increasing hydrophobicity of the mineral surfaces is calcite > mica > quartz. At 323 K, 25 MPa, and a stearic acid concentration of $10^{-2}$ mol/L, quartz became intermediate-wet with a CO$_2$-brine equilibrium contact angle of 89.8°, whereas mica and calcite became CO$_2$-wet with CO$_2$-brine equilibrium contact angles of 117.5° and 136.5°, respectively. This work provides insight into the effects of organic acids inherent in CO$_2$ geo-storage formations and caprocks on rock wettability and rock-fluid interfacial interactions.

Credit author statement

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1. Introduction

The extensive build-up of carbon dioxide (CO₂) in the atmosphere from fossil fuel burning and other human activities has resulted in global warming and undesired climate change (Blunet et al., 1993; IPCC, 2013; Iglauser et al., 2022). Carbon capture and sequestration is the practice of capturing CO₂ from the atmosphere or stationary sources and storing it in depleted hydrocarbon reservoirs and other subsurface geological formations, such as deep saline aquifers (Birkholzer et al., 2009; Busch et al., 2008; Metz et al., 2005; Orr, 2009).

Recently, various enhanced oil recovery techniques have been developed using various chemicals, such as surfactants, polymers, and nanoparticles (Afolabi et al., 2021; Okunade et al., 2021a; Pal et al., 2017, 2019a, 2019b; Pal and Mandal, 2020; Yekeen et al., 2021a). However, among these techniques, CO₂ flooding is superior in cost and efficiency (Ali et al., 2015, 2017; Pal et al., 2022). Carbon capture and sequestration are promising for reducing global warming and alleviating the high concentration of atmospheric greenhouse gases (Ali, 2018, 2021). However, the effectiveness of the CO₂ geo-storage and oil recovery potential in hydrocarbon reservoirs depends on the rock wettability in brine-CO₂ systems and the rock-fluid interfacial interactions (Yekeen et al., 2020).

Wettability and interfacial tension are crucial parameters that drive gas pore-scale distribution (Hosseini et al., 2022b). It is also responsible for fluid flow through porous media, the CO₂ injection rate, and containment security (Al-Yaseri et al., 2021b; Ahnii et al., 2018; Faziah et al., 2018, 2020; Hosseini et al., 2022a; Okunade et al., 2021b). The CO₂ containment security reduces as the rock surface becomes CO₂-wet, resulting in premature gas leakage from rock pores, causing a substantial decrease in residual and structural trapping abilities of the storage rock or caprock (Al-Khdheeawi et al., 2020, 2021; Yekeen et al., 2020).

However, wettability is a critical factor, and assessing its influence at realistic downhole conditions is quite complicated (Ali et al., 2021b). Moreover, the ideal subsurface conditions are anoxic or reductive (Ali et al., 2020a; Hosseini et al., 2022c), demonstrating the existence of organics in CO₂ geo-storage formations (Akob et al., 2015; Lundegard and Kharaka, 1994). Although the organic molecule concentrations in geo-storage formations are small, such a low concentration is sufficient to modify the rock wettability into oil-wet (Ali et al., 2019a, 2019b, 2020a). Thus, wettability is severely affected by organic molecules.

There is a considerable alteration of initially water-wet CO₂-storage formation rock into the CO₂-wet state because of the adsorption of small quantities of organic molecules in CO₂ geo-storage formations (Ali et al., 2019a, 2019b, 2020a, 2021b; Pan et al., 2021). Previous studies have shown that water-wet surfaces could initially become CO₂-wet with organic content in the pore matrix (Ali et al., 2019a, 2019b, 2020a, 2021b; Pan et al., 2021). Hydrophilic rock-forming minerals could attain intermediate or absolute hydrophobic conditions when aged in oil because of organic molecule adsorption on rock surfaces (Tabar et al., 2020; Yekeen et al., 2020).

The minimum concentration of organic acid contamination that could affect rock wettability in CO₂-brine systems was investigated by Ali et al. (2019a, 2019b, 2020a). Specifically, a threshold concentration (10⁻¹⁰ mol/L) of organic acids, such as lignoceric, hexanoic, lauric, and stearic acids, was sufficient to reduce the hydrophilicity of the strongly water-wet calcite, quartz, and mica mineral surfaces. The rock surface became more CO₂-wet with rising concentrations of organic acids at 25 MPa and 323 K.

These results suggest that the residual and structural trapping capabilities of CO₂ storage formations decrease as the rock becomes CO₂ wet in organic acids. Ideally, the storage rock and caprock should remain water-wet (contact angle < 90°) for CO₂ to remain immobilized in storage media and for the optimum sealing capacity of caprock, where it acts as an effective seal (Ali et al., 2021c, 2021d, 2022a, 2022b; Tabar et al., 2020; Yekeen et al., 2020). However, whenever θₐ is higher than 90° (CO₂-wet condition), the stored CO₂ is more likely to mobilize within the storage formation. Likewise, at θₐ > 90°, there is migration and interaction of the stored CO₂ with caprock, resulting in upward percolation (flow) and leakage of CO₂ via the caprocks.

In studies by Ali et al. (2019a, 2019b, 2020a, 2021b), the influence of organic molecules (acids) on the wettability of rock-CO₂–brine systems was inferred from advancing and receding contact angle datasets. The interfacial interaction between the rock and fluids also significantly contributes to CO₂ entrapment in storage formations and caprocks. However, rock-fluid interfacial data for assessing the influence of organic acids on the entrapment of CO₂ in storage formations and caprocks are rarely reported in the literature (Abdulelah et al., 2021).

Solid-brine and solid-CO₂ interfacial tension (IFT) values cannot be measured conveniently through laboratory experiments; hence, researchers usually compute these parameters from CO₂-brine IFT values and contact angle datasets (Abdulelah et al., 2021; Al-Yaseri et al., 2021a; Arif et al., 2016b; Pan et al., 2020, 2021).

Arif et al. (2016b) employed Neumann’s equation of state method to calculate the clay-coated quartz-CO₂ and clay-coated quartz-CH₄ IFT values from advancing and receding contact angles of clay-coated quartz-CO₂–brine systems (measured via DSA 100 tilted at 17°), CH₂-brine and CO₂-brine IFT (measured with the same Krüss DSA 100 using the pendant drop method). They found that coating quartz substrate with clay (montmorillonite and kaolinite) has minor effects on clay-coated quartz-CO₂ and clay-coated quartz-CH₄ IFT values but makes the substrate surface less water-wet at 300 K and more water-wet at 353 K. Increasing CO₂ pressure generally resulted in less hydrophilic conditions for coated and uncoated quartz substrates. Moreover, Al-Yaseri et al. (2021a) and Abdulelah et al. (2021) recently employed Neumann’s equation of state to compute the rock-CO₂ IFT for shale and basalt rock, respectively.

However, all previous computations of the rock-fluid IFT at CO₂ geo-storage conditions were conducted without accounting for the organic contamination inherent in storage formations. Pan et al. (2021) is the only researcher who has investigated the effect of organic acids on the rock-fluid IFT. However, the rock substrates were quartz and basalt, and their results only provide insight into solid-CO₂ interfacial energy during CO₂ storage in sandstone formations. To the best of the authors’ knowledge, no existing study has assessed the influence of organic acid contamination on solid-CO₂ and solid-water IFT values at geo-storage temperatures and pressures for mica, quartz, and calcite. Consequently, the effect of organic acid contamination on quartz-CO₂–brine, calcite-CO₂–brine, and mica-CO₂–brine systems was investigated systematically by computing the equilibrium contact angles and rock-fluid IFT. A modified form of Neumann’s equation of state was used to calculate solid-brine and solid-CO₂ IFT values at 0–25 MPa, a constant salinity of 10 wt% NaCl, and a constant temperature of 323 K. Afterward, the implications of the results on CO₂-trapping capacities and containment security in storage rocks and caprocks were explained. The storage rock is the underground formation geologically capable of keeping CO₂ immobile, whereas caprock is the nonpermeable formation (seal) that traps CO₂, preventing further migrating to the surface.

2. Experimental materials and methodology

2.1. Materials

Three minerals were used in this study: quartz, calcite, and mica, which represent the geo-storage formations and caprocks. These samples were acquired from Ward’s Natural Science, USA. The surface roughness was measured using atomic force microscopy. The root mean square (RMS) of pure substrates was 1 nm for quartz, 24 nm for calcite, and 2 nm for mica. Earlier studies confirmed that a smooth surface (RMS
<1 μm) does not affect the contact angle measurements (Al-Yaseri et al., 2016a, 2016b; Ahnili et al., 2018).

### 2.2. Aging procedure of mineral surfaces

Each sample was cleaned properly to avoid surface contamination and achieve a representative aging process (Bikkina, 2011; Iglauer et al., 2014; Love et al., 2005; Mahadevan, 2012). The samples were washed with deionized water, blown with ultrapure N₂ gas, left in the oven to dry at 273 K for 2 h, and finally exposed to air plasma (Diemer Yocto instrument) for 15 min (Ali et al., 2019a, 2019b).

All samples were first immersed in acidic solution (2 wt% of NaCl brine and hydrochloric acid, pH = 4) for 30 min at ambient conditions to increase organic acid adsorption on calcite, mica, and quartz surfaces. A detailed explanation of this procedure is provided in previous studies (Ali et al., 2020a, 2021a). Afterward, the samples were dried using ultrapure N₂ gas then placed in a stearedic acid solution (10⁻² and 10⁻³ mol/L of stearic acid dissolved in n-decane) for 7 days under room conditions (Jardine et al., 1989; Madsen and Ida, 1998). The surface of pure and aged samples was also scanned using a scanning electron microscope to verify the aging process (Fig. 1).

### 2.3. Contact angle measurement

The contact angles of mineral-brine-CO₂ were measured via the sessile drop method on a tilted plate (17°), following the procedure detailed in earlier studies (Al-Yaseri and Jha, 2021; Ali et al., 2021c; Iglauer et al., 2020, 2021; Lander et al., 1991, 1993). The measurements were performed at high pressure (reaching 25 MPa) and high temperature (323 K) to simulate actual CO₂ storage conditions. The brine (10 wt% of NaCl) water droplet was mixed with CO₂ to obtain thermodynamic equilibrium before contact angle measurement (El-Maghrary et al., 2012; Pentland et al., 2011). Then, the advancing (θₐ) and receding (θₑ) contact angles were measured, and the equilibrium contact angles were calculated (further explained in Section 2.4).

### 2.4. Interfacial tension calculations

The determination of the IFT is conducted using Young’s equation (1805), representing the expression of the equilibrium contact angle as a function of solid-CO₂ (γsolid-CO₂), solid-liquid (γsolid-liquid), and liquid-CO₂ (γliquid-CO₂) as illustrated in Eq. (1):

$$\cos \theta_i = \frac{\gamma_{sc} - \gamma_{sl}}{\gamma_{lc}}$$

where θᵢ denotes the equilibrium contact angle. Tadmor’s (2004) correlation is described in Eqs. (2)–(4) and is used to compute the equilibrium contact angles (θₑ):

$$\theta_e = \arccos \left( \frac{\gamma_{sc} - \gamma_{ss} \cos \theta_a}{\gamma_{sc} + \gamma_{ss} \cos \theta_a} \right)$$

$$\gamma_{sc} = \frac{\sin \theta_a}{2 - 3 \cos \theta_a + \cos \theta_a}$$

$$\gamma_{sc} = \frac{\sin \theta_e}{2 - 3 \cos \theta_e + \cos \theta_e}$$

The empirical approaches must be used to determine solid-CO₂, γsolid-CO₂, or solid-liquid, γsolid-liquid, IFT. The Fowkes (1964) method, Neumann’s method (Neumann et al., 1974), the harmonic-mean approach (Wu, 1971), Zisman method (Fox and Zisman, 1952), and Van Oss-Good method (Van Oss et al., 1986) are the most prevalent empirical methodologies. Determining γsolid-CO₂ and γsolid-liquid is important for explicit insight into CO₂ wetting behavior, which is important for evaluating CO₂ geo-storage potential (Al-Yaseri et al., 2015).

To calculate γsolid-CO₂ and γsolid-liquid, we used the adjusted Neumann equation of state (Neumann et al., 1974). This approach is practical because it is designed for use in systems with CO₂ brine, and rock. For solid-liquid, solid-CO₂, and liquid-CO₂ IFT values, Neumann’s equation of state can be represented as follows:

$$f(\gamma_{solid-CO₂}, \gamma_{solid-liquid}, \gamma_{solid-liquid}) = 0$$

According to Eq. (1), the free adhesion energy (free energy needed to detach a particle from the surface) is equal to the geometric mean of the solid and liquid cohesion work, the geometric mean of the force applied to the solid and liquid for separation. Solid-liquid (γsolid-liquid), solid-CO₂ (γsolid-CO₂), and liquid-CO₂ (γliquid-CO₂) IFT values were characterized by Ameri et al. (2013):

$$\tau_w = \tau_a + \tau_e - 2\sqrt{\tau_a \tau_e} \left[ 1 - \beta (\tau_e - \tau_a) \right]^2$$

$$\cos \theta_i = 1 - 2 \sqrt{\frac{\tau_a}{\tau_e}} \left[ 1 - \beta (\tau_e - \tau_a) \right]^2$$

Where β is a constant. These equations assume that γsolid-liquid remains constant with pressure, and β is calculated alongside γsolid-liquid. Using Eq. (7) by fitting a given set of θ and γliquid-CO₂ data with a least-squares fit. After determining γsolid-liquid and β, Eq. (6) is used to determine γsolid-CO₂.

To calculate β and τₑ (Figs. 1, 2, 3, 4, 7, 8, and 9) for each mineral sample using Eq. (7), additional pressures of 0.1, 10, 15, and 25 MPa at 323 K were used to measure the contact angles (θₑ) and τₑ. Then, the computed values of β and τₑ were input into Eq. (6) to determine τₑ (Figs. 3, 6, and 9). Table 1 describes the β and R² values for pure and organic-aged samples from various formation types.

### 3. Results and discussion

Understanding the influence of organic contamination on the wetting phenomenon via rock-fluid IFT data is crucial for the success of gas geo-storage in storage formations and caprocks (Ali et al., 2022). The wetting phenomenon determines the pore-scale distribution and CO₂ containment security (Zhou et al., 2017). The CO₂ trapping capacity in CO₂ geo-storage formations is projected to decrease with trace organic acid concentrations because the rock pore surfaces could become intermediate-CO₂-wet (Ali et al., 2019a, 2019b; 2020a, 2021b). The smallest organic concentration sufficient to influence the trapping
Fig. 2. Brine-quartz interfacial tension (IFT) at different pressures and 323 K for clean quartz after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations.

Fig. 3. Carbon dioxide-quartz interfacial tension (IFT) at different pressures and 323 K for clean quartz after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations.

Fig. 4. Carbon dioxide-brine equilibrium contact angles at diverse pressures and 323 K for clean calcite after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations ($sd = \pm 3^\circ$).

Fig. 5. Brine-calcite interfacial tension (IFT) at different pressures and 323 K for clean calcite after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations.

Fig. 6. Carbon dioxide-calcite interfacial tension (IFT) at different pressures and 323 K for clean calcite after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations.

Fig. 7. Carbon dioxide-brine equilibrium contact angles at diverse pressures and 323 K for clean mica after aging with $10^{-5}$ (optimum) and $10^{-2}$ mol/L (maximum) stearic acid concentrations ($sd = \pm 3^\circ$).
Before the measurements of advancing and receding angles, the scanning electron micrographs of the pure quartz, calcite, and mica substrates and those aged in stearic acid solution were compared to demonstrate the influence of aging with stearic acid solutions (Table 2). The images of the unaged surfaces were relatively clear. However, the stearic acid coverage on the quartz, calcite, and mica surfaces was significantly noticed after the rock surfaces were treated with $10^{-2}$ mol/L of the organic acid. This incident suggests that the alteration of the wettability of quartz, calcite, and mica surfaces from strongly water-wet conditions into weakly water-wet, intermediate-wet, or CO$_2$-wet states results from the exposure of substrate surfaces to different concentrations of stearic acid solutions.

### 3.1. Quartz–CO$_2$–brine wettability (contact angle datasets)

The effects of varying concentrations of organic acid on quartz wettability in brine-CO$_2$ systems at different pressures and a constant temperature (323 K) are portrayed in Fig. 1. The graphs demonstrate that pure quartz became less hydrophilic when the quartz substrate was aged in a stearic solution. By increasing the concentration from $10^{-5}$ to $10^{-2}$ mol/L, the quartz surface wettability was changed from strongly water-wet to weakly water-wet conditions due to the adsorption of stearic acid on the rock surfaces. At a constant temperature (323 K) and 0.1 MPa, the equilibrium contact angles increased from 0° to 53.1° and subsequently to 64.2° with an increasing stearic acid concentration from $10^{-5}$ to $10^{-2}$ mol/L, respectively.

These results suggest that the aging of pure quartz in a stearic acid solution altered the surface wettability into weakly water-wet conditions at ambient pressure (Ali-Anssari et al., 2017; Ali, 2018, 2021). Contact angles are generally higher at elevated pressure (Yekeen et al., 2020, 2021b). In this study, at 25 MPa and 323 K, the equilibrium contact angles increased from a weakly water-wet state (53.1°) to intermediate-wet conditions (76.55°) when aged in $10^{-5}$ mol/L stearic acid solution, with a contact angle of 89.75° in $10^{-2}$ mol/L solution. Such a modification in surface wettability of the quartz due to organic contamination and high CO$_2$ pressure decreases the capillary trapping abilities of CO$_2$ at subsurface conditions in sandstone storage formations.

Previous studies have demonstrated that CO$_2$-wet or oil-wet rocks have low residual trapping capabilities and that residual saturations of CO$_2$ are smaller in quartz when the rock is CO$_2$- or oil-wet compared to hydrophilic rock surfaces (Ali, 2021; Ali et al., 2019a, 2019b, 2022a; Iglaier et al., 2015). The results of this study agree with the previous findings on the influence of organic acids on the wettability of quartz in brine-CO$_2$ systems. The results further confirm that the adsorption of a slight concentration of organic acid molecules ($10^{-5}$ mol/L of stearic acid) onto the surface of sandstone rock significantly increases rock surface hydrophobicity (Ali et al., 2019b, 2021b). Neglecting the organic acid contamination effect on quartz-CO$_2$–brine wettability during CO$_2$ storage in sandstone formation could result in over-prediction of the capillary trapping abilities and CO$_2$ containment security in such formations.

### 3.2. Quartz–CO$_2$–brine wettability from rock-fluid interfacial tension data

Rock-fluid IFT data were computed to describe and explain the change in the contact angle as a function of interfacial interactions within the rock and interacting fluids. The Young–Laplace equation (Eq. (2)) (Arif et al., 2021; Young, 1805) described the relationship between wettability (contact angle) represented by $\theta$ and the rock-CO$_2$, CO$_2$-brine, and rock-brine IFT values. Figs. 2 and 3 illustrate the brine-quartz IFT and CO$_2$-quartz IFT determined at different pressures and a constant temperature (323 K).

Fig. 2 indicates that the brine-quartz IFT remained the same at constant temperature (323 K), irrespective of the change in pressure. For

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**Table 1**

Organic acid concentrations, sample types, and $\beta$ values.

| Sample | Organic concentration | $\beta$ (m/mN)$^2$ | $R^2$ |
|--------|-----------------------|-------------------|-------|
| Quartz | 0                     | 0.000211          | 0.91  |
|        | $10^{-5}$             | 2.53E-05          | 0.95  |
|        | $10^{-2}$             | 1.78E-05          | 0.95  |
| Calcite| 0                     | 0.000212          | 0.90  |
|        | $10^{-5}$             | 8.90E-05          | 0.95  |
|        | $10^{-2}$             | 7.8E-09           | 0.91  |
| Mica   | 0                     | 0.000211          | 0.96  |
|        | $10^{-5}$             | 4.42E-05          | 0.90  |
|        | $10^{-2}$             | 4.24E-05          | 0.92  |

The influence of the organic acid concentration on CO$_2$ containment securities was deduced from contact angle measurements. We assessed the effect of two stearic acid concentrations ($10^{-5}$ and $10^{-2}$ mol/L) on CO$_2$ geo-storage rocks and caprocks (using quartz, calcite, and mica substrates as representatives of rock-forming minerals) from contact angle values and fluid-rock interfacial interactions at 323 K and different pressures (0.1–25 MPa).
instance, the brine-quartz IFT of the unaged quartz was obtained as 1.0786 mN/m and remained unchanged, despite the increasing pressure from 0.1 to 25 MPa. The brine-quartz IFT datasets generally suggest that the interfacial interaction or tension between the brine and solid rock surfaces is unaffected by the alteration of the CO₂ pressure for rock–CO₂–brine systems. The quartz substrate is incompressible and has a constant volume and shape, whereas liquids have low compressibility. Pressure only slightly reduces the distance between the closely packed molecules; therefore, increasing the pressure has no significant influence on the interfacial energy between the quartz and water (Al-Yaseri et al., 2016a, b; Arif et al., 2016a; Roshan et al., 2016).

Fig. 2 further reveals that the brine-quartz IFT increased with the increased stearic acid concentration. The IFT of the unaged quartz increased from 1.0786 to 3.4257 mN/m when the quartz substrate was soaked in 10⁻⁵ mol/L of acid. In 10⁻² mol/L of stearic acid, the IFT between the brine and quartz increased to 6.4639 mN/m. This result implies that the aging of the quartz substrate in the organic acid solution increased the adsorption of stearic acid solution molecules on a quartz substrate, resulting in almost 218% and 499% increments in the interfacial energy between the quartz surface and brine.

"Interfacial energy" is the free energy of the surfaces at an interface, resulting from differences in the tendencies of each phase to attract its own molecules. As the rock surface becomes hydrophobic (e.g., oil-wet or CO₂-wet) due to the adsorption of organic acid molecules, the water contact angles are higher, suggesting that the interfacial energy between the rock and CO₂ is lower, whereas the interfacial energy between the rock and brine is higher (Arif et al., 2016b). The CO₂ strongly adheres to the pore surface, occupying smaller rock pores, whereas the nonwetting phase (brine) occupies more open channels (Ganat, 2020; Singh et al., 2016).

The Young–Laplace equation (Eq. (1)) displays a direct relationship between the contact angle and quartz-brine IFT. Hence, such a remarkable increase in brine-quartz IFT interfacial energy and cohesive force strength in the presence of organic acid molecules is expected to cause a considerable increase in the advancing and receding angles in brine by making the rock surface more hydrophobic or CO₂-wet. The quartz-brine IFT data confirmed that, in realistic reservoir conditions, a trace organic contamination in the sandstone CO₂ geo-storage formation
3.3. Calcite geo-storage formation.

The CO₂ storage capacity of calcite is critical for enhancing CO₂ storage security. This assertion is confirmed by the plots of CO₂-quartz IFT at different pressures and 323 K, portrayed in Fig. 3. As shown in Fig. 3, the CO₂-quartz IFT decreases sharply with increased pressure. The CO₂-quartz IFT for the unaged quartz was higher than for quartz aged in a stearic solution. The CO₂-quartz IFT decreases with increased pressure because the pressure raises the cohesive energy density of the CO₂. The contamination of the quartz surface with organic acid significantly decreases the equilibrium contact angles against different pressures (0.1–25 MPa) (Fig. 6). An inverse relationship exists between cosθ and CO₂-quartz IFT; thus, the value of the contact angle (θ) becomes larger as the CO₂-quartz IFT becomes negative. Hence, the lower CO₂-quartz IFT values obtained in organic acid confirm the increasing quartz surface hydrophobicity with the adsorption of organic molecules on the quartz surface.

The lower CO₂-aged quartz interfacial energy and higher CO₂-unaged quartz interfacial energy suggest that the quartz substrate is more favorable and conventionally wetted by CO₂ when the interfacial energy between the CO₂ and quartz is lower, and the solid-brine interfacial energy is higher (Arif et al., 2016b). The CO₂-solid quartz data demonstrate that, at 0.1 MPa, the CO₂-quartz IFT of the pure quartz substrate decreased from 71.67 to 46.77 mN/m in a 10⁻⁵ mol/L acid solution and eventually to 37.74 mN/m when the quartz was aged in a 10⁻² mol/L solution. At 25 MPa, the CO₂-quartz IFT of quartz reduced from 21.55 to 14.01 mN/m and eventually to 9.30 mN/m when the substrate was aged in 10⁻⁵ and 10⁻² mol/L organic acid concentrations, respectively. The contact angle datasets and rock-fluid IFT data collectively confirmed that the contamination of the quartz surface with organic acid significantly influences the wetting phenomenon in the sandstone CO₂ geo-storage formation.

3.3. Calcite–CO₂–brine wettability (contact angle datasets)

The CO₂ wettability of calcite is quantified in the graph of equilibrium contact angles against different pressures (0.1–25 MPa) at 323 K (Fig. 4). Similar to the case of quartz-CO₂ wettability, the CO₂-brine equilibrium contact angles increased with rising pressure, suggesting that high pressure is less favorable for CO₂ geo-storage in limestone-carbonate storage formations. The calcite surface also demonstrated an increasing tendency to become hydrophobic (CO₂-wet) when aged in stearic acid. However, compared to quartz-CO₂ wettability at different pressures, a constant temperature (323 K), and the presence of organic acid, higher contact angle values were obtained for calcite-CO₂ systems, suggesting that the calcite surface was more hydrophobic (Sun and Bourg, 2020).

With calcite substrate aging in 10⁻² mol/L acid, the wetting state was modified from the intermediate-wet state (97.9°) to CO₂-wet (136.5°) as the CO₂ pressure was raised from 0.1 to 25 MPa. Similarly, the equilibrium angle rose from weakly water-wet (53.4°) to an intermediate-wet state (92°) when the calcite was aged in a lower stearic acid concentration (10⁻² mol/L). The CO₂-water equilibrium contact angle datasets at varying pressures and a constant temperature (323 K) confirmed that the carbonate CO₂ storage rock became more CO₂-wet in organic acid at elevated pressures. All et al. (2019a) demonstrated that, at 323 K and 10 MPa, the brine advancing contact angle of the calcite-CO₂ system increased from weakly water-wet (63.9°) to the CO₂-wet state (126.0°) with an increased stearic acid concentration. At 25 MPa, the contact angle rose from 95.4° (intermediate-wet state) to CO₂-wet (141.2°). The higher hydrophobicity of the calcite surface when aged in stearic acid was attributed to the esterification of the hydroxyl groups on the calcite surface by the stearic acid molecules via a condensation reaction, resulting in chemically bonding (covalently) the stearic acid octadecenoate groups to the calcite surface (Ali et al., 2019a; Yekeen et al., 2020).

3.4. Calcite–CO₂–brine wettability from rock-fluid interfacial tension data

An amended form of Neumann’s equation of state (Neumann et al., 1974) was used to calculate the brine-calcite and CO₂-calcite IFT values to explain the change in wettability in different stearic acid concentrations and at higher pressures as a function of the rock-fluid interfacial interaction. Fig. 5 presents the plots of brine-calcite IFT versus the varying pressures at a constant temperature (323 K). The plotted graphs reveal that, similarly to the brine-quartz IFT, the brine-calcite IFT remained constant with increasing pressure because of the insignificant effect of the pressure on incompressible solid and water molecules.

However, the values of the brine-calcite IFT were higher for aged calcite. In addition, the brine-calcite IFT computed in a 10⁻² mol/L stearic acid concentration was higher than the value computed when 10⁻⁵ mol/L of acid was used for aging the calcite substrate. When the CO₂-calcite and CO₂-brine IFT values are kept constant, the increasing brine-calcite IFT with an increasing stearic acid concentration decreases the magnitude of cosθ in Eq. (1). Thus, higher values of the CO₂-brine equilibrium contact angles are obtained whenever the computed values of the brine-calcite IFT are higher, confirming that the calcite surface becomes hydrophobic.

The brine-calcite IFT values were also higher than the brine-quartz IFT values. For instance, the brine-quartz IFT value for pure quartz was 1.0786 mN/m, whereas the brine-calcite IFT value for pure calcite was 2.7520 mN/m at 0.1 MPa and 323 K. With the 10⁻⁵ mol/L stearic acid solution, the brine-calcite IFT value was computed as 3.4257 mN/m, whereas the value of the brine-calcite was reported as 6.4639 mN/m. Similarly, when the stearic acid concentration became 10⁻² mol/L, the brine-quartz IFT was calculated as 7.0729 mN/m, whereas the brine-calcite IFT was computed as 21.0494 mN/m at 0.1 MPa and 323 K. These results confirm that calcite is more hydrophobic and provides higher active sites for adsorbing organic molecules than quartz surfaces. Hence, organic acids in CO₂ storage formations could significantly reduce the CO₂ storage capacities in limestone or carbonate formations compared to sandstone formations.

Generally, the CO₂-calcite IFT decreased abruptly with increased pressure from 0.1 to 25 MPa (Fig. 6). Specifically, the CO₂-calcite IFT of the pure calcite decreased from 72.38 to 16.82 mN/m with a 0.1–25 MPa change in pressure. Similar trends were discovered for the CO₂-calcite IFT of the calcite substrate aged in 10⁻⁵ and 10⁻² mol/L stearic acid solutions. However, the CO₂-calcite IFT was noticeably higher for clean calcite than aged calcite. For instance, at 0.1 MPa and a constant temperature (323 K), the CO₂-calcite IFT was 72.38 mN/m for pure calcite, 44.50 mN/m for the substrate soaked in 10⁻⁵ mol/L acid, and 13.77 mN/m in the 10⁻² mol/L stearic acid concentration. Similarly, at increased pressure (25 MPa), the CO₂-calcite IFT for unaged calcite was 16.82 mN/m, whereas the CO₂-calcite IFT values were determined as 9.23 and 0.91 mN/m when the calcite was aged in 10⁻⁵ and 10⁻² mol/L organic acid concentrations (Fig. 6).

The CO₂-calcite IFT values (Fig. 6) demonstrated that hydrophilic surfaces have significantly higher solid-CO₂ interfacial energy and lower brine-solid interfacial energy than hydrophobic surfaces. The propensity of the calcite surface to be wet with CO₂ is higher when the solid-CO₂ surface energy is lower, whereas the surface has a higher affinity to water when the solid-CO₂ surface energy is higher, and the solid-brine surface energy is lower. The research findings agree with those of Arif et al. (2016b), who adopted a similar method for calculating the pure mica-CO₂ IFT at different pressures and temperatures. They observed that the IFT between the CO₂ and mica was estimated at 4.6 mN/m for...
oil-wet mica surfaces and 40 mN/m for water-wet mica surfaces, suggesting that water-wet mica has a higher mica-CO$_2$ interfacial energy, whereas the oil-wet mica has a lower mica-CO$_2$ interfacial energy.

3.5. Mica–CO$_2$–brine wettability (contact angle datasets)

The plots of the CO$_2$–brine-mica equilibrium contact angles versus various pressures at 323 K are presented in Fig. 7, which presents a consistent pattern of the plots of the equilibrium contact angles against pressure for quartz–CO$_2$–brine and calcite–CO$_2$–brine systems. The contact angles were higher with a high concentration of organic acids and higher pressures. However, the wettability variation was substantial for calcite–CO$_2$–brine systems compared with mica–CO$_2$–brine and quartz–CO$_2$–brine systems. The order of increasing contact angles with the rising concentration of stearic acid and pressure is CO$_2$–brine-calcite > CO$_2$–brine-mica > CO$_2$–brine-quartz. The contact angle dataset of the CO$_2$–brine-mica system was smaller than that of the CO$_2$–brine-calcite system but higher than that of the CO$_2$–brine-quartz system (Arif et al., 2016a). At 10 MPa and 323 K, when the substrate was contaminated by 10$^{-2}$ mol/L stearic acid, the CO$_2$–brine-mica equilibrium contact angle was 85.2$^\circ$, higher than the measured contact angle values of 72.9$^\circ$ and 112.3$^\circ$ for the CO$_2$–brine-quartz and CO$_2$–brine-calcite systems, respectively.

These results demonstrate that the stearic acid presence in caprocks could significantly affect CO$_2$-storage by rendering the rock more CO$_2$-wet, decreasing the structural trapping capacities (Al-Yaseri et al., 2015). The higher contact angles of the mica substrates aged in organic acids could be attributed to the chemisorption of carboxylic acid on the mica surface (Al-Anssari et al., 2016; Ali et al., 2020a). The contact angle increased with the increased pressure because the pressure increased the intermolecular interactions between CO$_2$ molecules and the rock surface (Al-Anssari et al., 2016; Ali et al., 2020a).

Generally, quartz has ample hydrophilic sites compared to mica and calcite, and the contact angle measured on the quartz surface is expected to be lower than that of the mica and calcite surfaces. Moreover, the computed quartz-CO$_2$ IFT was the highest in all experimental conditions because the pure quartz surface has an almost 100% silanol (SiOH) group compared to mica and calcite. The lower the percentage of SiOH coverage on the surface, the higher the surface hydrophobicity. The abundance of sufficient hydrophilic sites in quartz and the absence of such sites in mica and calcite are the reasons for the higher solid-CO$_2$ IFT for quartz and the lower solid-CO$_2$ IFT for calcite.

Previous studies have shown that hydrophobic surfaces, such as calcite and mica surfaces, have significantly lower CO$_2$-solid interfacial energy than the hydrophobic quartz surface (Arif et al., 2016b). The adsorption of organic acid molecules on the aged substrate surfaces was responsible for the low surface energy of the aged calcite, mica, and quartz substrates.

3.6. Mica–CO$_2$–brine wettability from rock-fluid interfacial tension data

The graphs of the brine-mica and CO$_2$–mica IFT values in Figs. 8 and 9 are consistent with the calculations of the brine and CO$_2$ IFT for calcite and quartz substrates. The brine-mica IFT was constant at all investigated pressures due to the insignificant effect on the liquid and solid molecules and lower compressibility. However, a higher brine-mica IFT was obtained when the substrate was aged in a stearic acid solution. The brine-mica IFT increased with the increased organic acid concentration. However, similar to the case of CO$_2$-calcite and CO$_2$-quartz systems, the CO$_2$–mica IFT decreased with increased pressure and stearic acid concentration (10$^{-5}$ to 10$^{-2}$ mol/L). The increasing brine-mica IFT and decreasing CO$_2$–mica IFT ultimately increased the value of the contact angle ($\theta$) according to Eq. (1).

The mica-fluid IFT computation and CO$_2$–brine equilibrium contact angles established that a trivial organic acid concentration profoundly affects the structural trapping capacities and CO$_2$ containment security in caprock formations. Hence, these effects should be included and evaluated in reservoir scale modeling to prevent CO$_2$ geo-storage failure in caprock formations.

4. Conclusions

The viability of CO$_2$ geo-storage projects in storage formation and caprocks could be determined by the influencing parameters, such as salinity, temperature, surface roughness, pressure, and organic acid presence (Ali et al., 2020b, 2021a; Guo et al., 2020; Iglauer, 2017). A paucity of information exists on the influence of organic acids on the CO$_2$-geo-storage potential and containment safety in storage rocks and caprocks. Moreover, previous attempts to examine the effect of organic acid contamination on the rock-wetting phenomenon during CO$_2$ geo-storage have been limited to contact angle measurement (Ali et al., 2019a, 2019b; 2020a; 2020b; 2021a; 2021b). No other studies have attempted to highlight the influence of organic acid contamination on the rock-wetting phenomenon during CO$_2$ geo-storage from interfacial interaction between the rock and fluids because rock-fluid IFTs cannot be measured experimentally (Abdulelah et al., 2021; Al-Anssari et al., 2018, 2020).

A modified form of Neumann’s equation of state was employed to compute the rock-brine and rock-CO$_2$ IFT values for CO$_2$-geo-storage and caprock representative minerals (quartz, calcite, and mica) at a constant temperature (323 K) and different pressures (0.1–25 MPa). The influence of organic acid (stearic acid) contamination on the rock-wetting phenomenon was explained by the rock-fluid IFT data and equilibrium contact angle values. The following inferences were drawn from the study results.

1. At 323 K, 25 MPa, and a stearic acid concentration of 10$^{-2}$ mol/L, quartz became intermediate-wet, and calcite and mica became CO$_2$-wet with CO$_2$–brine equilibrium contact angles of 89.75$^\circ$, 117.45$^\circ$, and 136.5$^\circ$, respectively. This outcome suggests that the hydrophobicity of rock surfaces increased at high pressure and with an increased stearic acid concentration.

2. The adsorption of organic acid molecules on rock surfaces and the high cohesive energy density of CO$_2$ at high pressure could decrease the CO$_2$ trapping potential and containment security in storage rocks and caprock. These effects should be considered to ensure the success of CO$_2$ geological sequestration projects.

3. The brine-rock IFT was higher with organic acids and remained constant with increased pressure because the liquid and solids are incompressible, whereas the CO$_2$–rock IFT was lower with organic acid contamination due to low solid-gas surface energy. The CO$_2$–rock IFT decreased with increased pressure due to the favorable CO$_2$–rock intermolecular interaction at high pressure.

4. The rock-brine IFT and CO$_2$–brine equilibrium contact angles were lower, whereas the rock-CO$_2$ IFT was higher for the quartz–CO$_2$–brine system than the calcite–CO$_2$–brine sand mica–CO$_2$–brine system. This result is due to ample hydrophilic sites on quartz, suggesting that hydrophobic surfaces are characterized by higher rock-brine and lower rock-CO$_2$ IFT values.

5. The predicted rock-fluid IFT values agree with the measured contact angle data, suggesting that the modified Neumann equation of state could satisfactorily predict the rock-fluid IFT values. Hence, the developed equations and contact angle datasets can be used to assess the change in wetting phenomenon from organic contamination in CO$_2$ geo-storage formations and caprocks.

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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