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Impact of solid surface energy on wettability of CO₂/brine/mineral systems as a function of pressure, temperature and salinity

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Abstract

CO₂ storage refers to the methods employed to inject CO₂ in depleted oil and gas reservoirs and deep saline aquifers for long term storage of CO₂ with the objective to reduce the anthropogenic CO₂ emissions. Wettability and interfacial tension are two important multiphase parameters which are used to characterize the flow behavior of CO₂ in reservoirs. Numerous studies have reported wettability data of CO₂/brine systems on various rock forming minerals as a function of pressure, temperature and salinity. However, the associated trends have not been physically well-understood and require considerable attention which is objective of our present work.

In this work, we apply Neumann's equation of state method to compute solid/CO₂ and solid/water interfacial tension using our measured contact angle data for CO₂/brine on mica and quartz. Our results indicate that solid/CO₂ interfacial tension decrease with pressure and increase with temperature for both quartz and mica while the solid/water interfacial tension decrease with temperature for mica but increase with temperature for quartz. Moreover, the solid/water interfacial tension increased with water salinity.

We further demonstrate that the interplay of these interfacial tensions lead to a typical behavior of contact angle as a function of pressure temperature and salinity. We thus conclude that hotter reservoirs with lower injection pressure and lower brine salinities exhibit relatively better water wetting state and hence better seal capacity leading to higher CO₂ storage potential. We also conclude that solid surface energy approach adequately explains the dependency of wettability on pressure, temperature and salinity.

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1. Introduction

Carbon capture and storage in depleted hydrocarbon reservoirs or deep saline aquifers is a reliable technique to reduce the anthropogenic greenhouse gas emissions [1]. CO₂ is also injected into hydrocarbon reservoirs for enhanced oil recovery [2-4]. Certain trapping mechanisms render CO₂ immobile in porous medium which include structural trapping [5, 6], residual trapping [7], dissolution trapping [8], mineral trapping [9], and adsorption trapping in coal seams [10]. Structural and residual trapping are by far the most important trapping mechanisms during the first decade of a storage project [11]. In this context, wettability of rock/fluid systems plays a vital role in deciding the fate of the injected CO₂ within the geological formation. Many publications have reported experimental CO₂-wettability data as a function of pressure, temperature and salinity for quartz [12, 13] and mica [5, 6]. However, no significant attention has been given to evaluate the factors which are responsible for wettability variation with pressure, temperature and salinity despite the variations in trends reported in literature. For instance, θ increased with temperature for quartz/CO₂/brine [12] and decreased with temperature for mica/CO₂/brine [5].

Nomenclature

θ	Contact angle
θ_e	Equilibrium contact angle
γ_{sc}	Solid/CO ₂ interfacial tension, mN/m
γ_{sw}	Solid/brine interfacial tension, mN/m
γ_{cw}	CO ₂ /brine interfacial tension, mN/m
β	Fitting parameter (dimensionless)

Theoretically, it is well-established that the contact angle is a function of the interplay of the three interfacial tensions (solid/CO₂, solid/brine and CO₂/brine) as depicted by Young-Laplace equation below:

$$\cos\theta = \frac{\gamma_{sc} - \gamma_{sw}}{\gamma_{cw}} \quad (1)$$

In equation (1), γ_{sc} , γ_{sw} and γ_{cw} are the solid/CO₂, solid/brine and CO₂/brine interfacial tensions respectively. Thus wettability is dependent on the three interfacial tensions and to assess this dependence, the quantification of these three interfacial tensions is essential. The experimental CO₂/brine interfacial tension data has been reported [5, 14], however, solid/fluid interfacial tension cannot be measured experimentally [15]. Neumann [16] developed equation of state that allows the computation of solid energy [17]. Ameri et al. [18] evaluated solid/CO₂ interfacial tension as a function of pressure using Neumann's equation of state and found that the solid/CO₂ interfacial tension decreased with pressure. In this work, we extend the use of Neumann's equation of state for computation of solid/CO₂ and solid/brine interfacial tensions as a function of pressure, temperature and salinity for quartz and mica. Essentially, we then explain how these computed interfacial tensions explain the dependence of wettability on pressure, temperature and salinity.

In this context, we used advancing and receding contact angle (θ_a and θ_r respectively) data for CO₂/brine systems for quartz (from Al-Yaseri et al. [12]) and mica (from Arif et al. [5, 6]), at a wide range of operating conditions and computed solid/CO₂ and solid/brine interfacial tensions and analyzed the associated trends. Our results depict that solid/CO₂ interfacial tension decreased with pressure and increased with temperature for both quartz and mica. However, solid/water interfacial tension decreased with temperature for mica but increased with temperature for

quartz. The interfacial tension data reported in this paper can also be used to estimate contact angle from Young's equation at any pressure, temperature and salinity using known values of surface energies. Finally, we conclude that the quantification of surface energies is not only helpful in understanding the CO₂/solid interactions but also adequately explain the factors influencing wettability and thus considerably improve the understanding of geological storage processes and provide independent estimates for surface energies for various other engineering applications.

2. Methodology

In this work, we selected Neumann's equation of state method to compute solid/CO₂ and solid/water interfacial tensions for quartz and mica as a function of pressure, temperature and salinity. This approach is convenient in its application since it requires equilibrium contact angle (θ_e), and CO₂/water interfacial tension (γ_{cw}) data which are readily available.

Thermodynamically, Neumann's equation of state [16] relates the solid/CO₂, solid/water and CO₂/water interfacial tensions as follows:

$$\gamma_{sw} = f(\gamma_{sc}, \gamma_{cw}) \quad (2)$$

According to Neumann et al. [16], the free energy of adhesion per unit area of a solid-liquid pair is equal to the work required to separate a unit area of solid-liquid interface and that free adhesion energy was proposed to be equal to the geometric mean of the solid cohesion work and the liquid cohesion work. These geometric means were combined so that equation (3) resulted (for a complete derivation the reader is referred to Ameri et al. [18]).

$$\gamma_{sw} = \gamma_{sc} + \gamma_{cw} - 2\sqrt{\gamma_{cw}\gamma_{sc}}[1 - \beta(\gamma_{cw} - \gamma_{sc})^2] \quad (3)$$

The equation (4) below was then derived by Ameri et al. [18] to find an expression for γ_{sc} instead of γ_{sw} as shown:

$$\gamma_{sc} = \gamma_{sw} + \gamma_{cw} - 2\sqrt{\gamma_{cw}\gamma_{sw}}[1 - \beta(\gamma_{cw} - \gamma_{sw})^2] \quad (4)$$

' β ' is a constant which is determined by the non-linear regression of contact angle (θ) and CO₂/water interfacial tension data (γ_{cw}) as further explained below.

Combining Eq. (1) and (4), we get the following expression:

$$\cos \theta_e = 1 - 2 \frac{\gamma_{sw}}{\sqrt{\gamma_{cw}}} [1 - \beta(\gamma_{cw} - \gamma_{sw})^2] \quad (5)$$

Equation (4) and (5) are then used to determine solid/CO₂ interfacial tension as a function of pressure, temperature and salinity. It is notable that solid/brine interfacial tension is dependent on temperature and salinity but not on pressure (Ameri et al. [18], Neumann et al. [16]). This is the basic assumption of the Neumann's equation of state.

Our computations begin with input data acquisition which includes a) advancing and receding contact angle data for quartz (Al-Yaseri et al. [12], Table 1) and mica (Arif et al. [6], Table 1) and b) CO₂/water interfacial data (Sarmadivaleh et al. [13]), listed in Table 2. Then, $\cos\theta_e$ (cosine of the equilibrium contact angle) is calculated using advancing and receding contact angle data for all cases analyzed (results listed in Table 1) using Tadmor's correlation (Tadmor, [19]). In the next step, γ_{sw} and the constant ' β ' are determined by least squares fitting of the $\cos\theta_e$ and γ_{cw} data. To accomplish this, $\cos\theta_e$ is first calculated by using equation (5) for any trial values of γ_{sw} and ' β ' and is plotted against γ_{cw} (this data is referred as model data). Moreover, the experimental $\cos\theta_e$ (Table 1) is also plotted against γ_{cw} (such a plot is shown in Figure 1 for both quartz and mica data at 343 K), the regression analysis of these data-sets yield final values of γ_{sw} and ' β ' corresponding to the best-fit. The R²-values, fitting parameters ' β ' and γ_{sw} were computed for each case from the regression fits and the results are tabulated in Table 3. The model and experimental data are in a good agreement, however the model predictions are sensitive to CO₂/water interfacial tension values and

thus reliable CO₂/brine interfacial tension input is required for reliable modelling of solid/fluid interfacial tensions. Finally, using these calculated values, solid/CO₂ interfacial tension is computed using equation (4) as a function of pressure, temperature, salinity and type of the mineral. The standard deviations in experimental contact angle and interfacial tension data used were $\pm 3^\circ$ and ± 3 mN/m respectively.

Table 1: Advancing, receding and equilibrium contact angle data for quartz/CO₂/water and mica/CO₂/water systems used in this study.

Temperature (K)	Pressure (MPa)	Quartz			Mica		
		θ_a (°)	θ_r (°)	Equilibrium, θ_e (°)	θ_a (°)	θ_r (°)	Equilibrium, θ_e (°)
308	0.1	0	0	0	10	5	6
	5	15	11	12.9	33	25	28.7
	10	23	17	19.8	55	50	52.4
	15	30	20	24.2	71	63	66.7
	20	37	23	29	80	72	75.7
323	0.1	0	0	0	4	0	2
	5	19	13	15.7	30	24	26.8
	10	30	25	27.4	48	40	43.7
	15	38	28	32.5	59	54	56.4
	20	42	35	38.3	70	62	65.7
343	0.1	0	0	0	0	0	0.5
	5	22	19	20.4	27	22	24.3
	10	42	30	35.3	43	36	39.3
	15	45	38	41.3	52	48	49.9
	20	50	42	45.7	62	53	57.1

Table 2: CO₂/DI-water and CO₂/brine interfacial tension data used.

Temperature (K)	Pressure (MPa)	CO ₂ /DI-water IFT ^a (mN/m)	CO ₂ /brine* IFT ^b (mN/m)
308	0.1	75.8	72.9
	5	40.2	50.1
	10	28.4	38.2
	15	22.7	33.9

	20	21.0	32.3
323	0.1	73.1	72.0
	5	49	55.3
	10	35.5	42.6
	15	29	38.7
	20	26	36.0
343	0.1	65	69.2
	5	52.18	57.7
	10	43	44.8
	15	34.5	39.7
	20	27	37.7

Table 3: Results obtained from regression fit of the experimental and model data.

Case	Temperature (K)	R ²	β	γ_{sw} (mN/m)
Quartz	308	0.898	0.000205	0.058
	323	0.943	0.000219	0.284
	343	0.988	0.0002524	0.952
Mica	308	0.899	0.00022	2.178
	323	0.935	0.00023	2.048
	343	0.992	0.00027	1.98

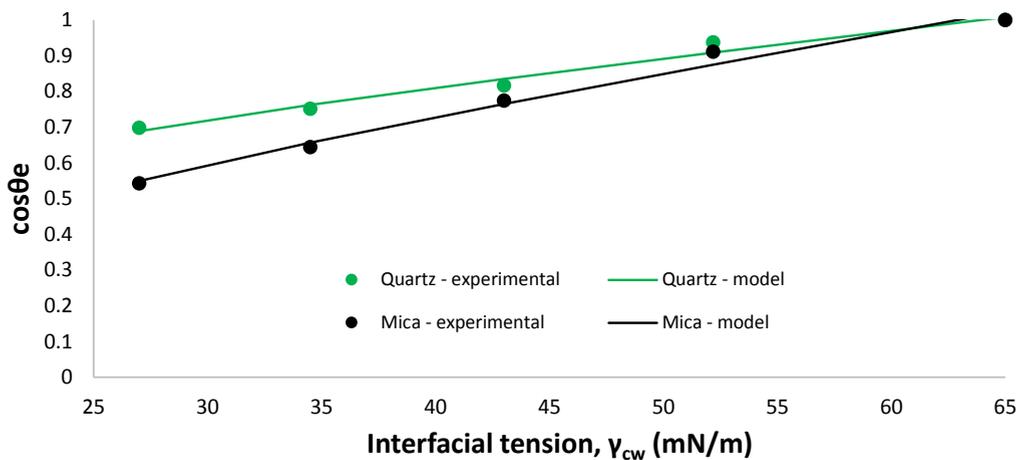


Figure 1: Regression plot between CO₂/water interfacial tension and cosine of equilibrium contact angle at 343 K

3. Results and Discussion

Solid/CO₂ interfacial tension are computed for quartz and mica using the equation of state. The results are obtained as a function of pressure, temperature and salinity. Moreover, solid/water interfacial are also computed as a function of temperature and salinity. The results lead to a broad understanding of rock/fluid interaction properties. Specifically, the results allow the interpretation of the impact of surface energy on rock wettability as a function of pressure, temperature, salinity, and type of mineral which thus contribute to ensure containment security [20, 21].

3.1. Effect of pressure and temperature on quartz/CO₂ interfacial tension

Solid/CO₂ interfacial tension decreased with pressure and increased with temperature for both quartz and mica as shown in Figure 2 and 3 respectively. As the pressure increased from 0.1 MPa to 10 MPa, quartz/CO₂ interfacial tension decreased sharply from 75 mN/m to 31 mN/m at 323 K (Figure 2). However, the decrease flattened for additional pressure increment from 15 MPa to 20 MPa and the quartz/CO₂ interfacial tension changed from 25 mN/m to 22 mN/m, a reduction of only 3 mN/m (Figure 2). A similar trend was found at elevated temperature, 343 K and the major difference was that the values of quartz/CO₂ were higher at elevated temperatures.

Physically, as the pressure increases, the cohesive energy density of CO₂ increases and approaches to the cohesive energy of the substrate (Dickson et al. [22]). Eventually, the interactions between solid and CO₂ become more favorable and as a result quartz/CO₂ interfacial energy decreases with pressure. Note that at pressure = 0.1 MPa, a switch in temperature occurs due to a switch in CO₂/water interfacial tensions; Table 2.

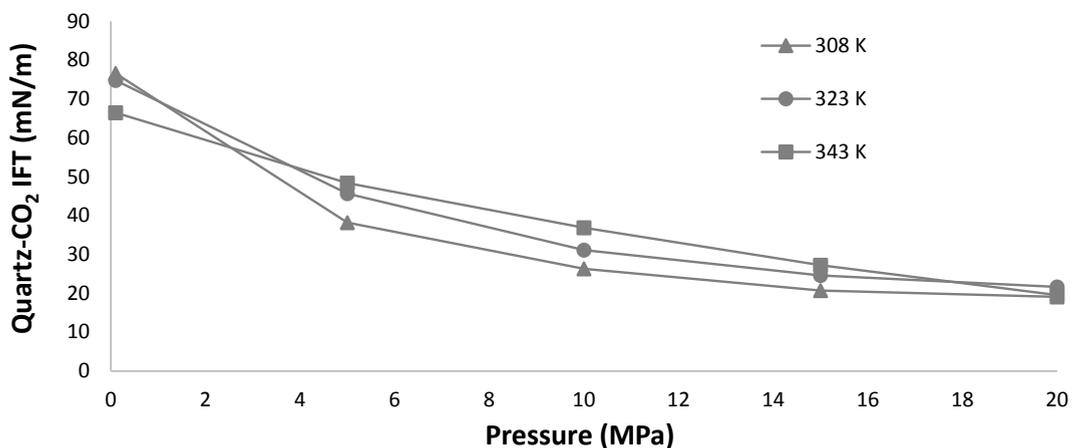


Figure 2: Quartz/CO₂ interfacial tension as a function of pressure and temperature.

In literature, a few studies report surface free energies of quartz at ambient conditions. Janczuk and Zdziennicka [23] calculated the surface energy of quartz at ambient conditions against air using the van Oss-Good method (van Oss et al. [24]) and the values ranged from 57 mN/m to 126 mN/m, consistent with our value (~74 mN/m) estimated for a similar condition (0.1 MPa and 308 K).

Dickson et al. [22] is the only major study who computed surface energies as a function of pressure for silica (glass)/CO₂ systems and found that for a partially methylated glass surface (63% of the surface was covered by methyl groups, the remaining 37% by SiOH groups) surface solid/CO₂ interfacial tension decreased with pressure. The values

reported were 38 mN/m at a CO₂ activity of 0 (equivalent to a pressure of 0.1 MPa) and reduced to ~10 mN/m at a CO₂ activity of 1.4 (equivalent to 20 MPa) at 296 K. The decrease in quartz/CO₂ interfacial tension with pressure is thus consistent with Dickson et al. [22], however, the difference in values is due to the fact that the surface they used had only 37% silanol group coverage (while in our case it is 100%, i.e. pure quartz). Furthermore, Dickson et al. [22] reported solid/CO₂ interfacial tension for a 12% SiOH surface (now 88% of the surface was methylated), for which lower γ_{sc} values were reported (20 mN/m at 0.1 MPa and ~0 mN/m at 20 MPa) which is due to the higher hydrophobicity of the 12% SiOH surface (when compared with the 37% SiOH surface). Due to the limited number of silanol groups available, only a minimal amount of CO₂ is expected to cap these hydrophilic sites, thus γ_{sc} values were lower for lower silanol coverage (e.g. for our case γ_{sc} = 20 mN/m at 20 MPa, and for Dickson et al. γ_{sc} = 10 mN/m for 37% SiOH surface, and ~0 mN/m for 12% SiOH surface).

For all cases analyzed, the solid/CO₂ interfacial tension increased with temperature (Figures 2). Quartz/CO₂ interfacial tension increased from 21 mN/m to 27 mN/m when temperature increased from 308 K to 343 K (Figure 2).

For all cases analyzed, the increase in γ_{sc} with temperature is attributed to a decrease in cohesive energy density of CO₂ with temperature [25] while the cohesive energy density of the solid is expected to stay approximately constant with temperature [26], which leads to an increase in the difference of solid/CO₂ cohesive energies with temperature. Consequently, the interactions between solid and CO₂ become less favorable, thus γ_{sc} increases with temperature which promotes water-wetting of the surface. Moreover, reduction in CO₂ density with temperature leads to fewer van der Waals interactions which leads to an increase in γ_{sc} with temperature.

3.1. Effect of pressure and temperature on mica/CO₂ interfacial tension

The results indicate that, likewise quartz, mica/CO₂ interfacial tension decreased with pressure and increased with temperature (Figure 3). When pressure increased from 0.1 MPa to 5 MPa, mica/CO₂ interfacial tension decreased sharply from 78 mN/m to 41 mN/m. The decrease flattened out gradually with further increase in pressure (24 mN/m at 10 MPa and 16 mN/m at 20 MPa).

Mica/CO₂ interfacial tension also followed a similar trend. It increased from 11.5 mN/m to 24 mN/m when temperature increased from 308 K to 343 K.

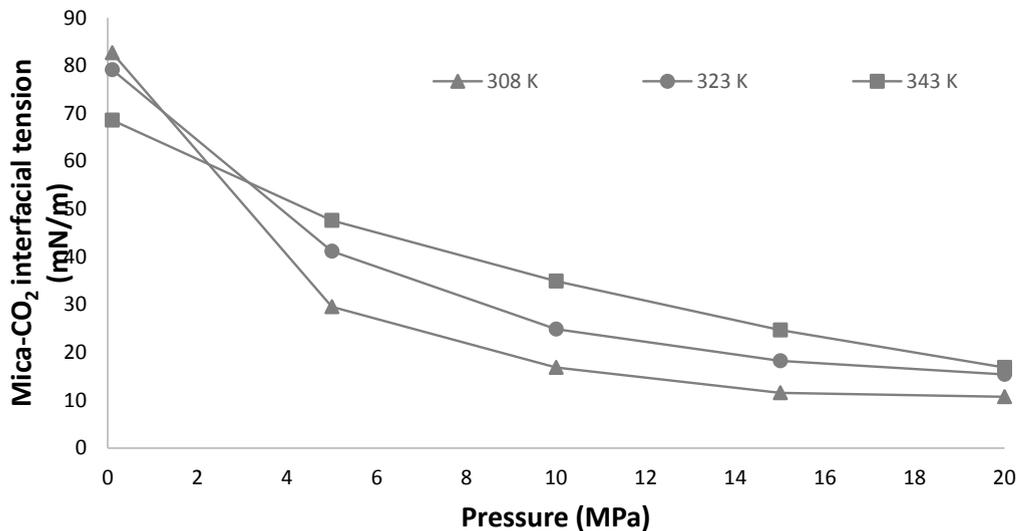


Figure 3: Mica/CO₂ interfacial tension as function of pressure and temperature.

3.3. Effect of temperature on solid/water interfacial tension

Solid/water interfacial tensions were directly obtained from the non-linear regression fit of the experimental and model data (such a plot is shown in Figure 1) and the results are tabulated in Table 3. It is clear from the results shown in Table 3 that the solid/water interfacial tension increased with temperature for quartz and decreased with temperature for mica. However, the changes in γ_{sw} for quartz were quite insignificant as compared to mica. When temperature increased from 308 K to 343 K the quartz/water interfacial tension increased from 0.058 mN/m to 0.952 mN/m which is consistent with Shojai Kaveh et al. [27] who computed shale/water interfacial tension and reported that the shale/water interfacial tension was also very low (0.58 mN/m at 318 K). The increase in quartz/water interfacial tension with temperature can be attributed to desorption of water molecules from the surface.

For mica, at any temperature, the solid/water interfacial tensions were higher than those of quartz. (e.g. $\gamma_{sw} = \sim 2$ mN/m for mica 0.2 mN/m for quartz at the same temperature, 323 K). The larger solid/liquid interfacial tension values for the more hydrophobic surface is consistent with Dickson et al. [22] who reported that the glass surface with higher silanol coverage had lower solid/liquid interfacial tensions (note: a higher concentration of surface silanol groups creates a more hydrophilic surface (Chen et al. [28])).

Further, we point out that the proposed methodology assumes that γ_{sw} is constant versus pressure. In reality, however, the solid/water interactions are expected to change due to increase in solubility of CO₂ in water with pressure (El-Maghraby et al. [29]), and associated lower pH values [30], which leads to increased protonation of the silanol surface groups (Brown et al. [31]).

3.4. Effect of salinity on solid/CO₂ and solid/water interfacial tension

We compared solid/CO₂ interfacial tension (as function of pressure and temperature) for 20 wt% NaCl brine in mica/CO₂ systems and compared it with that of mica/water systems. The results showed that the mica/CO₂ interfacial tension for DI-water at a particular pressure and temperature is quite similar to the mica/CO₂ interfacial tension for 20 wt % NaCl brine case (Figure 4). For instance, at 323 K, and 10 MPa, the mica/CO₂ interfacial tensions were 22.4 mN/m for liquid comprising of 20 wt% NaCl brine, and 24.8 mN/m for DI-water, thus a difference of only 2.4 mN/m (Figure 4). Moreover, at the same temperature but at 15 MPa, mica/CO₂ interfacial tension for two different liquids (DI water and 20 wt % NaCl brine) is the same (~ 18.5 mN/m, Figure 7). In summary, the R²-values for the correlation between mica/CO₂ interfacial tensions for the two liquids were 0.997, 0.998 and 0.985 at 308 K, 323 K and 343 K, respectively, indicating a strong correlation. This implies that solid/CO₂ interfacial tension is not much changed by altering the type of the liquid in the same system. We point out that this result verifies this methodology and our predictions (of mineral/CO₂ and mineral/water interfacial tensions) to some extent.

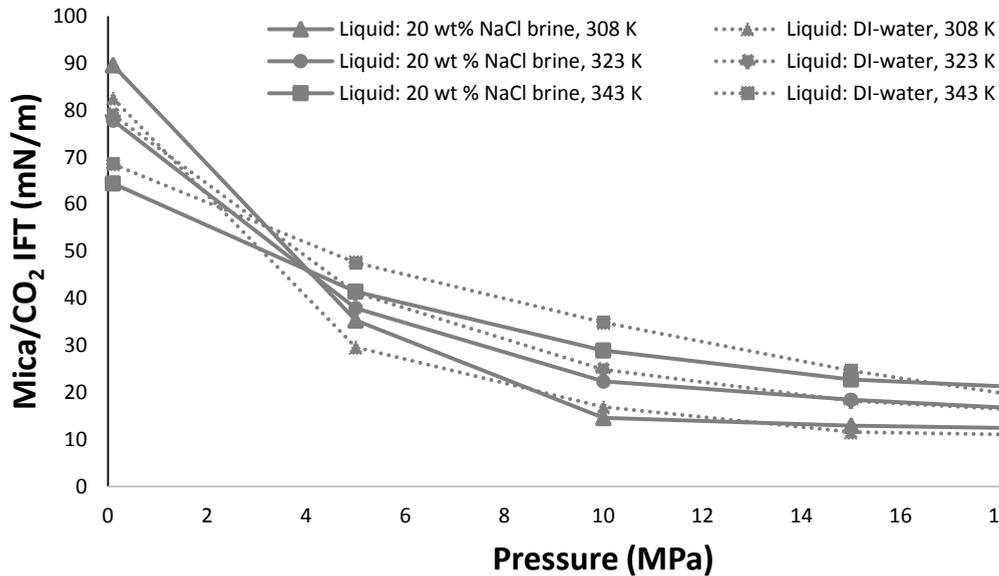


Figure 4: Mica/CO₂ interfacial tension as a function of pressure and temperature for two different liquids (DI-water and 20 wt% NaCl brine)

To analyze the effect of salinity on the solid-water interfacial energies, we compared γ_{sw} for DI water with that of 20 wt% NaCl brine (Figure 4). The β values from the non-linear regression fit of cosine of the equilibrium contact angle data were 0.000267, 0.000284, and 0.00034 at 308 K, 323 K and 343 K, respectively. The Pearson coefficients were 0.846, 0.921 and 0.941, indicating good fits. The mica/brine (20wt% NaCl) interfacial tensions were 10.5 mN/m, 6.27 mN/m and 4.4 mN/m at 308 K, 323 K and 343 K, respectively implying that mica/brine interfacial tension decreased with temperature, consistent with the solid/DI-water system (discussed above). However, at any given temperature, mica/brine interfacial tension was larger than the mica/water interfacial tension. For instance, at 308 K, mica/brine (20 wt % NaCl brine) interfacial tension was 10.5 mN/m in comparison to 2.1 mN/m for mica/DI water at the same temperature (308 K). This result is consistent with Ameri et al. [18] who found that when salinity increased from 0wt% NaCl to 3.5 wt% NaCl, γ_{sw} increased slightly. The increase in solid/brine interfacial tension with salinity is related to the intermolecular forces and the zeta potential which arises due to charged species on the surface. As salinity increases, more counter ions are available to reduce the net charge and thus reduces the polarity of the surface, which again leads to a reduction in water-surface van der Waals forces. Lower van der Waals interactions result in higher interfacial tensions.

4. Implications

In order to evaluate the net effect of the three interfacial tensions on wettability (or equivalently contact angle), the right hand side (RHS) of Young's equation (the value of $\cos\theta$, equation 1) was calculated using the computed values of γ_{sc} and γ_{sw} and experimental values of γ_{cw} . We found that for quartz, $\cos\theta$ decreased with pressure and temperature because quartz/CO₂ interfacial tension decreases with pressure and increases with temperature, and the quartz/water interfacial tension increases with temperature. Thus the net effect of the three interfacial tension results in decrease in $\cos\theta$ with pressure and temperature and consequently θ increases with pressure and temperature for quartz (consistent

with experimental data, Table 1). For mica, the right hand side of Young's equation i.e. ' $\cos\theta$ ' decreases with pressure and increases with temperature because solid/ CO_2 interfacial tension decreases with pressure and increases with temperature and the solid/water interfacial tension also decreases with temperature, thus θ increases with pressure and decreases with temperature (consistent with experimental data, Table 1).

In summary, the increase in contact angle with pressure is due to a reduction in the difference of solid and CO_2 cohesive energies with pressure which leads to more favorable interactions between solid and CO_2 . Consequently, γ_{sc} decreases with pressure and thus promotes de-wetting of the surface (i.e. higher water contact angle).

5. Conclusions

We computed solid/ CO_2 and solid/brine interfacial tensions as a function of pressure, temperature and salinity for quartz and mica to demonstrate the wettability dependency on the interfacial tensions by applying Neumann's equation of state. We found that solid/ CO_2 interfacial tension decreased with pressure (consistent with Ameri et al. [18] and Dickson et al. [22]), which is due to increased CO_2 -mineral intermolecular interactions (e.g. Arif et al. [32]). It was also found that solid/ CO_2 interfacial tensions increased with temperature which is due to an increase in the difference of solid/ CO_2 cohesive energies with temperature which thus leads to less favorable interactions between solid and CO_2 . Moreover, we found that solid/brine (or solid/water) interfacial tension decreased with temperature for mica and increased with temperature for quartz. The effect of salinity was also analyzed and it was found that solid/water interfacial tension increased with salinity. Moreover, contact angles were predicted by Young's equation using the computed values of interfacial energies, and the predicted θ values were in good agreement with the experimental θ values. We conclude that the approach used here is adequate to quantify the solid surface energy and that the results showed a significant influence of surface energy in controlling the wettability dependence on pressure, temperature and salinity for both quartz and mica.

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