

Thermodynamic Computations for Ion Exchange and Surface Protonation Reactions and the Implications for Acid Induced Contact Angle Evolution in Silica Rich Saline Aquifer Systems

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Abstract

To reduce current high concentrations of anthropogenic greenhouse gases in the atmosphere to levels stipulated by the Intergovernmental Panel on Climate Change, geological sequestration has been universally proposed. On the basis of cost analysis and global availability, deep saline aquifers are the prime targets for most proposed commercial and pilot scale projects.

While the geological storage of anthropogenic carbon dioxide is expected to mitigate global warming, the technical aspects of the injection deserve to be considered for efficient injection projects. The water rock interaction phenomenon occurs due to carbonic acid generation which causes surface protonation reactions and has the potential to decrease water wettability of the system leading to enhanced water mobility and efficient gas injection. Therefore, for a saline aquifer rock with minerals capable of ion exchange reactions that consume solution protons, the wettability of such a system is likely to be preserved leading to reduced water mobility and poor gas injection. Generally, the extents to which surface protonation and ion exchange reactions occur depend on the free energy change of the reaction.

In this paper, we have carried out thermodynamic computations for the free energies of surface protonation and ion exchange reactions. Based on the values of computed free energies, which show that ion exchange reactions have lower free energies, we have discussed the wettability implications for geological storage in silica rich saline aquifer systems.

Keywords: Gibbs free energy, surface protonation, ion exchange, dielectric constant, wettability, contact angle

1. Introduction

As global warming, due to anthropogenic emission of carbon dioxide assumes alarming dimensions, the capture and geological isolation of this gas is considered necessary though there exist some limitations (Meer, Investigations regarding the storage of carbon dioxide in aquifers in the Netherlands, 1992). To isolate anthropogenic carbon dioxide at a rate commensurate with the rate at which it is being emitted, geologic repositories, notably saline aquifers have been endorsed by the Intergovernmental Panel on Climate Change (IPCC) (Bert, Davidson, Coninck, Manuela, & Meyer, 2005). This is due to their promising global storage capacity (Szulczewski, MacMinn, Herzog, & Juanes, 2012).

To be able to achieve efficient displacement of formation brine while storing large volumes of anthropogenic carbon, the wettability of the saline aquifer must be reduced to ensure enhanced relative mobility of resident formation brine. Generally, the relative permeability of a particular phase tends to decrease with increases in rock wetting with respect to that phase (Anderson, 1987). However, in view of the water rock interaction of carbon dioxide under subsurface condition (Matter & Kelemen, 2009), the extent to which water wettability of the system can be altered depends on the types of diagenetic minerals in the aquifer rock (Ketzer, *et al.*, 2009). Siliciclastic (quartz rich) (Mcbride, A Classification of Common Sandstones, 1963) saline aquifer rocks with diagenetic minerals such as glauconite and muscovite will have the potential for ion exchange reactions. In these reactions, hydrogen ions produced from the dissociation of carbonic acid, which are supposed to reduce formation water pH and reduce wettability (Jung & Wan, 2012) will be exchanged for frame work potassium ions (Sainz-Diaz & Coudros, 2001). On the other hand, monomineralic rocks such as those consisting of nearly 99% quartz and quartz cement will lack ion exchange reactions, which will enhance surface protonation reactions and increase solid-water interfacial tension leading to wettability reduction (Jung & Wan, 2012).

However, the extent to which ion exchange reactions and surface protonation reactions occur and compete for hydrogen ions produced from the dissociation of carbonic acid (McGrail, *et al.*, 2006) will depend on the thermodynamic free energy of the reactions (Miller, Calcaterra, & Closs, 1984). This is because, the thermodynamic free energy of a reaction measures the extent of feasibility. This means, depending on the values of the thermodynamic free energies, the order of feasibility of two possible reactions can be inferred. One reaction is where cation exchange reactions maintain wettability by pH buffering despite carbon dioxide dissolution. The other is where there is wettability reduction due to increases in hydrogen ion concentration from dissolved carbon dioxide. The order of feasibility of these reactions depends on the magnitudes of the free energies. Generally, the one with the most negative value will be more feasible. The objective of this paper is to carry out thermodynamic computations for surface protonation and ion exchange reactions and to use these as the bases for determining which of these reactions will be more feasible. The thermodynamic implications in light of contact angle evolution will be further discussed for saline aquifers under geological carbon storage.

2. Literature Review

2.1 Relationship of Interfacial Free Energies to Contact Angle

In the geologic environment, the system carbon dioxide-brine-solid/mineral surface is characterized by three distinct interfacial free energies or interfacial tensions. They are solid-liquid, solid-gas and gas-liquid interfacial free energies. These interfacial energies arise from intermolecular interactions at the interfaces (Wu, 1971) and they together control the wettability state of the system at a given pH of aqueous solution in light of Young's equation (Good, 1952). The wettability parameter of the system carbon dioxide-water-rock is the cosine of the contact angle which depends on the interfacial tension between the individual interfaces and it is given by Young's equation as: (Good, 1952):

$$\cos \theta_{(CO_2-brine)} = \frac{\sigma_{CO_2-solid} - \sigma_{solid-liquid}}{\sigma_{CO_2-liquid}} \quad 1$$

In which $\sigma_{CO_2-brine}$ is the interfacial tension between water and carbon dioxide interface [Nm^{-1}], $\sigma_{CO_2-solid}$ is the interfacial tension between carbon dioxide and rock interface [N/m] and $\sigma_{solid-liquid}$ is the interfacial tension between solid and water interface [N/m]

Equation 1 was deduced by Yong when he applied the condition of mechanical equilibrium along the point where the three interfaces meet the contact line. In principle, this equation expresses the ratio of the difference between two interfacial tensions or interfacial free energies ($\sigma_{CO_2-solid}$, $\sigma_{solid-liquid}$) to vapor-liquid interfacial tension and equates this to the cosine of the contact angle, which has a bearing on wettability. In the carbon dioxide-water-solid system, any changes in water pH, which generate physiochemical reaction through water rock interaction will contribute to solid-liquid interfacial tension changes to impact wettability. Changes in the other two surface tensions can also lead to wettability changes.

3. Wettability Evolution during Geological Storage of Carbon Dioxide

Different types of wettability regimes can be identified during geological storage of carbon dioxide in saline aquifers. One is where interfacial tension and wettability of the system remain constant. This is typical of deep saline aquifer geological storage where the pressure effect of gas solubility is neutralized by temperature effect. The second case is where wettability and interfacial tension change continuously. In the latter case, wettability changes mean changes in all the three interfacial tensions of the system or a change in any of them while others remain constant. The third case is where the wettability of the system immediately changes to a new wettability state determined by new values of all the three interfacial tensions and remains constant. The third case can be realized in carbon dioxide injection when the injected gas enters the formation under overburden pressures above 13 MPa. Figure 1 shows that for all formation brine salinities, geological sequestration of carbon dioxide at pressures typically above 13 MPa will result in approximately constant carbon dioxide-brine interfacial tension.

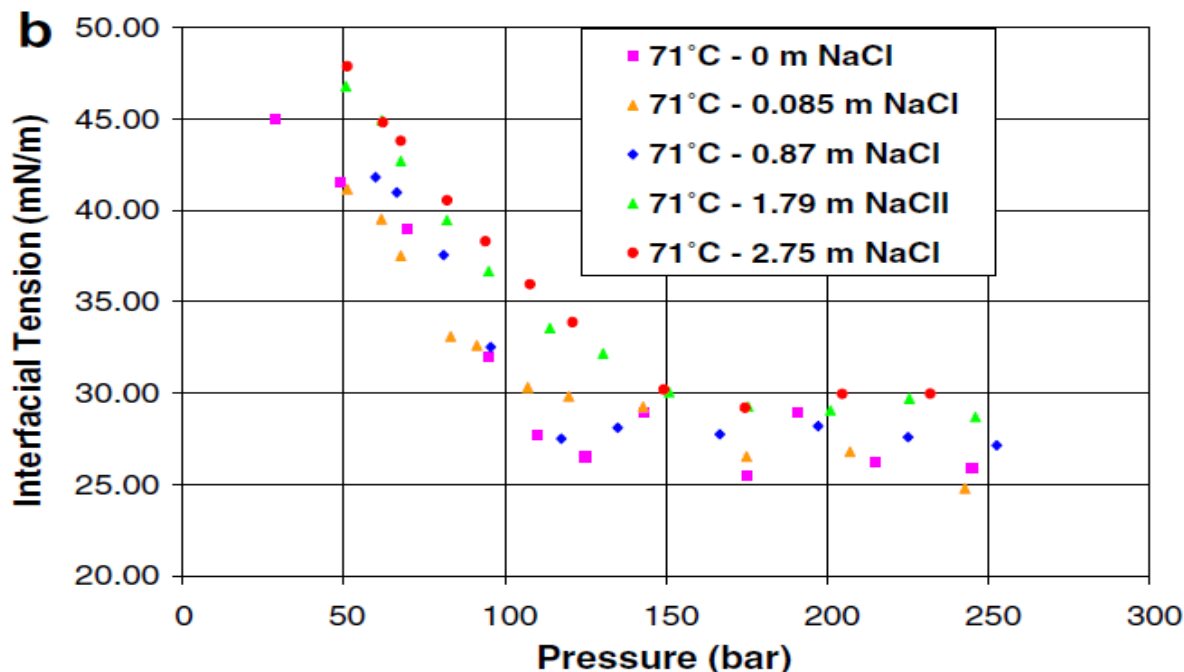


Figure 1. Interfacial tension between carbon dioxide and brine at different salinities versus pressure (Chalbaud *et al.*, 2009)

Under this condition, the solubility of carbon dioxide will be fixed by aquifer temperature, salinity and pressure. Solid-liquid interaction will occur at a given pH determined by the solubility of carbon dioxide (Søreide & Whitson, 1992) at the prevailing aquifer temperature and salinity. Since gas solubility is constant, the interfacial tension between gas and water will be constant. Generally, it is the dissolved species of carbon dioxide that interact with the solid surface and not the gaseous phase. Therefore, solid-gas interfacial tension is also constant. Water rock-rock interactions between hydrogen ions produced from the dissociation of injected carbon dioxide will produce a new solid-liquid interfacial tension at the given pH of formation brine determined by carbon dioxide solubility. Therefore, for pressures more than 13 MPa, where carbon dioxide-brine interfacial tension is practically constant (Chalbaud, *et al.*, Interfacial tension measurements and wettability evaluation for geological CO₂ storage, 2009), the injection of carbon dioxide into a saline aquifer will result in a new wettability state of the system.

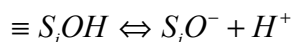
4. Thermodynamic Computations

4.1 Thermodynamics of Protonation and Cation Exchange Reactions

The extent of reduction of the wettability of rock/mineral surface with regard to formation brine depends on the extent to which solid-liquid interfacial tension is increased by the adsorption of protons from carbonic acid dissociation. This is because, there are two contributions to solid-liquid interfacial tension. They are the contribution due to the free energy at the point of zero charge pH of solid surface and the contribution due to the free energy at the prevailing pH relative to the point of zero charge pH of solid surface (Chatelier, *et al.*, 1995). For significant contact angle increase, which corresponds to wettability decrease in light of Young’s equation, surface protonation reaction leading to solid-liquid interfacial tension increase must be more feasible compared the cation exchange reaction. Therefore, the thermodynamic free energies of proton adsorption and cation exchange reaction, which measure how far the reactions are from equilibrium and for that matter how feasible they will occur (Aagaard & Helgeson, 1982) deserve to be considered and the following section will be devoted to that.

4.2 Gibbs Free Energy Change for Surface Protonation Reaction

Under formation water pH conditions typical of carbon geosequestration in sandstone saline aquifers (typically neutral) the surface of silica will be negatively charged. The pertinent geochemical reaction is given as (Sverjensky, 1996):



2

Hydrogen ions will be provided by the dissociation of carbonic acid. The Gibbs free energy for the reaction is given as (Sverjensky, 1996).

$$\Delta G_r^o = -2.3RT \log K \quad 3$$

ΔG_r^o = Standard Gibbs free energy change for the reaction-KJ/mole

K = equilibrium constant for the reaction-mol/l

4.3 Thermodynamics of Ion Exchange

Cation exchange reaction involving potassium leaching from glauconite in sandstone under acidic conditions is described by the following reaction (Clearfield, 1988):



The Gibbs free energy change for this reaction is considered based on the following thermodynamic analyses (Clearfield, 1988):

For a monovalent ion that must be brought from the bulk of a dilute solution into contact with a fixed ionic grouping (of opposite charge) of an ion exchanger, two types of interactions have to be taken into consideration. They are the following:

1. The electrostatic interaction between the fixed grouping and the counterions or the exchanging ions
2. The free energy changes involving the hydration of the counterions and the fixed grouping

By regarding the fixed grouping and the counterions as being point charges, each at the center of an incompressible sphere, Eisenmann (Eisenman, 1967), deduced that if the fixed grouping is anionic with radius r_f^- , then the electrostatic energy arising from the interaction with a cation A^+ of radius r_A^+ is given as:

$$\Delta G^o = \frac{e^2}{r_f^- - r_A^+} \quad 5$$

Where e is the electronic charge

Similarly, the interaction of the fixed grouping with cation B^+ would give rise to a change in standard Gibbs free energy as:

$$\Delta G^o = \frac{e^2}{r_f^- + r_B^+} \quad 6$$

The total standard Gibbs free energy change for the cation exchange reaction gives:

$$\Delta G^o = -\frac{e^2}{r_f^- + r_A^+} - \frac{e^2}{r_f^- + r_B^+} \quad 7$$

To proceed further in the thermodynamic formulation, we have assumed that the free energy change due to hydration is related to the free energies of hydration of the ionic groups (Eisenman, 1967)

The total standard Gibbs free energy change for cation exchange reaction is then (Clearfield, 1988)

$$\Delta G^o = \frac{e^2}{r_f^- + r_A^+} - \frac{e^2}{r_f^- + r_B^+} - (\Delta G_A^+ - \Delta G_B^+) \quad 8$$

The free energy of hydration from Born's equation is given as (Jayaram, Sharp, & Honig, 1989):

$$\Delta G_h = \frac{-q^2 \left(1 - \frac{1}{\epsilon}\right)}{2a} \tag{9}$$

Where

ΔG_h = Gibbs free energy change of hydration

q = charge on ion -C

ϵ = dielectric constant of solution

\mathcal{E} = cavity radius-nm

4.4 Modification

To achieve the objective of this paper, Eismann’s equation will be modified. This is because, this equation considers a dilute solution where the dielectric constant is very big. The final equation for the total change in Gibbs free energy of ion exchange will be written in this paper as:

$$\Delta G^o = \frac{e^2 \left(1 - \frac{1}{\epsilon}\right)}{r_f^- + r_A^+} - \frac{e^2 \left(1 - \frac{1}{\epsilon}\right)}{r_f^- + r_B^+} - (\Delta G_A^+ - \Delta G_B^+) \tag{10}$$

This modification takes account of the fact that under typical conditions of aquifer salinity (hypersaline conditions) for carbon dioxide injection, we have high salinities leading to a decrease in dielectric constant. From Born’s equation Eq. 9, the reciprocal of the dielectric constant of brine under this condition is quite substantial to be neglected for the case of Eismann’s equation and hence Eq. 10.

4.5 Final Equation

By linking the electrostatic free energy of interaction in the hydration sphere to Avogadro’s number, permittivity of vacuo and the dielectric constant of the medium, Eq. 10 for the total Gibb’s free energy can be written by using the equation in (Bazhin, The Born Formula Describes Enthalpy of Ions Solvation, 2012) as:

$$\Delta G^o = \frac{z^2}{8\pi\epsilon_o} \frac{e^2 \left(1 - \frac{1}{\epsilon}\right)}{(r_f^- + r_A^+)} - \frac{z^2}{8\pi\epsilon_o} \frac{e^2 \left(1 - \frac{1}{\epsilon}\right)}{(r_f^- + r_B^+)} - \left(\frac{ze^2}{2a_{K^+} 8\pi\epsilon_o} \left(1 - \frac{1}{\epsilon}\right) - \frac{Ze^2}{2a_{H^+} 8\pi\epsilon_o} \left(1 - \frac{1}{\epsilon}\right) \right) \tag{11}$$

z = valence of ion

a_{K^+} = radius of potassium ion-nm

N_A = Avogadro’s number-mol⁻¹

ϵ_o = permittivity of vacuo-F/m

4.6 Salinity Effect on Dielectric Constant

The dependence of static dielectric constant of formation brine on salinity is given as (Gadani, Rana, Bhatnagar, Prajapati, & Vyas, 2012)

$$\epsilon_o = (T, N) = \epsilon_o(T, 0)a(N)$$

$$a(N) = 1.000 - 0.2551N + 5.15 * 10^{-2} N^2 - 6.889 * 10^{-3} N^3 \tag{12}$$

$$b(NT) = 0.1463 * 10^{-2} NT + 1.0000 - 0.04896N - 0.02967N^2 + 5.644 * 10^{-3} N^3 \tag{13}$$

$$\epsilon_o(T,0) = 87.74 - 0.40008T + 9.398 * 10^{-4} T^2 + 1.410 * 10^{-6} T \quad 14$$

T is the temperature of the water in °C and N is the normality of the solution

4.7 Calculation of Normality for a Case Study

To contain anthropogenic carbon dioxide under supercritical conditions in the sedimentary basin, the threshold depth is 800 meters based on a mean geothermal gradient of 25 °C per kilometre. The mean concentration of chloride and sodium ions based on a strong regional diagenetic imprint across Arkansas and North Louisiana are 171.7 and 69 g/l respectively (Moore & Druckman, Burial Diagenesis and Porosity Evolution, Upper Jurassic Smackover, Arkansas and Missouri, 1981), Table 3. The mean Total Dissolve Solute (TDS) is 279 g/l (Moore & Druckman, Burial Diagenesis and Porosity Evolution, Upper Jurassic Smackover, Arkansas and Missouri, 1981). Using the equivalent sodium chloride concept (Moore *et al.*, 1966), the percentage of chloride and sodium ions regarding TDS is 86. The following ions will be used to represent formation brine composition:

Na = 67 g/l

Mg = 3.4 g/l

Cl = 171.7 g/l

Ca = 34.5 g/l

Total dissolved solute is the sum (276.6 g/l)

The ratio of Calcium to magnesium is 10:1

By using the cation correction chart (Moore, Sasz, & Whitney, 1966) the cation correction factor is 0.58. The equivalent sodium chloride concentration is 0.58 multiplied by total dissolved solute which gives 160.4 g/l

This is equivalent to 2.77 moles per liter. The number of equivalent is calculated as the equivalent sodium chloride (g/l) divided by valence (1). The normality is thus 2.77 mol/l.

4.8 Calculation of Dielectric Constant

By assuming the threshold depth of 800 m for carbon geosequestration, the temperature of injected carbon dioxide is supercritical (31°C). Application of Eq. 12 through Eq.14 gives the dielectric constant of brine in a saline aquifer with the equivalent concentration of sodium chloride and temperature as 48.5 F/m.

4.9 Thermodynamic Free Energy Computation for Ion Exchange Reaction

We assume an ion exchange between glauconite potassium and hydrogen ion from solution produced by the dissociation of carbonic acid formed during the injection of anthropogenic carbon dioxide into a glauconitic sandstone saline aquifer. In this approach, Eq. 11, for the total Gibbs free energy of ion exchange by glauconite framework potassium and solution hydrogen is used. Calculated dielectric permittivity of saline aquifer brine is used with the value of Avogadro's number ($6.23 * 10^{23}$ /mole) and electronic charge ($6.22 * 10^{19}$ Coulomb). The fixed ion in the glauconite is assumed to be oxygen anion of radius of 0.145nm (Lal, 2006). The radius of potassium and Hydrogen ions are taken as **0.138 nm and 0.030 nm, respectively** (Marcus, 1991), the calculated Gibbs free energy change is -7704 kJ/mo. In this calculation we assume the valency, z, to be one.

4.10 Thermodynamic Free Energy of Surface Protonation Reaction

In this regard, we consider surface protonation reaction where there is proton adsorption on the surface of silica or quartz mineral of the saline aquifer as another proton sink (proton consumption reaction). This reaction will compete with the ion exchange reaction for proton consumption and the extent to which any of the reactions will proceed will depend on the free energy change of the reaction. Equation 5 for the Gibbs free energy change for the surface protonation reaction is used with a value of the surface protonation equilibrium constant being 7.5 (Sverjensky, 1996). The calculated free energy change is -5078 KJ/mol.

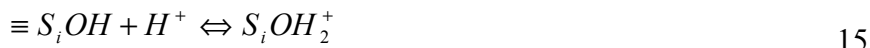
5. Implications of Thermodynamic Free Energy of Protonation and Cation Exchange for Different Saline Aquifers

To discuss the implications of the difference in thermodynamic free energies of cation exchange and surface protonation reactions on contact angle/wettability evolution for the system carbon dioxide-brine-mineral surface requires understanding the mechanism of interfacial free energy changes under conditions of formation brine pH evolution. The following sections will be devoted to this.

5.1 Mechanism of Interfacial Free Energy Change

5.1.1 Carbon dioxide Brine–Mineral System

This system is characterized by water rock interaction (Matter, Takahashi, & Goldberg, 2007). In light of interface chemistry, this reaction is characterized by protonation and deprotonation of surface hydroxyl functional groups in siliciclastic saline aquifers consisting predominantly of silica and subordinate amount of diagenetic minerals (Lanson, *et al.*, 2002). The reactions can be described by the following equilibrium reaction (Duval, Mielczarski, Pokrovsky, Mielczarski, & Ehrhardt, 2002):



In which $\equiv S_iOH$ is a neutral surface species, S_iO^- is a deprotonated surface species H^+ is hydrogen ion and $\equiv S_iOH_2^+$ is protonated surface species.

The equilibrium constants for these reactions are given as:

$$K_1 = \frac{[S_iOH_2^+]}{[S_iOH][H^+]} \tag{17a}$$

$$K_2 = \frac{[S_iO^-][H^+]}{[S_iOH]} \tag{17b}$$

In which K_1 is the equilibrium constant for the reaction described by Eq. 15 [mol/ l], K_2 is the equilibrium constant for the reaction described by Eq. 16 [mol l], $[S_iOH]$ is the concentration of surface neutral species [mol/l], $[S_iO^-]$ is the concentration of surface deprotonated species [mol⁻¹] and $[S_iOH_2^+]$ is the concentration of surface protonated species [mol/l] and $[H^+]$ is hydrogen ion concentration [mol/ l].

5.2 Dependence of Solid-Liquid Interfacial Tension on pH from Molecular Theory

Based on the molecular theory of interfacial tension, the solid-liquid interfacial tension is calculated as (Van Oss, Good, & Chaudhury, 1988):

$$\gamma_{SL} = \left((\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2} \right)^2 + 2 \left((\gamma_S^+ \gamma_S^-)^{1/2} + (\gamma_L^+ \gamma_L^-)^{1/2} - (\gamma_S^+ \gamma_L^-)^{1/2} - (\gamma_S^- \gamma_L^+)^{1/2} \right) \tag{18}$$

In which γ_{SL} is solid liquid interfacial tension [N/m], γ_S^{LW} is dispersion force contribution to solid-liquid interfacial tension due to solid surface [N/m], γ_L^{LW} is the dispersion forces contribution to solid-liquid interfacial tension due to water [N/m], γ_S^- is the electron donor contribution to sold-liquid interfacial tension due to sold [N/m] , γ_S^+ is the electron acceptor contribution to solid-liquid interfacial tension due to solid [N/m], γ_L^+ is the electron acceptor contribution to solid-liquid interfacial tension coming from liquid [N/m] and γ_L^- is electron donor contribution to interfacial tension due to water [N/m].

Under conditions typical of deep aquifer geologic storage (above 13 MPa) the pH of formation water is closer to neutral. Therefore, for a sandstone saline aquifer with predominant silica content, the surface charge of silica will be predominantly negative because the point of zero charge pH of this mineral is 3 (Kosmulski, 2006). Protonated surface

species will be lacking and therefore Eq. 18 can be written as:

$$\gamma_{SL} = \left((\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2} \right)^2 + 2 \left((\gamma_L^+ \gamma_L^-)^{1/2} - (\gamma_S^- \gamma_L^+)^{1/2} \right) \quad (19)$$

For the system carbon dioxide-brine-mineral surface, solid-liquid interfacial tension will be pH dependent.

Generally, the electron acceptor and donor components of interfacial tension are related to the protonated and deprotonated species given in Eqs. 15 and 16. These species are pH dependent through the following equation (Glover, Meredith, Sammonds, & Murrell, 1994):

$$R_{pH}^- = \frac{[H^+]_{pzc}^2}{[H^+]_{pzc}^2 + [H^+]^2} \quad (20)$$

$$R_{pH}^+ = 1 - R_{pH}^- = \frac{[H^+]_{pH}^2}{[H^+]_{pzc}^2 + [H^+]_{pH}^2} \quad (21)$$

In which R_{pH}^- is the fraction of surface sites available for the adsorption of positive species [-]. R_{pH}^- is the fraction of surface sites available for the adsorption of negative species, $[H^+]_{pzc}$ is the hydrogen ion concentration of aqueous solution at the point of zero charge of rock surface mol^{-1}] and $[H^+]$ is the concentration of hydrogen ions of aqueous solution [mol/ l]

To derive the pH dependence of solid-liquid interfacial tension we will assume here that the extent of electron donor contribution from solid will depend on the fraction of these sites available on the surface at a given pH of formation brine. The following equation will be written:

$$\gamma_S^- = KR_{pH}^- = K \frac{[H^+]_{pzc}^2}{[H^+]_{pzc}^2 + [H^+]^2} \quad (22)$$

K = Constant of proportionality

For pH conditions, typical of carbon dioxide injection, Eq. 22 can be combined with Eq. 19 to give:

$$\gamma_{SL} = \left((\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2} \right)^2 + 2 \left((\gamma_L^+ \gamma_L^-)^{0.5} - \left(K \left(\frac{[H^+]_{pzc}^2}{[H^+]_{pzc}^2 + [H^+]_{pH}^2} \right) \gamma_L^+ \right)^{0.5} \right) \quad (23)$$

Equation 23 clearly shows the effect of hydrogen ion inputs on solid-liquid interfacial tension. Specifically, it shows that as hydrogen ion concentration increases due to CO₂ dissolution, the expression involving hydrogen ions and the electron acceptor contribution to solid-liquid interfacial tension from liquid will decrease. The net effect is an increase in solid-liquid interfacial tension. The interfacial tension between gas and water is practically constant (Chalbaud, *et al.*, 2009) at deeper depths of storage. Going by Young's equation, (Eq. 1), this corresponds to increase in contact angle and decrease wettability with increasing hydrogen ions or pH decreases.

6. Implications for Different Saline Aquifer Rocks

Saline aquifer rocks can be divided into two categories based on the ability of minerals found in the rocks to buffer formation water pH. Normally, carbonate cement and mica minerals found in sandstones saline aquifers will tend to buffer formation water pH through hydrogen ion reaction with carbonate cement minerals (iron and magnesium carbonate) (Kharaka, *et al.*, 2006) and through cation exchange reactions respectively (Lorenz, 1999). Any of these reactions has the capacity to deplete added hydrogen ions from carbonic acid dissociation leading to formation water pH buffering.

The other types of siliciclastic saline aquifers are the predominantly monomineralic or quartz arenites with very clean

sands (Smith, Browne, Heinz, & Wise, 1996). These aquifers will not be capable of formation water pH buffering and wettability changes during carbon dioxide injection into these aquifers will depend on variations of the three interfacial tensions found in Yong's equation. These saline aquifers will experience significant increases in solid-liquid interfacial tensions to cause significant contact angle changes, which will decrease water wetting of pore walls.

7. Implications for Differences in Gibbs Free Energy Changes for Protonation and Cation Exchange Reaction

The Gibbs free energy of a chemical reactions measures how far it is from chemical equilibrium (Hellmann & Tisserand, 2006). The farther the reaction is from equilibrium evidenced by low Gibbs free energy reaction, the more feasible it is. Comparison of thermodynamic Gibbs free energies of ion exchange and surface protonation reactions from section 4.8 and section 4.9 shows that the bigger negative value of the ion exchange reaction implies a greater feasibility of this reaction. Therefore, under the given aquifer temperature and salinity conditions, ion exchange reaction will be more feasible compared to surface protonation reactions. The thermodynamic implication is that for sandstones with high proportions of glauconite or clay minerals, surface protonation reactions, which are the causes of solid-liquid interfacial tension increases will be less feasible compared to ion exchange reactions of the glauconites, which exchange framework cation (K^+) for solution hydrogen (Carroll, 1959). This means that interfacial tension increases, which are the causes of wettability reductions will be grossly impaired. By Young's equation, the wettability of the system will tend to be preserved during carbon dioxide injection as hydrogen ions from dissolved carbon dioxide are preferably exchanged for potassium ions in octahedral framework of clay minerals, leading to formation water pH buffering as cation exchange fraction increases (Appelo, 1994)(Figure 1). Consequently, water relative mobility in such systems will be low. This is because local displacement efficiency depends on the fraction of resident brine that is contacted by injected carbon dioxide (Jessen, Kovscek, & Orr Jr., 2005). The more wetting the aquifer is with regard to water, the smaller the fraction of brine contacted by injected gas.

Similarly, for sandstone saline aquifers where there are no glauconites, the absence of ion exchange reactions renders more hydrogen ions produced from the dissociation of carbonic acid available for surface protonation reactions. This will lead to significant increases in solid-liquid interfacial tension, which is the requirement for decreased water wettability of the system (Kim *et al.*, 2012; Jung and Wan, 2012). leading to higher relative mobility of water. Generally, protonation reactions involving the interaction of hydrogen ions with surface negative species of deprotonated surface hydroxyl groups at pH above the point of zero charge pH of aquifer rock surface will promote water dewetting. For a predominantly sandstone saline aquifer, this will be predominant as carbon dioxide is injected. However, for a sandstone saline aquifer with significant proportion of clay minerals capable of cation exchange reaction there will be competition between surface protonation reaction and cation exchange reaction. The extent to which any of these reactions will occur will depend on the magnitude the free energy of reaction as revealed by our this paper.

8. Conclusion

Saline aquifer systems are mineralogically heterogeneous, consisting of predominant minerals with subordinate amounts of other accessory minerals. Depending on the diagenetic imprint, a saline aquifer rock can have significant amount of accessory minerals. For siliciclastic saline aquifers with significant amount of clay minerals capable of formation water pH buffering reactions, competition between cation exchange and surface protonation reactions can impact wettability/contact angle evolution during carbon dioxide for geological storage. The extent to which cation exchange or surface protonation reaction will impact wettability evolution in such systems will depend on the thermodynamic free energy of the reaction. We have used thermodynamic approaches to calculate free energies of protonation and cation exchange reactions under geological conditions of carbon storage. The following sum up the conclusions of this paper.

1. Thermodynamic calculations under conditions typical of geological carbon storage show that the free energy of cation exchange reactions is lower than that of protonation reaction.
2. On the basis of the dependence of reaction feasibility on the magnitude Gibbs free energy, the lower value of this energy for cation exchange reaction means that it will be more feasible compared to surface protonation reaction.
3. For sandstone saline aquifers that are predominantly silica or siliciclastic, surface protonation reaction will be predominant during carbon dioxide injection and this will promote silica dewetting with regard to water (Jung and Wan, 2012, Kim *et al.*, 2012)
4. For sandstone saline aquifers with significant proportions of clay minerals, the greater feasibility of cation exchange reaction compared to surface protonation reaction will lead to pH buffering to enhance water wetting of silica surface (pore walls). These systems will be characterized by low water relative mobility

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