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Key Points:

- Rock wettability strongly correlates with gas density
- Water wettability decreases with increasing gas density
- Wettability depends on gas density (and not gas type)

Supporting Information:

- Supporting Information S1

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Dependence of quartz wettability on fluid density

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Abstract Wettability is one of the most important parameters in multiphase flow through porous rocks. However, experimental measurements or theoretical predictions are difficult and open to large uncertainty. In this work we demonstrate that gas densities (which are much simpler to determine than wettability and typically well known) correlate remarkably well with wettability. This insight can significantly improve wettability predictions, thus derisking subsurface operations (e.g., CO₂ geostorage or hydrocarbon recovery), and significantly enhance fundamental understanding of natural geological processes.

1. Introduction

Carbon geostorage (CGS) has recently been explored as a technology to reduce anthropogenic greenhouse gas emissions and thus mitigate climate change [Intergovernmental Panel on Climate Change (IPCC), 2005; Orr, 2009; Lackner, 2003]. CGS containment security and storage efficiency rely on several storage mechanisms of which structural and residual trapping are the most important ones during the first several decades of a storage project [IPCC, 2005; Orr, 2009]. Both mechanisms depend on strong capillary forces, which are present in the pore network of the rock. The capillary forces counter balance the buoyancy forces exerted by the (lower density) CO₂, and they are determined by the contact angle (θ) between the rock, water, and gas in the pore space as well as pore geometry [Iglauer et al., 2015a]. Specifically, small water contact angles ($<50^\circ$) lead to good structural [Iglauer et al., 2015b] and residual trapping capacities [Pentland et al., 2011; Iglauer, 2011; Andrew et al., 2013], while high contact angles ($>90^\circ$) dramatically reduce structural [Iglauer et al., 2015a, 2015b] and residual trapping capacities [Chaudhary et al., 2013; Rahman et al., 2016]. However, there is a large uncertainty associated with such contact angle data reported in the literature [Mahadevan, 2012; Bikkina, 2012; Iglauer et al., 2014; Palamara et al., 2015], and such experiments are generally expensive and difficult to perform. Theoretical predictions based on molecular dynamics computations are also laden with uncertainty and the difficulty to mimic the solid surface in a representative way [Liu et al., 2010; Iglauer et al., 2012; McCaughan et al., 2013; Javanbakht et al., 2015; Chen et al., 2015]. It is therefore highly desirable to well constrain θ to make reliable reservoir flow predictions and related economic and safety risk assessments.

In this context, we demonstrate that the density of gas (ρ_g) in a brine/gas/quartz system correlates remarkably well with θ , and therefore, ρ_g can be used to significantly simplify θ predictions. Implementation of such correlations in reservoir simulators will significantly improve CGS planning and derisk projects.

2. Experimental Methodology

An alpha-quartz crystal was selected as it is the most common constituent mineral found in mudrocks and sandstone storage rocks [Blatt and Schultz, 1976; Hawkes et al., 2005; Chiquet et al., 2007; Qi et al., 2009; Linstrom and Mallard, 2011; Grate et al., 2012; Wang et al., 2012; Broseta et al., 2012; Al-Yaseri et al., 2015; Sarmadivaleh et al., 2015; Gallé, 2000; Iglauer et al., 2015a, 2015b; Al-Yaseri et al., 2016]. The smooth sample (root-mean-square surface roughness is 56 nm [Al-Yaseri et al., 2016]) was cleaned with acetone and then exposed to air plasma for a period of 15 min to remove surface contaminants prior to each test [Love et al., 2005; Mahadevan, 2012; Bikkina, 2012; Iglauer et al., 2014]. Subsequently, the substrate was placed in a high-pressure cell and flooded with gas for a minimum period of 10 mins. The gas pressure in the cell was then incrementally increased to preset values of 0.1, 5, 10, 15, and 20 MPa using a high-precision syringe pump (ISCO pump model 500D), while the temperature was kept constant (343 K). A droplet of brine (20 wt % NaCl + 1 wt % KCl in deionized water; degassed under vacuum for a period of 10 h) was then dispensed onto the tilted

substrate, so that advancing and receding water contact angles could be measured [Lander *et al.*, 1993], with a high-performance video camera. Each experiment was repeated thrice, and therefore, the average values of contact angle with associated error bars are shown in the results. The density of the different gases (note that some of the components are supercritical at certain conditions, e.g., CO₂ above 304.8 K and 7.39 MPa, but for simplicity, we call all volatile phases “gas” here; the purity of all gases used was ~99.9 mol %) at different pressures was calculated using the real gas law (PV = ZnRT) [Linstrom and Mallard, 2011]. Considering the fact that only quartz was tested (in the presence of water), we limit our discussion to this material only; however, we hypothesize that similar trends could hold for other geological materials; this is further discussed below.

3. Results and Discussion

As abovementioned the contact angle is a key parameter required to predict subsurface flow processes [e.g., Oren *et al.*, 1998; Blunt, 2001; Valvatne and Blunt, 2004]. The difficulty, however, lies in acquiring accurate data, and we present here a much simpler way to determine θ , namely, through a correlation with the density of the gas phase. The contact angle of liquid (θ_l) can be related to the gas-solid (γ_{gs}), gas-liquid (γ_{gl}), and liquid-solid (γ_{ls}) interfacial tensions by Young’s equation [Young, 1805]:

$$\cos\theta_l = \frac{(\gamma_{gs} - \gamma_{ls})}{\gamma_{gl}} \quad (1)$$

With the use of the sharp-kink approximation [Dietrich and Napiórkowski, 1991; Merath, 2008] and Young’s equation (equation (1)), the following macroscopic equation can be obtained [Garcia *et al.*, 2009; Gatica *et al.*, 2004; Cheng *et al.*, 1991]:

$$\cos\theta_l = \frac{I}{\gamma_{lg}} \Delta\rho - 1 \quad (2)$$

where $I = -\int_{z_{\min}}^{\infty} V(z)dz$ is the van der Waals potential integral (I) [Garcia *et al.*, 2009; Gatica *et al.*, 2004], and $\Delta\rho = \rho_{lf} - \rho_g$ (ρ_g is the gas density and ρ_{lf} is a function of the liquid and gas densities for a specific substrate), [Merath, 2008]. Rearranging equation (2) therefore yields:

$$\cos\theta_l = -\frac{I}{\gamma_{lg}} \rho_g + \left(\frac{I}{\gamma_{lg}} \rho_{lf} - 1 \right) \quad (3)$$

Detailed discussion of equation (3) and how it has been derived is given in the supporting information. In order to use equation (3), the measured advancing-receding water contact angles (Figure 1) were combined to obtain the Young’s contact angle [Chibowski and Terpilowski, 2008; Tadmor, 2004]:

$$\theta_l = \arccos\left(\frac{r_A \cos\theta_A + r_R \cos\theta_R}{r_A + r_R}\right) \quad (4)$$

$$\text{With } r_A = \left(\frac{\sin^3\theta_A}{2 - 3\cos\theta_A + \cos^3\theta_A}\right)^{1/3} \text{ and } r_R = \left(\frac{\sin^3\theta_R}{2 - 3\cos\theta_R + \cos^3\theta_R}\right)^{1/3}$$

The measured advancing (θ_a) and receding (θ_r) water contact angles increased with pressure but to different degrees based on the gas type (Figure 1), consistent with literature data [Chiquet *et al.*, 2007; Espinoza and Santamarina, 2010; Jung and Wan, 2012; Saraji *et al.*, 2013; Iglauer *et al.*, 2014, 2015b; Al-Yaseri *et al.*, 2016; Sarmadivaleh *et al.*, 2015]. The physicochemical reason for this increase is the strengthening of gas-quartz intermolecular interactions, which increase with increasing pressure [Iglauer *et al.*, 2012]. Note that the associated Wenzel contact angles were computed and used in Figure 1 to filter out the effect of surface roughness (Al-Yaseri *et al.* [2016] noticed that the effect of surface roughness is only minor).

The measurement (or estimation) of the van der Waals forces (term I in equation (3)) is a significant challenge and typically requires substantial effort [Cheng *et al.*, 1991; Gatica *et al.*, 2004; Garcia *et al.*, 2009], and therefore we propose to use the concept presented in equation (3) and plot $\cos\theta_w$ versus ρ_g for the measured

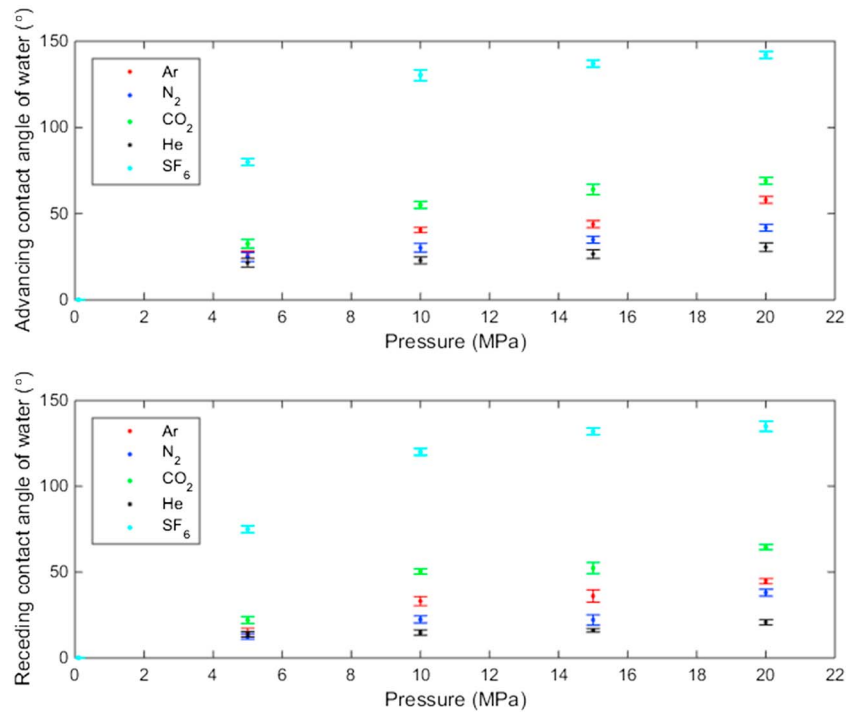


Figure 1. (top) Advancing and (bottom) receding water contact angles for SF₆, CO₂, N₂, Ar, and He/brine/quartz as a function of pressure at constant temperature (343 K and salinity, 4.48 M ionic strength).

water-gas-quartz contact angles (Figure 2); note that the density of different gases is readily available in the literature [e.g., Georgiadis et al., 2010; Linstrom and Mallard, 2011].

Remarkably, there is a linear relationship (equation (5), $R^2 \approx 0.98$) between $\cos \theta_w$ and ρ_g for a wide range of gases. This implies that the contact angle for such a system can be comfortably related to ρ_g :

$$\cos \theta_w = (-0.0012) \rho_g + 0.99 \tag{5}$$

where the slope of the line represents $-\frac{\gamma_{lg}}{\gamma_{lg}} \rho_{lf} - 1$ (which remarkably stays constant with changes in pressure or gas type) and the intersection represents $\left(\frac{\gamma_{lg}}{\gamma_{lg}} \rho_{lf} - 1\right)$. It is, however, important to point out that this correlation

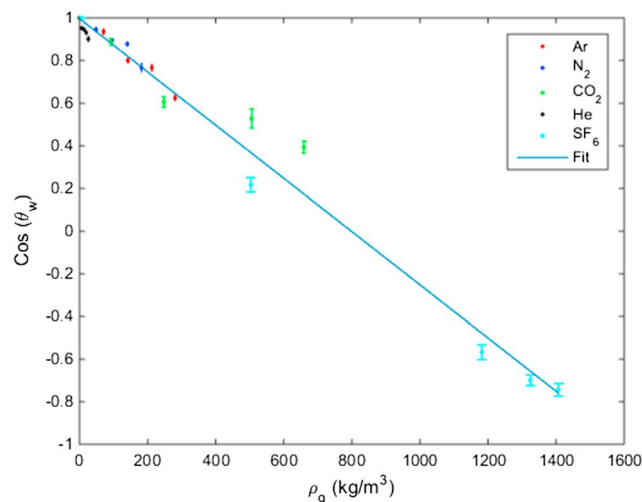


Figure 2. Cosine of the equilibrium water contact angles for SF₆, CO₂, N₂, Ar, and He/brine/quartz as a function of gas density at constant temperature (343 K) and salinity (4.48 M ionic strength). The blue line is the fitted equation (5) ($R^2 = 0.98$).

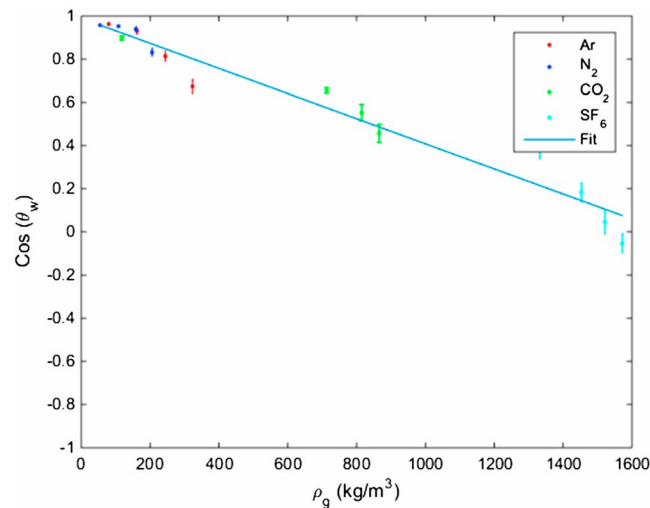


Figure 3. Cosine of the equilibrium water contact angles for SF₆, CO₂, N₂, Ar, and He/brine/quartz as a function of gas density at constant temperature (308 K) and salinity (4.48 M ionic strength). The blue line is the fitted equation ($\cos \theta = (-0.0006)\rho_g + 0.99$, $R^2 = 0.96$).

holds only for quartz, a specific salinity (20 wt % NaCl + 1 wt % KCl = 4.48 M ionic strength) and temperature (343 K) as θ is also a function of salinity, temperature, and the substrate itself [e.g., Arif *et al.*, 2016; Chiquet *et al.*, 2007; Broseta *et al.*, 2012; Al-Yaseri *et al.*, 2016; Sarmadivaleh *et al.*, 2015; cf. Iglauer *et al.*, 2015a]. Nevertheless, this correlation can be extended to other salinity and temperature conditions, e.g., lower temperature as presented in Figure 3.

4. Conclusions and Implications

We have shown that gas densities can be used to predict water contact angles on quartz for a specific temperature and brine composition, and thus rock wettability. Effectively, the impact of pressure and gas type can be correlated by gas density, which represents a remarkable simplification of a complex phenomenon. Thus, these findings enable a much more rapid and simplified determination of θ and associated with that more reliable pore scale [Valvatne and Blunt, 2004] and reservoir scale [Qi *et al.*, 2009; Iglauer *et al.*, 2015a] predictions as gas densities can be swiftly and reliably calculated [Linstrom and Mallard, 2011]. One word of caution is required, however, for each temperature, substrate, and salinity, a similar set of experiments needs to be acquired to adjust the correlations (see above). Furthermore, we conclude that variability in rock wettability with depth can be expected as pressure, and thus, gas density increases with depth [Hawkes *et al.*, 2005; Linstrom and Mallard, 2011].

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