Experimental and simulation study of carbon dioxide, brine, and muscovite surface interactions

Craig M. Tenney[a],[*], Thomas Dewers[a], Kuldeep Chaudhary[b], Edward N. Matteo[a], M. Bayani Cardenas[b], Randall T. Cygan[a]

[a] Sandia National Laboratories, Albuquerque, NM, United States
[b] University of Texas, Austin, TX, United States

ABSTRACT

Capture and subsequent geologic storage of CO_2 in deep brine reservoirs plays a significant role in plans to reduce atmospheric carbon emission and resulting global climate change. Subsurface injection of CO_2 is also used industrially in enhanced oil and natural gas recovery operations to increase the amount of hydrocarbon that can be economically recovered from a geologic reservoir. The interaction of CO_2 and brine species with mineral surfaces controls the ultimate fate of injected CO_2 at the nanoscale via surface chemistry, at the pore-scale via capillary trapping, and at the field-scale via relative permeability. High resolution micro X-ray CT scanning, optical contact angle measurements, and large scale molecular dynamics simulations were used to investigate the behavior of supercritical CO_2 and aqueous fluids on basal surfaces of muscovite, a common phyllosilicate mineral. Experimental results demonstrate partial wetting by the aqueous phase and a dependence of contact angle upon aqueous phase brine composition. This contrasts with simulation results, which predict that supercritical CO_2 forms a non-wetting droplet, separated from direct interaction with the muscovite surface by distinct layers of water and charged species. Simulations with trace amounts of acetate or acetic acid added to the CO_2/water/mineral system were used to investigate the potential effect of contamination with small organic molecules. While the observed contact angle was not significantly altered, these simulations demonstrate the influence of pH on species partitioning, with acetic acid molecules partitioning to the CO_2/water interface and acetate ions adsorbing to the mineral surface. Similar simulations using hexanoate displayed a greater surfactant effect and significantly increased wetting by the CO_2 phase, suggesting that small concentrations of secondary species or contaminants can significantly influence macroscopic wetting behavior.

1. Introduction

Capture and subsequent geologic storage of CO_2 in deep brine reservoirs plays a significant role in plans to reduce atmospheric carbon emission and resulting global climate change (Metz, 2005). Evaluation and implementation of proposed scenarios for injecting CO_2 into sedimentary reservoirs requires understanding the interactions between supercritical CO_2, aqueous brines, and the mineral phases found in the reservoir and overlying caprock. In particular the relative wetting of pore surfaces in the rock matrix by CO_2 and brine, characterized macroscopically by contact angles, controls the capillary pressure of the fluids in the pore and strongly influences the transport and ultimate distribution of CO_2 in the reservoir (Saadatpoor et al., 2010; Krevor et al., 2011). Knowledge of meso- and molecular-scale interactions between fluid and mineral phases can be used to develop

larger-scale conceptual models for multi-phase surface wetting to help evaluate the fate of supercritical CO_2 in the reservoir (Wang et al., 2013; Parmigiani et al., 2011).

Wettability of supercritical CO_2 in subsurface aquifers is of interest for storage efficiency and leakage concerns during geologic carbon storage (GCS) (Iglauer et al., 2015). Because of the ubiquity of clay minerals in both reservoir and caprock lithologies, many researchers have examined wettability in brine-muscovite-CO_2 systems as muscovite surfaces are similar in molecular structure to clay mineral surfaces to act as a proxy for clay mineral wettability. Experimental studies have been conducted to determine the wettability of caprock and reservoir materials in CO_2–brine systems (Chiquet et al., 2007, 2007; Espinoza and Santamarina, 2010; Bikkina, 2011; Kim et al., 2012; Saraji et al., 2013), but reported wetting trends with respect to temperature, pressure, and brine composition are not always consistent (Heath

et al., 2012; Mahadevan, 2012).

Iglauer et al. and Wan et al. provide a review of literature on muscovitebrine-CO$_2$ wettability, and show a large range in contact angles as a function of conditions (temperature, pressure, and ionic strength) (Iglauer et al., 2015; Wan et al., 2014). In general previous works report increases in wetting phase (water) contact angles in mica systems with increasing pressure and with greater contact time between CO$_2$ and mica surfaces (up to 50 days) (Wang et al., 2013; Chiquet et al., 2007; Wan et al., 2014; Broseta et al., 2012; Farokhpoor et al., 2013). Advancing contact angles can range up to 100°, while receding angles are much less (perhaps ~20°) (Wan et al., 2014; Broseta et al., 2012). Static contact angles obtained by workers have intermediate values with somewhat less scatter showing consistent increases with pressure (Wan et al., 2014; Farokhpoor et al., 2013).

Progressive reaction of muscovite surfaces results in alteration and surface roughening which appears to favor CO$_2$ wettability and increases in wetting phase contact angle (Wan et al., 2014). Much has been made in the literature concerning surface treatments and potential contamination and the collective influence on wettability measurements. Iglauer et al. (2014) address contamination and cleaning effects on silica surfaces and propose cleaning all surfaces with strongly oxidizing solutions prior to measurement to ensure surfaces are contaminant free. Saraji et al. (2014) suggest that such cleaning may alter surface properties of silicate minerals, creating an artificial hydrophobicity.

Ionic strength effects on wettability are well known from oil field, environmental, and soil literature (Buckley, 2001; Jr et al., 1997; Leelamanie and Karube, 2013) as well the GCS literature (Wan et al., 2014; Farokhpoor et al., 2013; Jung and Wan, 2012). In CO$_2$-brine-silicate mineral systems, a general increase in contact angle with ionic strength is noted (Farokhpoor et al., 2013; Jung and Wan, 2012) but other authors have noted very little or uncertain influence (Chiquet et al., 2007; Wan et al., 2014; Broseta et al., 2012). No literature exists on the potential influence of various cations in mica wettability in CO$_2$ systems, although a slight difference is noted when using, e.g., CaCl$_2$ vs NaCl in other systems (Jr et al., 1997; Leelamanie and Karube, 2013). In this work, we examine wettability variations in brine-CO$_2$-muscovite systems as a function of ionic strength with attention to any potential divalent vs monovalent cation effects. We present new experimental results that show a slight increase in wettability with ionic strength with little or no difference noted as a function of cation content.

A contact angle θ_C is defined here as the angle formed between the interface of a droplet and solid surface and the interface of the droplet and the surrounding bulk fluid phase (see Fig. 1). For wetting fluids $\theta_C < \pi/2$ and for non-wetting fluids $\theta_C > \pi/2$. As described by Young's equation,

$$\gamma S1 = \gamma S2 + \gamma 12 cos\theta C \qquad (1)$$

the equilibrium contact angle results from the balance of forces between the interfacial tensions (or surface free energies) γ_{ij} between two fluids (subscripts 1 and 2) and a solid surface (subscript S). Note that this definition and Eq. (1) only truly apply to macroscopic systems, and complications may arise when contact angle is considered at the nanoscale. For example, as droplet size decreases, the free energy associated with creating the three-phase contact line may become significant and needs to be added to Eq. (1) (Amirfazli and Neumann, 2004; Tadmor, 2008; Brinkmann et al., 2005). Also, near the three-phase line molecular interactions between two phases can be altered by the presence of the third phase, resulting in a local nanoscale contact angle that may differ from its macroscopic value. While the simulation work described in this paper is primarily concerned with general wetting trends and details of molecular ordering at interfaces, we attempted to minimize the potential for nano- versus macro-scale complications by simulating relatively large systems with cylindrical, as opposed to spherical, droplet geometries. The systems used in this study are described in greater detail in the next section. For the

purposes this paper, we will generally assume an interpretation of contact angle akin to that depicted in Fig. 1.

In this study we used molecular dynamics simulations (Plimpton, 1995; Plimpton) to investigate interfacial behavior and evaluate contact angles for CO$_2$-brine-mineral systems.

Previous studies of contact angles using molecular simulation include water on graphene (Taherian et al., 2013; Sergi et al., 2012; Scocchi et al., 2011), water and surfactant on hydrocarbon surfaces (Halverson et al., 2009), water on gold (Wu et al., 2012), epoxy on SiO$_2$ (Holck et al., 2012), CO$_2$ and brine on quartz (Iglauer et al., 2012), water on kaolinite (Solc et al., 2011), and CO$_2$ and brine on kaolinite (Tenney and Cygan, 2014). Molecular simulation has also been used to study interfacial tension in CO$_2$-water systems (Nielsen et al., 2012; Li et al., 2013). Accurate interatomic potentials (Cygan et al., 2004; Cygan et al., 2012) were used to evaluate the energy and forces associated with hundreds of thousands of atoms for various fluid droplet configurations within slit pores formed between basal surfaces of muscovite, a common phyllosilicate mineral. Clay and clay-like minerals are present in many potential sites being considered for carbon sequestration, where these phases occur as coatings on sandstone grains and as the dominant mineral phase of shale caprocks. Muscovite is easily cleaved to expose relatively uniform and hydrophilic basal surfaces that are suitable for experimental determinations of contact angles, which allows relatively easy comparison with simulation results. In addition to providing the foundational science for understanding the molecular control in wetting processes, such results can be used to improve capillary flow and capillary trapping models to better assess the disposition of CO$_2$ in sequestration reservoirs.

2. Experimental details

2.1. Micro X-ray CT scanning

The wetting characteristics of muscovite/CO$_2$/brine systems were investigated by laboratory experiments to quantify the contact angle θ_C (Eq. (1)). A novel experimental technique was developed using high resolution micro X-ray CT scanning for imaging the interface of fluids with a solid surface (Chaudhary et al., 2015). Rectangular chips (20 mm×7 mm) of muscovite were oriented in a parallel-plate arrangement and vertically placed inside a PEEK column (7.5 mm ID) heated with a carbon fiber sleeve (Fig. 2). Temperature was maintained at 333 K and pressure at 13.8 MPa. Three different aqueous phase salt concentrations (100% DI-water, 1.26 wt% CaCl$_2$ brine, and 2.00 wt% NaCl brine) were used. In addition, 1.00 wt% NaBr was used to enhance the image contrast during X-ray CT scanning. The column was pressurized with brine and CO$_2$ and allowed 4 h of dissolution-equilibration time. The column was scanned using an Xradia MicroXCT-400 scanner, which provided images of the CO$_2$-brine interface with muscovite surfaces. The spacing between the parallel muscovite chips was optimized based on the Bond Number B_o given as

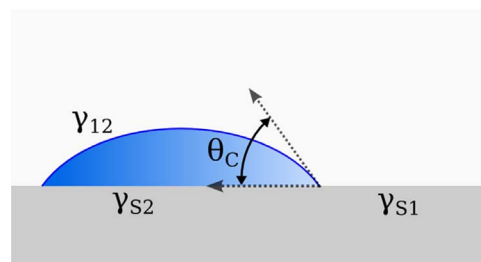$$B_o = \frac{(\Delta\rho)gL^2}{\gamma} \qquad (2)$$

Fig. 1. Contact angle θ_C resulting from the balance of forces between interfacial tensions γ_{ij} between two fluids (subscripts 1 and 2) and a solid surface (subscript S).