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CO 2 -wettability of sandstones exposed to traces of organic acids: Implications for CO 2 geo-storage

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CO_2-wettability of sandstones exposed to traces of organic acids; implications for CO_2 geo-storage

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Abstract

Wettability of CO_2-brine-mineral systems plays a vital role during geological CO_2-storage. Residual trapping is lower in deep saline aquifers where the CO_2 is migrating through quartz rich reservoirs but CO_2 accumulation within a three-way structural closure would have a high storage volume due to higher CO_2 saturation in hydrophobic quartz rich reservoir rock. However, such wettability is only poorly understood at realistic subsurface conditions, which

are anoxic or reducing. As a consequence of the reducing environment, the geological formations (i.e. deep saline aquifers) contain appreciable concentrations of various organic acids. We thus demonstrate here what impact traces of organic acids exposed to storage rock have on their wettability. Technically, we tested hexanoic acid, lauric acid, stearic acid and lignoceric acid and measured wettability as a function of organic acid concentration at realistic storage conditions (i.e. 25 MPa and 323 K (50 °C)). In addition, measurements were also conducted at ambient conditions in order to quantify the incremental pressure effect on wettability. Clearly, the quartz surface turned significantly less water-wet with increasing organic acid concentrations, even at trace concentrations. Importantly, we identified a threshold concentration at ~10^{-6} M organic acid, above which quartz wetting behaviour shifts from strongly water-wet to an intermediate-wet state. This wettability shift may have important consequences for CO_2 residual trapping capacities, which may be significantly lower than for traditionally assumed water-wet conditions where CO_2 is migrating through quartz rich reservoirs.

1. Introduction

CO_2 geological storage can significantly contribute towards a green environment via permanent CO_2 immobilization in deep underground formations, e.g. deep saline aquifers and depleted hydrocarbon reservoirs (Blunt et al., 1993, IPCC, 2005, Orr, 2009;). Efficient and safe CO_2 geological storage involves a qualitative and quantitative assessment of the contribution of the different functional trapping mechanisms which prevent the buoyant CO_2 from migrating back to the surface (IPCC, 2005; Juanes et al., 2010). These trapping mechanism include structural trapping (Iglauer et al., 2015a, Arif et al., 2016a,b, 2017a;), capillary or residual trapping (Juanes et al., 2010; Iglauer et al., 2011a,b; Pentland et al., 2011; Krevor et al., 2012), mineral trapping (Gaus 2010; Golding et al., 2011; Pearce et al., 2015,) and dissolution trapping

(Iglauer 2011c; Agartan et al., 2015). In addition, adsorption trapping has been identified as another storage mechanism functional in coal seams and organic rich shales (Busch et al., 2008; Shojai Kaveh et al., 2012, 2016; Arif et al., 2016c, 2017b).

Structural and residual trapping are strongly influenced by the CO_2-brine-rock wettability (Chaudhary et al., 2013; Iglauer et al. 2015a,b; Al-Menhali et al. 2016a,b; Rahman et al., 2016; Al-Khdheeawi et al., 2017; Arif et al. 2017a; Iglauer 2017; Wan et al., 2018), however, wettability is a complex parameter which is not well understood, particularly for realistic subsurface conditions. One key aspect of realistic subsurface conditions is their anoxic or reducing character, which results in the existence of organic molecules in target storage formations (Meredith et al., 2000; Watson et al. 2002).

It is shown in previous studies that water receding contact angle on the cap rock (i.e. CO_2 displacing water) is related to structural trapping (below an impermeable caprock; Broseta et al., 2012). Whereas, the advancing water contact angle (water displacing CO_2) is related to capillary trapping in the reservoir rock (Chiquet et al. 2007; and thus the amount of residually trapped CO_2; Chaudhary et al., 2013, Rahman et al. 2016, Al-Menhali et al. 2016a). Note further that dissolution trapping in the reservoir rock is significantly affected by the wettability and it is thus necessary to know the wettability for accurate reservoir simulations and storage capacity predictions (Al-Khdheeawi et al. 2016, 2017).

Although the concentrations of organic molecules in deep aquifers is normally low (Stalker et al. 2013), their prevailing concentrations are potentially sufficient to significantly influence the rock's wettability characteristics (Standnes and Austad, 2003; Gomari et al., 2006; Iglauer et al., 2014). Indeed, a partial mono-molecular layer adsorbed to the mineral surface would be sufficient for this (Shafrin et al., 1962; Gaines 1966; Kuhn et al., 1971; Zasadzinski et al., 1994; Adamson and Gast 1997; Maboudian et al., 1997; Bikkina 2011; Mahadevan 2012).

These minute organic concentrations can adversely affect the storage capacities and containment security via their impact on CO_2 wettability (Iglauer et al. 2015a,b; Al-Khdheeawi et al. 2016, 2017). It is therefore important to understand at what organic concentration the impact on CO_2/Water/Mineral wettability becomes significant for trapping capacities. Thus, this work aims to benchmark the influence of trace concentrations of such organics and the effect of their carbon chain length on CO_2-rock wettability.

2. Experimental Methodology

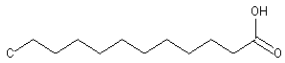
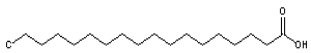
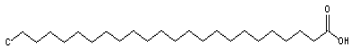
2.1. Materials

Nine pure quartz samples (Quartz (single crystals; testing chips from WARD'S Natural Science; sample range = 12 mm to 19 mm x 10 mm x 10 mm) were used as a model for sandstone storage formations. The surface roughnesses of all nine surfaces were provided by the supplier and the values ranged from 1 nm to 2 nm (root-mean-square (RMS) surface roughness, which is very smooth (Sarmadivaleh et al. 2015).

CO_2 (purity ≥ 99.999 mol%; from BOC, gas code-082), N_2 (purity ≥ 99.999 mol%; from BOC, gas code-234) and 10 wt% NaCl brine (NaCl purity ≥ 99.9mol%; from Scharlab) were used. The NaCl was dissolved in deionized water (Ultrapure from David Gray; electrical conductivity = 0.02 mS/cm). Subsequently, the NaCl brine was equilibrated with CO_2 at experimental conditions in a high pressure mixing reactor (according to the procedure described by El-Maghraby et al. 2012). To represent organic compounds, organic acids were selected due to their presence in hydrocarbon reservoirs and aquifers; these included hexanoic acid, lauric acid, stearic acid, and lignoceric or oleic acid (Jardine et al., 1989; Legens et al., 1998; Madsen and Ida, 1998; Hansen et al., 2000; Amaya et al., 2002; Hamouda and Gomari,

2006; Kharaka et al., 2009; Stalker et al., 2013; Yang et al., 2015), Tabe 1 (purchased from Sigma Aldrich, purity ≥ 98 mol%).

Table 1: Properties of organic acids used in this study.

Organic Acid	Physical state	Formula	Number of C atoms	Molar mass (g/mol)	Chemical Structure
Hexanoic acid	Liquid	$C_6H_{12}O_2$	6	116.158	
Lauric acid	solid	$C_{12}H_{24}O_2$	12	200.318	
Stearic acid	solid	$C_{18}H_{36}O_2$	18	284.4772	
Lignoceric acid	solid	$C_{24}H_{48}O_2$	24	368.63	

Acetone (≥ 99.9 mol%; from Rowe Scientific) was used as surface cleaning agent, and drops of aqueous hydrochloric acid (ACS reagent, concentration 37 vol%, Sigma Aldrich) were used to control the pH of the brine (see ageing procedure below for more details).

2.2. Sample preparation

2.2.1 Quartz surface preparation

Initially the mineral (quartz) substrates were cleaned with DI-water to remove any dust or surface fragments from the surface. The sample was then dried in an oven at 90°C for 60 mins and exposed to air plasma (using a DiemerYocto instrument) for 15 mins to remove any organic contamination (Love et al., 2005; Iglauer et al., 2014).

2.2.2 Ageing procedure

To mimic a typical storage formation, where the rock pore surfaces were exposed to formation water over geological times we adopted the following strategy (Davis 1982; Ulrich et al., 1988; Zullig and Morse, 1988; Ochs et al., 1994; Hoeiland et al., 2001; White et al., 2003; Nordbotten et al., 2005; Karoussi et al., 2008; Birkholzer et al., 2009; Ji et al., 2015; Kleber et al., 2015):

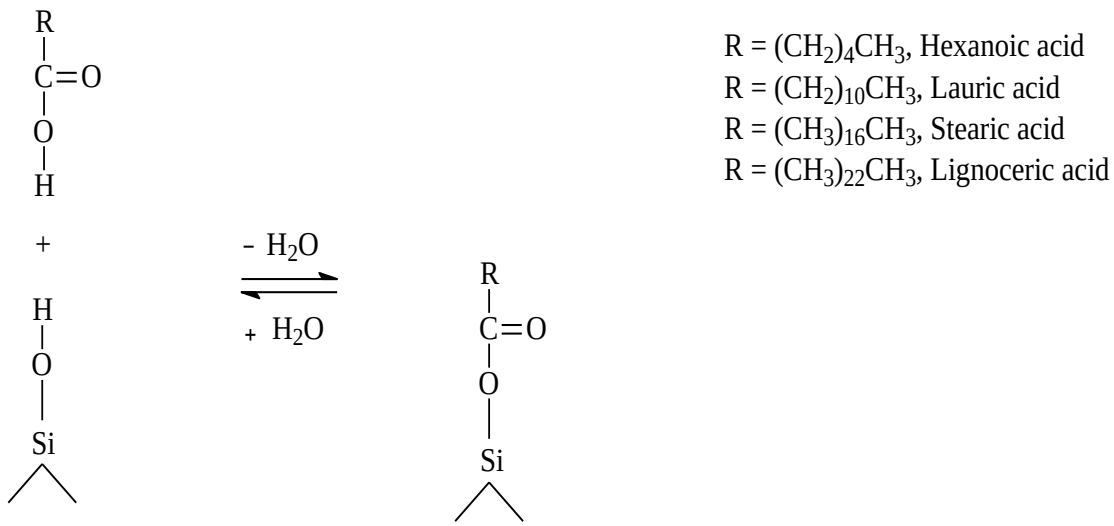
The quartz samples were immersed for 30 mins in 2 wt% NaCl brine at ambient conditions, while the acidity was maintained at pH = 4 by adding drops of aqueous hydrochloric acid; this procedure increases the adsorption rate of organics onto the substrate, and thus simulates adsorption of organic molecules over geological times (i.e. millions of years' exposure time) (Thurman 1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015). Ultraclean N_2 was then used to mechanically clean (blow away) the remaining water from the surface to avoid contamination. Subsequently the substrates were aged in different organic acid/n-decane solutions of prescribed molarity (10^{-2} M to 10^{-10} M organic acid concentration) for seven days to mimic exposure to formation fluid (which contains organic molecules) over geological time (Thurman 1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015).

Previously, silanes were used to render the wettability of quartz surfaces oil-wet. Typically, different silanes have different impacts on surfaces hydrophilicity (Dickson et al., 2006, Grate et al., 2012, Hobeika et al., 2017). However, organic acids including stearic acids represent more realistically subsurface environments (Al-Anssari et al., 2016, 2018, Paterson et al., 2011, Hamouda et al., 2006, Gomari et al., 2006); while silanes do not exist in the subsurface (due to their high reactivity).

It is vital to re-create such mineral surfaces to realistically mimic the subsurface behaviour, particularly with respect to their wettability characteristics (Davis 1982; Ochs et al., 1994;

Adamson and Gast 1997; Kleber et al., 2015). Note that it is proven that carboxylic acids and hydrocarbons both exist in deep saline aquifers (Bennett et al., 1993), as a result of biodegradation and organic matter diagenesis and subsequent migration into the water zones (Jones et al., 2008).

Mechanistically, the organic acid esterifies the hydroxyl groups on the quartz surface in a condensation reaction (Scheme 1).



Scheme 1. Chemisorption of organic acids on solid quartz surface (∧ indicates solid bulk).

Thus carboxylic components are chemically (covalently) bonded to the quartz surface, rendering them strongly hydrophobic (Al-Anssari et al., 2016).

2.3. Surface characterization of pure and aged quartz surfaces

The surface properties of the quartz samples were analysed via energy dispersive X-ray spectroscopy (EDS, Oxford X-act SSD X-ray detector with Inca and Aztec software) and contact angle (θ) measurements. Table 2 lists the EDS results before and after aging; these are average elemental surface concentrations (these are average over 45 data points: 5 data points

measured on each sample, on nine different samples) for each acid tested. Surface coverages with organic acid are also given (determined via the method defined by Dickson et al. 2006).

Table 2. Surface composition of pure and aged quartz samples and associated surface coverage with all organic acids.

Concentration (Molarity)	Pure Quartz			After ageing			Change due to ageing			Estimated surface coverage (after Dickson et al., 2006)
	wt% Si	wt% C	wt% O	wt% Si	wt% C	wt% O	wt% Si	wt% C	wt% O	$\left(1-\frac{wt\%\ C_{before\ aging}}{wt\%\ C_{after\ aging}}\right)\times 100$
Hexanoic Acid										
10^{-2}	31.9	2.3	65.8	38.1	4.8	57.1	+6.2	+2.5	-8.7	52.1
10^{-3}	33.3	4.1	62.6	30.3	7.5	62.2	-3.0	+3.4	-0.4	45.3
10^{-4}	35.4	2.8	61.8	37.0	4.9	58.1	+1.6	+2.1	-3.7	42.9
10^{-5}	34.7	3.2	62.1	34.2	5.1	60.7	-0.5	+1.9	-1.4	37.3
10^{-6}	29.0	3.5	67.5	32.9	5.2	61.9	+3.9	+1.7	-5.6	32.7
10^{-7}	29.5	4.2	66.3	29.0	5.8	65.2	-0.5	+1.6	-1.1	27.6
10^{-8}	32.8	1.8	65.4	48.0	2.3	49.7	+15.2	+0.5	-15.7	21.7
10^{-9}	29.9	3.4	66.7	33.1	4.1	62.8	+3.2	+0.7	-3.9	17.1
10^{-10}	31.8	2.6	65.6	32.0	2.9	65.1	+0.2	+0.3	-0.5	10.3
0	34.0	1.5	64.5	34.0	1.5	64.5	0	0	0	0
Lauric Acid										
10^{-2}	38.1	2.4	59.5	27.6	5.3	67.1	-10.5	+2.9	+7.6	54.7
10^{-3}	33.8	1.8	64.4	31.1	3.5	65.4	-2.7	+1.7	+1.0	48.6
10^{-4}	33.0	3.4	63.6	28.8	6.1	65.1	-4.2	+2.7	+1.5	44.3
10^{-5}	38.3	4.3	57.4	35.4	7.1	57.5	-2.9	+2.8	+0.1	39.4
10^{-6}	32.4	2.6	65.0	34.1	4.0	61.9	+1.7	+1.4	-3.1	35.0
10^{-7}	34.5	3.6	61.9	33.5	5.2	61.3	-1.0	+1.6	-0.6	30.8
10^{-8}	32.4	4.1	63.5	32.7	5.4	61.9	+0.3	+1.3	-1.6	24.1
10^{-9}	32.4	1.4	66.2	36.1	1.7	62.2	+3.7	+0.3	-4.0	17.6
10^{-10}	32.2	3.5	64.3	32.8	4.1	63.1	+0.6	+0.6	-1.2	14.6
0	31.6	2.3	66.1	31.6	2.3	66.1	0	0	0	0
Stearic Acid										
10^{-2}	35.4	1.3	63.3	32.2	3.1	64.7	-3.2	+1.8	+1.4	58.1
10^{-3}	34.3	3.7	62.0	26.8	7.6	65.6	-7.5	+3.9	+3.6	51.3
10^{-4}	37.0	4.5	58.5	26.7	8.4	64.9	-10.3	+3.9	+6.4	46.4
10^{-5}	36.8	1.6	61.6	32.3	2.8	64.9	-4.5	+1.2	+3.3	42.9
10^{-6}	35.8	2.4	61.8	41.7	3.8	54.5	+5.9	+1.4	-7.3	36.8
10^{-7}	36.0	4.3	59.7	22.0	6.3	71.7	-14.0	+2.0	+12	31.7
10^{-8}	38.2	2.9	58.9	23.8	4.0	72.2	-14.4	+1.1	+13.3	27.5
10^{-9}	34.1	4.2	61.7	23.5	5.2	71.3	-10.6	+1.0	+9.6	19.2
10^{-10}	36.5	4.1	59.4	45.4	4.9	49.7	+8.9	+0.8	-9.7	16.3
0	36.5	2.2	61.3	36.5	2.2	61.3	0	0	0	0
Lignoceric Acid										
10^{-2}	37.3	2.3	60.4	25.0	6.2	68.8	-12.3	+3.9	+8.4	62.9
10^{-3}	36.3	2.0	61.7	25.4	4.6	70.0	-10.9	+2.6	+8.3	56.5
10^{-4}	34.1	4.0	61.9	21.9	7.8	70.3	-12.2	+3.8	+8.4	48.7
10^{-5}	35.6	3.4	61.0	24.8	6.2	69.0	-10.8	+2.8	+8.0	45.2
10^{-6}	34.7	3.5	61.8	32.3	5.8	61.9	-2.4	+2.3	+0.1	39.7
10^{-7}	33.9	4.1	62.0	28.9	6.1	65.0	-5.0	+2.0	+3.0	32.8
10^{-8}	33.7	2.7	63.6	26.0	3.9	70.1	-7.7	+1.2	+6.5	30.8
10^{-9}	39.6	1.9	58.5	27.7	2.5	69.8	-11.9	+0.6	+11.3	24.0
10^{-10}	36.5	4.2	59.3	25.0	5.1	69.9	-11.5	+0.9	+10.6	17.6

0	34.0	3.6	62.4	34.0	3.6	62.4	0	0	0	0

Table 3. Average Elemental surface analysis of quartz samples before and after ageing.

Organic Acids	Before aging			After aging		
	Si (wt%)	C (wt%)	O (wt%)	Si (wt%)	C (wt%)	O (wt%)
Hexanoic acid	$32.2^{a} \pm 3.2^{b}$	$2.9^{a} \pm 1.4^{b}$	$64.8^{a} \pm 2.9^{b}$	$34.9^{a} \pm 9.5^{b}$	$4.4^{a} \pm 3.0^{b}$	$60.7^{a} \pm 7.8^{b}$
Lauric acid	$33.9^{a} \pm 3.4^{b}$	$2.9^{a} \pm 1.5^{b}$	$63.2^{a} \pm 4.4^{b}$	$32.4^{a} \pm 4.3^{b}$	$4.5^{a} \pm 2.7^{b}$	$63.2^{a} \pm 4.8^{b}$
Stearic acid	$36.1^{a} \pm 2.1^{b}$	$3.1^{a} \pm 1.6^{b}$	$60.8^{a} \pm 2.4^{b}$	$31.1^{a} \pm 11.7^{b}$	$4.8^{a} \pm 3.1^{b}$	$64.1^{a} \pm 11.3^{b}$
Lignoceric acid	$35.6^{a} \pm 3.0^{b}$	$3.2^{a} \pm 1.2^{b}$	$61.3^{a} \pm 2.6^{b}$	$27.1^{a} \pm 6.1^{b}$	$5.2^{a} \pm 2.7^{b}$	$67.7^{a} \pm 4.2^{b}$

[a] average surface concentration is based on the arithmetic average of 45 data points measured on five different sites for each of the nine samples at all concentrations tested.
[b] '±' values are the standard deviations of these observations.

Clearly, aging had a significant impact on the atomic surface concentrations irrespective of the type and concentration of organic acid (Table 3). A significant overall average increase in surface carbon concentration (+1.6 wt% C for Hexanoic Acid, +1.7 wt% C for Lauric Acid, +1.9 wt% C for Stearic Acid and +2.2 wt% C for Lignoceric Acid) was measured. These changes in atomic coverage were caused by the chemisorption of the carboxylic acid on the quartz surface, consistent with Zullig and Morse (1988); see also 2.2.2 and scheme 1 above.

Moreover, the brine contact angles on the pure quartz samples were 0° (advancing and receding) at ambient conditions, thus pure quartz was completely water-wet at ambient conditions. However, higher contact angles (advancing 56° and receding 54° ± 3°) were measured at reservoirs conditions on these pure quartz samples (323 K (50 °C), 25 MPa), consistent with literature data (Chiquet et al., 2007; Farokhpoor et al., 2013; Al-Yaseri et al.

2016a,b; Arif et al., 2016d;). However, aging of the quartz surfaces caused a significant change in contact angles and thus CO_2-wettability, this is discussed in detail below.

2.4. Contact angle measurements

Contact angle measurements are a standard technique for assessing the wettability behaviour of a given rock/fluid/fluid system. Here we used the tilted plate technique, which is regarded as the most effective contact angle measurement method as it can measure advancing and receding contact angles simultaneously (Lander et al., 1993).

The schematic of the experimental setup is shown in Figure 1. It consists of a high pressure-high temperature cell, which houses the sample inside on a tilted plate. The cell is connected to two pumps (Teledyne D-500, pressure accuracy of 0.1%) used for either discharging brine or CO_2. Furthermore, a CO_2 gas cylinder and the brine pump are both connected to a mixing reactor with which CO_2 and brine can be thermodynamically equilibrated (El-Maghraby et al. 2012).

Initially, the cell was charged with CO_2 at the desired measurement pressure and temperature (0.1 MPa, 25 MPa and 323 K (50 °C)). Temperature of the pumps was controlled through heating bath and the cell temperature was controlled through heating tape around it. The brine pump was initially filled with CO_2-equilibrated brine (equilibrated at experimental conditions) and a droplet of equilibrated brine (average drop volume was 6 µL (± 1 µL) was dispensed onto the quartz surface through a needle. The advancing (θ_a) and receding (θ_r) brine contact angles were then measured at the leading and trailing edge of the droplet just before the drop started to move (Lander et al., 1993). This process was recorded by a high performance video camera (Basler scA 640–70 fm, pixel size = 7.4 µm; frame rate = 71 fps; Fujinon CCTV lens: HF35HA-1B; 1:1.6/35 mm), which was connected to a computer system to display and analyse

the results. The standard deviation of the measurements was ± 3° based on replicated measurements.

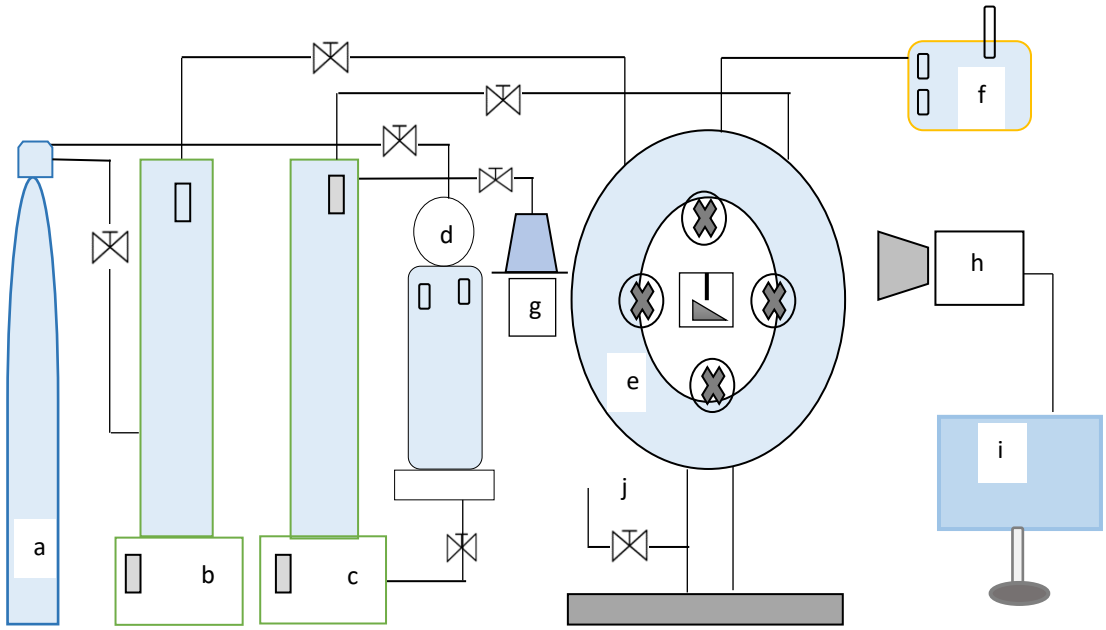


Figure 1. Experimental setting used in this study for measuring advancing and receding contact angles (modified after Arif et al., 2017a). (a) CO_2 cylinder (b) high precision syringe pump-CO_2, (c) high precision syringe pump-water, (d) High pressure Parr reactor for fluid equilibration e) high pressure cell with substrate housed on a tilted plate inside, (f) heating unit, (g) liquid feed/drain system, (h) high resolution video camera, (i) image visualization and interpretation software, (j) pressure relief valve.

3. Results and Discussion

Our results show that the quartz surface loses its water-wetness with increasing organic acid concentration. However, at organic acid concentrations ≤ 10^{-6} M, contact angles were only minimally affected, Figure 6, and thus structural trapping is not significantly affected (note:

even at low concentrations ≤ 10^{-6} M optimal residual trapping capacities are significantly affected). However, for concentrations > 10^{-6} M, quartz wetting behaviour shifts from strongly water-wet to an intermediate-wet state (Iglauer et al., 2015b). A recent study conducted on carbonate minerals (Ali et al., 2019) showed that even at low organic concentrations (≤ 10^{-6} M organic acid), optimal residual trapping capacities could be affected, which is due to the surface coverage of the mineral with organic acid and its tendency to alter the formation more CO_2-wet. Such wettability alteration changes the primary drainage capillary pressure curve (Morrow 1970, Anderson 1986, Masalmeh 2003), and thus the initial CO_2 saturation directly influencing the residual CO_2 saturation (e.g. Pentland et al. 2011; Wang et al., 2015, Heshmati et al., 2014, Akbarabadi et al., 2015).

3.1. Effect of acid concentration on quartz wettability

Advancing and receding brine contact angles increased significantly with an increase in organic acid concentration, as shown in Figures 2-5.

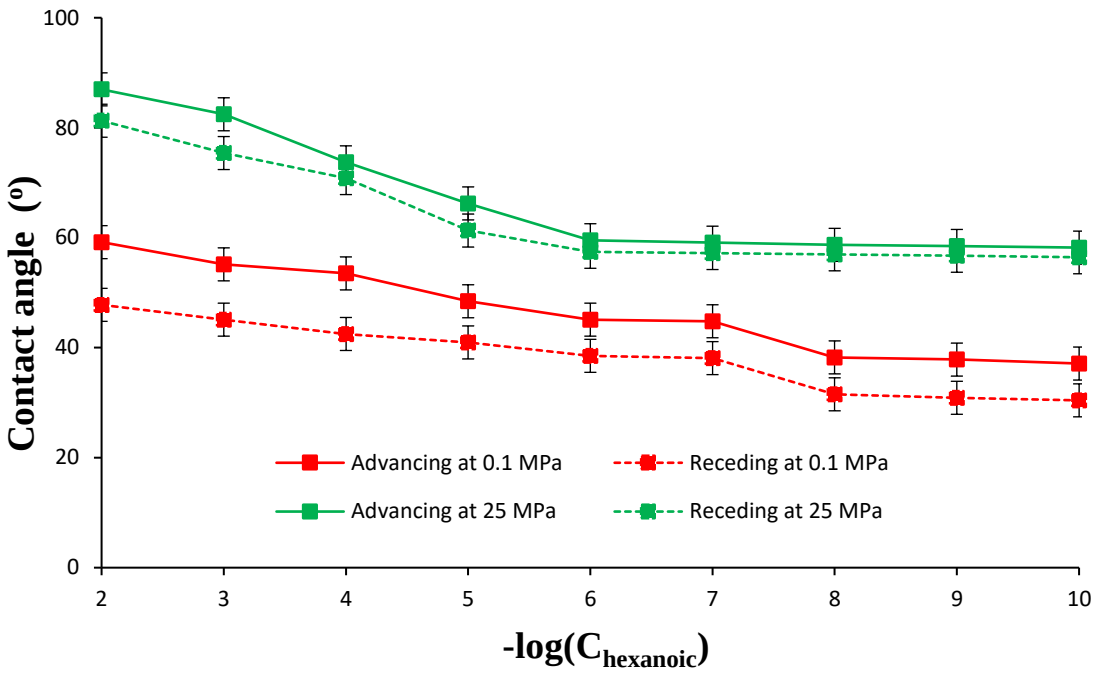


Figure 2. Quartz/CO_2/brine contact angles (measured through the water) as a function of hexanoic acid (C_6) concentration; $C_{hexanoic}$ is the hexanoic acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

The contact angle was significantly higher at high pressure, consistent with literature data (e.g. Dickson et al. 2006; Espinoza and Santamarina 2010; Broseta et al. 2012; Shojai Kaveh et al., 2012, 2016; Chen et al, 2015; Iglauer et al., 2015a,b; Al-Yaseri et al. 2016a,b; Iglauer 2017). For example, at 25 MPa and 323 K (50 °C), for the quartz surface aged in 10^{-10} M hexanoic acid, θ_a was 58° and θ_r was 55° implying that the quartz surface is weakly water-wet under such conditions. With an increase in hexanoic acid concentration up to 10^{-6} M, there was an insignificant change in θ. However, further organic acid concentration increase resulted in significant contact angle increase. For instance, when the hexanoic acid concentration increased to 10^{-2} M, at the same temperature and pressure (25 MPa, and 323 K (50 °C)), θ_a and θ_r increased to 87° and 82°, implying a wettability transformation from weakly water-wet to

intermediate-wet. Such a reduction in water wettability of the surface potentially leads to a reduction in residual trapping capacities where CO_2 plume is migrating in storage formation (Chaudhary et al., 2013; Iglauer et al., 2017; Al-Menhali et al., 2016a; Rahman et al., 2016). Note for instance that lower residual CO_2 saturations have been measured in more hydrophobic rock by x-ray micro-tomography (Al-Menhali et al., 2016a, Chaudhary et al., 2013, Rahman et al., 2016).

Lauric acid followed somewhat similar trends. For the quartz surface aged in 10^{-10} M lauric acid, quartz/CO_2/water contact angles were significantly lower than those measured on surfaces aged in 10^{-2} M lauric acid. Thus higher organic concentrations render the surface more non-wetting to water. For example, at 25 MPa and 323 K (50 °C), for the quartz surface aged in 10^{-10} M lauric acid, θ_a measured as 61° and θ_r as 56°, which increased to θ_a = 89° and θ_r = 84° when lauric acid concentration increased to 10^{-2} M (Figure 3).

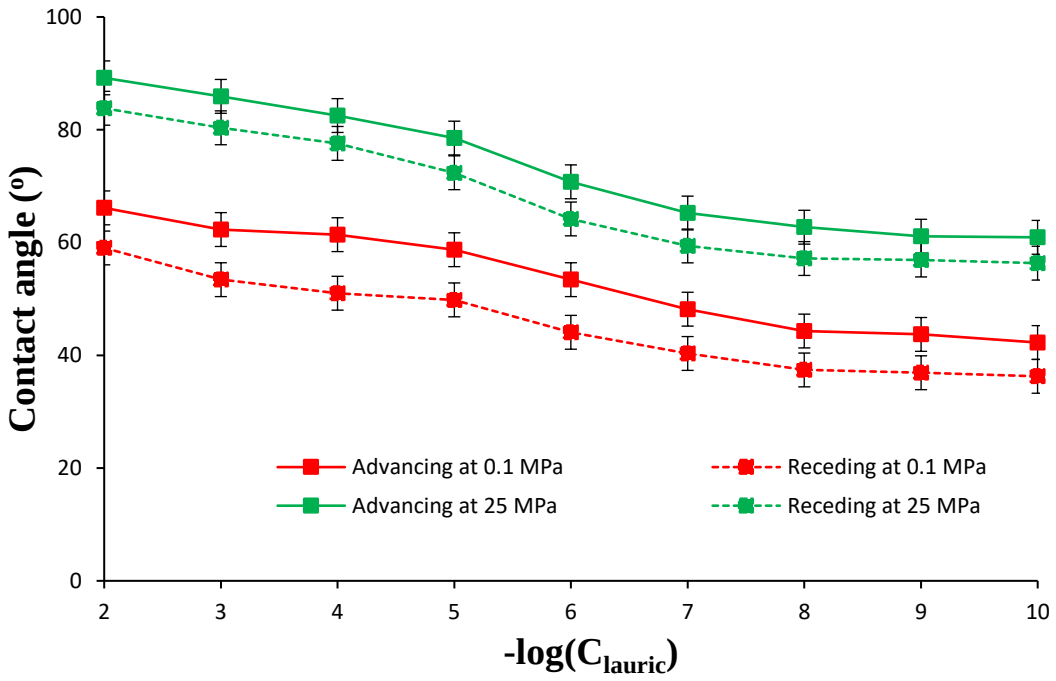


Figure 3. Quartz/CO_2/brine contact angles as a function of lauric acid (C_{12}) concentration; C_{lauric} is the lauric acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

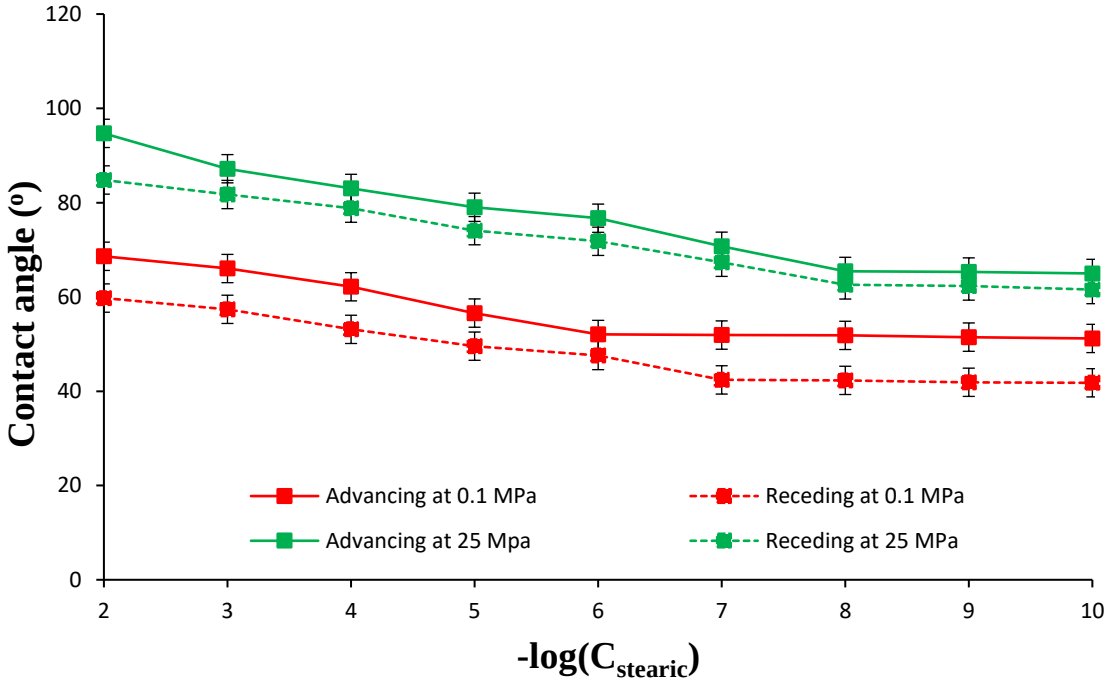


Figure 4. Quartz/CO_2/brine contact angles as a function of stearic acid (C_{18}) concentration; $C_{stearic}$ is the stearic acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

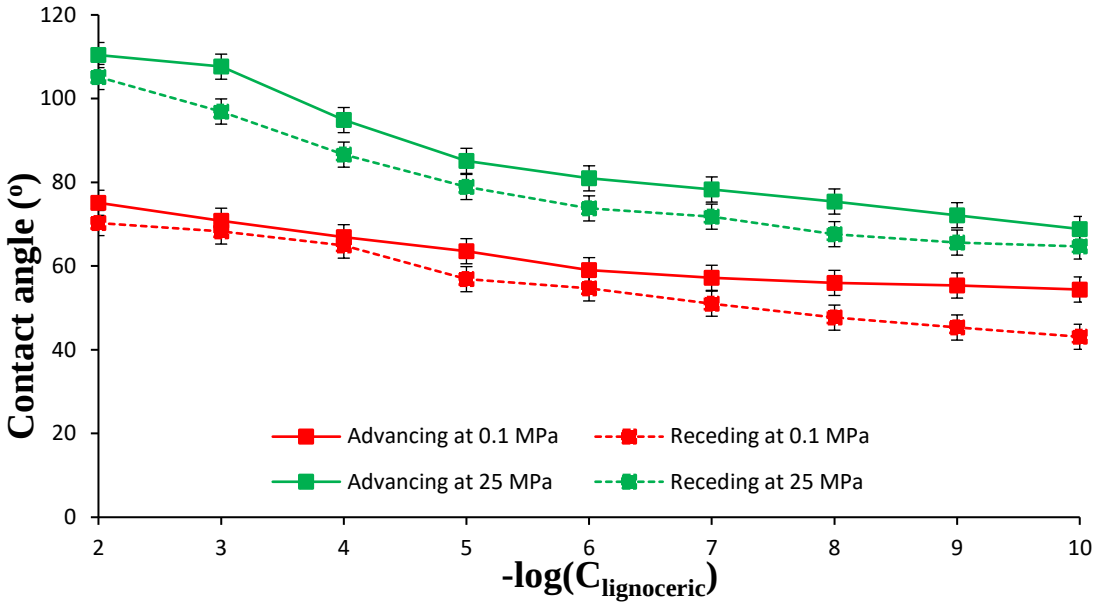


Figure 5. Quartz/CO_2/brine contact angles as a function of lignoceric acid (C_{24}) concentration; $C_{lignoceric}$ is the lignoceric acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

The results showed the same trend for quartz surfaces aged in stearic acid and lignoceric acid (Figures 4 and 5). In summary, the higher the organic acid concentration was, the higher were the values of both the advancing and receding water contact angles irrespective of the type of organic acid used for aging. Our results are consistent with literature data on wettability of calcite/oil/brine systems in the presence of organic acids (Hansen et al., 2000; Standness and Austad, 2003; Gomari et al., 2006). Mechanistically, carboxylic acid adsorbs onto the quartz surface leading to a wettability modification towards less water-wet surface conditions, see above.

When compared with CO_2-wettability of pure quartz surfaces, we find that higher contact angles are found, even at the lowest organic acid concentration (10^{-10} M, which is very low). For instance, for pure quartz/CO_2/brine system, at 20 MPa and 323 K (50 °C), θ_a was reported to be approximately 40° (Sarmadivaleh et al., 2015), whereas the lowest θ_a in the presence of

lowest chain organic acid (Hexanoic acid, C_6) was 57° (Figure 6). It is thus clear that even minute amounts of organic acid significantly increase the CO_2-wettability of mineral surfaces. As such minute concentrations always exist in the subsurface, even in aquifers (Bennett et al., 1993; Jones et al., 2008; Stalker et al. 2013), lower residual trapping capacities than previously thought are expected (Ali et al., 2019).

3.2 Influence of organic acid alkyl chain length on quartz wettability

It is clear that all organic acids influence the quartz wettability in a similar fashion i.e. both water advancing and receding contact angles increase with an increase in organic acid concentration and quartz rapidly loses its water-wetness, Figure 6. However, at a fixed organic acid concentration, the absolute values of contact angles were different for different acids (which differ in their alkyl chain length and their coverage on the quartz surface, as showed in Figure 6); surfaces aged in hexanoic acid (C_6) exhibited the lowest contact angles values, while surfaces aged in lignoceric acid (C_{24}) exhibited the highest contact angles values. Lauric acid and stearic acid fell in between. For instance, at 25 MPa and 323 K (50 °C), and a fixed organic concentration 10^{-2} M of hexanoic, lauric , stearic and lignoceric acid, θ_r = 81°, θ_r = 84°, θ_r = 85° and θ_r = 105°, respectively. Such a wettability transformation from intermediate-wet to CO_2-wet is attributed to the number of carbon atoms present in the acid, Table 1. Clearly, longer alkyl chains in the organic acid renders the surface more hydrophobic.

These effects have dramatic impact on the optimal residual trapping limit, which we consider here as the point where primary drainage is unaffected by wettability, i.e. at θ_a = 50° (Morrow 1970, Morrow 1976). For example, at 25 MPa and 323 K (50 °C) and a fixed trace organic concentration of 10^{-10} M, θ_a > 50° for all acids (note that this is a very minute concentration, and much higher organic concentrations were measured in deep saline aquifers (e.g. Thurman

1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015)); Figure 6.

Overall it is clear that a detailed knowledge of organic acids and its relative concentrations in storage formations is very important for assessing the feasibility of long-term geological storage projects.

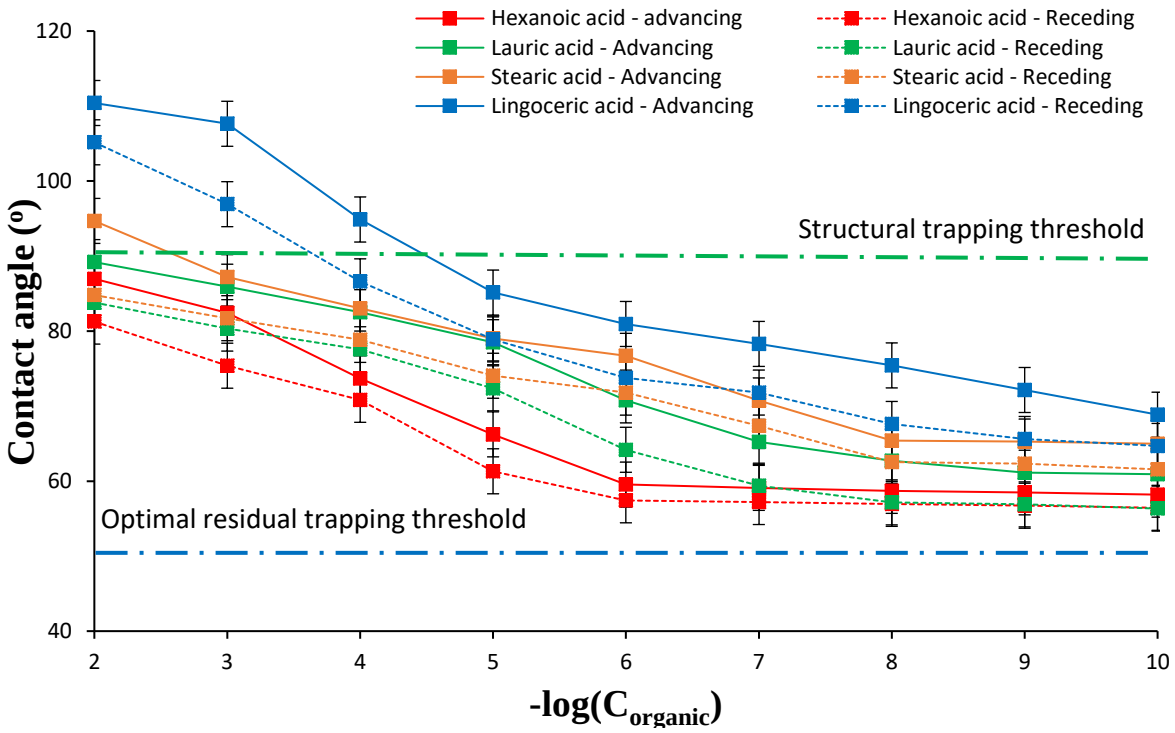


Figure 6. Quartz/CO_2/brine contact angles as a function of organic acid concentration and alkyl chain length at 25 MPa and 323 K (50 °C); $C_{organic}$ is the organic acid concentration (molarity). Dotted blue horizontal lines in the graph define the capillary trapping threshold ($\theta = 50°$), and dotted green horizontal lines in graph define the structural trapping ($\theta > 90°$) threshold.

4. Conclusions

Deep saline aquifers contain organic acids, which have a direct impact on the interfacial phenomena at the fluid/rock interface due to chemisorption. These effects are, however, only poorly understood; thus we measured the wettability of quartz/CO_2/brine systems in the presence of various organic acids. Four acids (hexanoic acid, lauric acid, stearic acid, lignoceric acid) were considered for a wide range of concentrations (10^{-9} M to 10^{-2} M), and advancing and receding contact angles were measured at typical storage conditions (25 MPa and 323 K (50 °C), as well as at ambient pressure) in order to mimic a realistic subsurface behaviour. We found that both advancing and receding contact angles increased with an increase in organic acid concentration throughout the tested experimental matrix. In addition, at a fixed organic acid concentration, the highest contact angles values were measured for lignoceric acid (C24), while relatively least values were recorded for hexanoic acid (C6). This behaviour is attributed to the number of carbon atoms in the organic acids alkyl chain, and hence a higher number of C atoms, resulting in more CO_2-wet/hydrophobic surfaces, which causes a reduction in residual trapping capacities.

We thus conclude that CO_2 geological storage capacities in certain geological scenarios (aquifers as an example) may be lower than previously thought. Reservoir-scale models thus need to take these effects into account so that accurate storage predictions are obtained thus de-risking carbon geological storage (CGS) projects.

Conflicts of Interest

There are no conflicts to declare.

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