CO₂ solubility in aqueous solutions containing Na⁺, Ca²⁺, Cl⁻, SO₄²⁻ and
HCO₃⁻: the effects of electrostricted water and ion hydration
thermodynamics.

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1 ABSTRACT: Dissolution of CO₂ into deep subsurface brines for carbon sequestration is
2 regarded as one of the few viable means of reducing the amount of CO₂ entering the atmosphere.
3 Ions in solution partially control the amount of CO₂ that dissolves, but the mechanisms of the
4 ion's influence are not clearly understood and thus CO₂ solubility is difficult to predict. In this
5 study, CO₂ solubility was experimentally determined in water, NaCl, CaCl₂, Na₂SO₄, and
6 NaHCO₃ solutions and a mixed brine similar to the Bravo Dome natural CO₂ reservoir; ionic
7 strengths ranged up to 3.4 molal, temperatures to 140°C, and CO₂ pressures to 35.5 MPa.
8 Increasing ionic strength decreased CO₂ solubility for all solutions when the salt type remained
9 unchanged, but ionic strength was a poor predictor of CO₂ solubility in solutions with different
10 salts. A new equation was developed to use ion hydration number to calculate the concentration
11 of electrostricted water molecules in solution. Dissolved CO₂ was strongly correlated ($R^2 =$
12 0.96) to electrostricted water concentration. Strong correlations were also identified between
13 CO₂ solubility and hydration enthalpy and hydration entropy. These linear correlation equations
14 predicted CO₂ solubility within 1% of the Bravo Dome brine and within 10% of two mixed
15 brines from literature (a 10 wt % NaCl+KCl+CaCl₂ brine and a natural Na⁺, Ca²⁺, Cl⁻ type brine
16 with minor amounts of Mg²⁺, K⁺, Sr²⁺ and Br⁻).

1. Introduction

Rising levels of CO₂ in the atmosphere that contribute to increased global heat trapping are driving the search for viable ways to reduce anthropogenic CO₂ emissions. To achieve this goal, many energy industry and world governments seek to reduce CO₂ emissions by capturing CO₂ at point sources and sequestering it in the deep subsurface for long-term storage (Benson et al., 2005). For carbon capture and geological storage (CCS), CO₂ will typically be compressed to a supercritical state, and pumped into brine aquifers to be stored by structural and pore-scale trapping, dissolution into brine, and mineral precipitation.

The effectiveness of CO₂ dissolution into brine as a trap depends directly on temperature, pressure, and chemical composition. While the influence of pressure and temperature are well characterized, chemical composition is more heterogeneous and less well understood; real solutions are more complex than the simple NaCl brines that have been widely discussed. In the study reported here, we measure CO₂ solubility in a wide range of aqueous electrolyte solutions to better understand behavior in real reservoirs.

At atmospheric pressure CO₂ solubility is proportional to the partial pressure of CO₂, (P_{CO_2}); it is adequately described by Henry's Law (Eq. (1)) using partial pressure. At higher pressures, such as those required for carbon sequestration, gases no longer behave ideally and effective pressure, or fugacity (f) must be used in place of partial pressure; fugacity is the tendency of CO₂ molecules to escape into the solution (Lewis, 1901). CO₂-phase fugacity is controlled by pressure and temperature (Fig. 1).

A small amount of the CO₂ that is dissolved into a solution hydrolyzes to form carbonic acid (Eq. 2), which dissociates to form bicarbonate (Eq. 3) and carbonate (Eq. 4):

$[H_2CO_3^*] = K_H^* [f]$	$K_H=10^{-1.47}$	1
$CO_2 + H_2O \rightarrow H_2CO_3$	$K=10^{-3.5}$	2
$H_2CO_3 \rightarrow H^+ + HCO_3^-$	$K_1=10^{-6.3}$	3
$HCO_3^- \rightarrow H^+ + CO_3^{2-}$	$K_2=10^{-10.3}$	4

$H_2CO_3^*$ is the sum of the activities of carbonic acid and aqueous CO_2 . At the pH conditions anticipated for a typical sequestration reservoir, the pH is generally below 4.0 and dissolved $CO_{2(aq)}$ is the dominant species (Appelo and Postma, 2005). The equilibrium constants reported in Eqs. (1-4) are at 25°C, and they vary with temperature. The effects of temperature on CO_2 solubility are important but complex. At higher temperatures CO_2 solubility decreases due to a lower Henry's law constant, K_H ($K_{H25} = 10^{-1.47}$, $K_{H140} = 10^{-2.06}$), yet it also increases the fugacity coefficient at a given pressure. Furthermore, temperature affects the equilibrium constants of solution complexes.

Another consideration of the total molal solubility of CO_2 in a subsurface reservoir is the ionic composition of the aqueous solution. Neutral species such as CO_2 in aqueous fluids are subject to salting out by dissolved electrolytes, and solubility typically decreases as ionic strength increases. CO_2 solubility in aqueous solutions of different compositions has been investigated. Dissolved CO_2 in pure water increases as PCO_2 increases and temperature decreases (Hu et al., 2007; Li et al., 2004; Teng and Yamasaki, 1997; Wiebe and Gaddy, 1941). However, increasing ionic strength decreases the CO_2 solubility in simple NaCl brines (Duan et al., 1995; Hu et al., 2007; Kruger and Diamond, 2001; Liu et al., 2011; Nighswander et al., 1989; Yan et al., 2011).

1 Numerous studies refer to ionic strength as the underlying control on salting out, but it is not
2 clear if brines that have the same ionic strength but different compositions will dissolve the same
3 amount of CO₂ or have different salting out potentials. Differences in dissolved CO₂ at the same
4 ionic strength may occur because of differences in ion size or charge, pH, complex formation,
5 mineral precipitation or other reactions (Liu et al., 2011; Millero and Huang, 2003).

6 Other possibilities may explain the salting out phenomenon. One possibility is a change in
7 water activity. Ions in solution electrostrict water molecules; that is, the ions pull in the water
8 molecules tightly and form a shell of highly ordered water. Electrostriction reduces water
9 availability for interaction with other ions or non-electrolytes (i.e. reduces availability of free
10 water) (Robinson and Stokes, 2002). This effect varies with ion size and charge.

11 Another potential approach for describing salting out is on a continuum basis using classical
12 thermodynamics. When an ion is dissolved, the pre-existing hydrogen bonded water structure is
13 disrupted resulting in an entropy increase with the addition of all but the smallest ions (e.g. F⁻
14 and Li⁺). In contrast, the dissolution of a non-polar gas (e.g. CO₂) into a polar solvent (e.g.
15 water) decreases the entropy of the system (Robinson and Stokes, 2002) as water forms an
16 ordered, cage-like structure, around the CO₂ molecule (Frank and Evans, 1945). The magnitude
17 of increasing entropy caused by the salts is usually larger than that of the decreasing entropy
18 caused by CO₂ dissolution, resulting in salting out. The solvation of the ion also results in a
19 change in enthalpy by making and breaking hydrogen bonds between water molecules upon
20 solvation (Robinson and Stokes, 2002).

21 Many CO₂ solubility models are based on simple NaCl solutions (Mao et al., 2013; Marin
22 and Patroescu, 2006; Søreide and Whitson, 1992). Natural brines, however, are not simple.

1 They often contain a complex mixture of ions including HCO_3^- , Ca^{2+} , Mg^{2+} , K^+ , and SO_4^{2-} , in
2 addition to organic acids and anions often found in deep reservoirs. Other models (Duan et al.,
3 2006; Pitzer, 1973; Rumpf and Maurer, 1993) predict CO_2 solubility in aqueous solutions
4 containing a larger set of electrolytes, but require experimentally-determined parameters that
5 change with reservoir conditions and brine composition. Through an investigation of the impacts
6 of reactive and divalent ions on CO_2 solubility, we present here an new mechanistic approach to
7 understanding salting out of CO_2 and provide a theoretical basis for predictive model
8 development.

9 **2. Methods**

10 The experimental approach used primarily single salt end-member solutions at varying
11 concentration, temperature, and pressure to identify solubility trends. In addition, brine from a
12 natural analog site (Bravo Dome) where high pressure CO_2 has been trapped over geologic time,
13 was characterized and used as an example of a complex mixed system. High purity salts from
14 Macron Chemical (NaCl), Fisher Scientific (anhydrous CaCl_2), Mallinckrodt (Na_2SO_4), MCB
15 (NaHCO_3), and Baker (MgSO_4) were used to prepare solutions in ultrapure deionized water. The
16 1 m NaHCO_3 solution was kept at 60°C to prevent precipitation due to solubility limits at lower
17 temperatures.

18 Bravo Dome is located on the eastern flank of the Sierra Grande uplift in northeast New
19 Mexico. The CO_2 is trapped in the Permian Tubb Formation arkosic sandstones by a
20 combination of fold structure, stratigraphic pinch-out, and possibly hydrodynamic forces
21 (Broadhead, 1990). The Bravo Dome field site has hundreds of wells and produced waters from
22 several wells are integrated and collected at a single gas-liquid separator. Because the gas was

1 very dry in the individual wells, insufficient sample could be collected for extensive
2 experimentation so a synthetic solution containing the six major ions in the natural brine was
3 prepared from NaCl, CaCl₂, NaHCO₃ and MgSO₄. The resulting brine had the following molal
4 composition: 0.402 m Na⁺, 0.047 m Ca²⁺, 0.024 m Mg²⁺, 0.395 m Cl⁻, 0.024 m SO₄²⁻ and 0.101
5 m HCO₃⁻, with an actual ionic strength of 0.542 (calculated using the LLNL database in PhreeqC
6 (Parkhurst and Appelo, 2013)).

7 All experiments were performed in high-pressure, 150 ml stainless-steel reactors initially
8 containing 100 ml of aqueous solution in either a constant temperature incubator or a constant
9 temperature water bath. Temperature was logged with an Onset HOBO temperature logger. The
10 average temperature in the incubator varied $\pm 2^{\circ}\text{C}$, which we estimate to induce error in CO₂
11 solubility in pure water of up to 2.5%. After CO₂ injection, gas-liquid equilibrium was
12 determined by logging change in pressure using temperature-compensated pressure transducers
13 (0-200 bar, Honeywell FP pressure transducer) through a National Instruments CompactDAQ
14 data acquisition system. A stable pressure indicated the system was at equilibrium.

15 Once the system equilibrated to each target pressure, an aliquot of CO₂-saturated brine was
16 collected into an evacuated thermally-equilibrated 5.75 ml stainless steel coil. A small pressure
17 dip of 0.5 – 1.0 MPa in the reactor was observed when valves were opened to collect the sample,
18 but a supercritical CO₂ pump quickly recovered reactor to the set point pressure. After the set
19 point pressure was re-established, the reactor remained open to the sample vessel for 30 minutes.
20 The sample coil was then removed and weighed, then the sample was expanded into an
21 evacuated 1.0 L expansion chamber and held at a constant temperature of 5°C. Starting absolute
22 pressure in the expansion chamber ranged from 0.0017 to 0.027 MPa; the final pressure was
23 recorded after steady state was reached. The expansion chamber remained under tension even

after expansion so that ideal behavior could be expected (fugacity coefficient ~ 1) and the ideal gas law could be used to calculate moles of CO_2 dissolved in the solution.

3. Results

Carbon dioxide solubility was measured in deionized water and salt solutions up to 3.4 molal from 30 to 140°C. Figs. 2-6 are shown to elucidate specific points. In the results section text and figures temperatures are referred to as 60°C and 30°C, but the actual average temperatures vary slightly. The actual temperatures for the measurements are listed in Table 1, which is a subset of the total data set. The complete data set is available in supplementary information.

Table 1 Measured CO_2 solubility versus T, PCO_2 , CO_2 fugacity and electrostricted water (h_a) with measurement uncertainty.

Solution	T (°C)	PCO_2 (Mpa)	CO_2 fugacity (MPa)	h_a (mol/kgw)	Measured CO_2 solubility (mol/kgw) +/- 0.78%
Water	35.0	21.0	6.91	0.0	1.18
Water	35.0	32.0	8.52	0.0	1.56
Water	70.0	10.4	7.34	0.0	0.80
Water	70.0	33.2	13.2	0.0	1.25
Water	100.0	10.9	8.46	0.0	0.77
Water	100.0	34.7	17.7	0.0	1.29
Water	140.0	20.0	14.9	0.0	1.09
Water	140.0	34.0	22.1	0.0	1.48
0.1m NaHCO_3	58.0	5.50	4.51	0.5	0.82
0.1m NaHCO_3	59.0	14.4	7.89	0.5	1.44
0.1 m CaCl_2	60.5	1.92	2.02	1.4	0.29

0.1 m CaCl₂	62.0	5.40	4.47	1.4	0.65
0.1 m Na₂SO₄	58.8	2.90	2.64	1.7	0.44
0.1 m Na₂SO₄	59.6	12.4	7.67	1.7	1.23
Bravo Dome	57.8	1.50	1.44	3.4	0.27
Bravo Dome	57.4	10.2	6.82	3.4	1.08
1 m NaHCO₃	60.5	5.70	4.67	5.0	0.66
1 m NaHCO₃	57.6	10.8	7.19	5.0	1.01
1.88 m NaCl	35.0	10.6	5.55	11.3	0.84
1.88 m NaCl	35.0	35.1	9.09	11.3	1.20
1.88 m NaCl	70.0	10.2	7.26	11.3	0.73
1.88 m NaCl	70.0	34.7	13.6	11.3	0.87
1.88 m NaCl	100.0	10.0	7.94	11.3	0.45
1.88 m NaCl	100.0	35.4	18.0	11.3	0.89
1.88 m NaCl	140.0	10.4	8.93	11.3	0.40
1.88 m NaCl	140.0	34.2	22.2	11.3	0.94
1 m CaCl₂	70.0	3.20	2.92	14.3	0.38
1 m CaCl₂	56.2	11.7	7.25	14.3	0.81
1 m Na₂SO₄	56.9	5.40	4.44	17.0	0.45
1 m Na₂SO₄	57.5	14.3	7.74	17.0	0.70
3.4 m NaCl	35.0	9.89	5.46	20.4	0.58
3.4 m NaCl	35.0	34.2	8.93	20.4	0.70
3.4 m NaCl	70.0	11.6	7.81	20.4	0.47
3.4 m NaCl	70.0	35.8	13.9	20.4	0.63
3.4 m NaCl	100.0	10.0	8.67	20.4	0.37
3.4 m NaCl	100.0	35.4	22.9	20.4	0.63
3.4 m NaCl	140.0	9.90	8.57	20.4	0.44
3.4 m NaCl	140.0	33.9	22.1	20.4	0.78

3.1 Pure water

The measured solubility of CO₂ in pure water at 60°C closely followed the findings at 55°C of previous authors (Liu et al., 2011) (Figs. 2 and 3), and predicted values using PhreeqC (PhreeqC.dat) and the Duan Group model at 60°C (Duan and Sun, 2003) (Fig. 3). CO₂ solubility increases in a non-linear fashion as CO₂ partial pressure increases (Fig. 2), but it is linear up to about 7 MPa (Fig. 3) when plotted as a function of fugacity. For this reason, all results are reported in terms of CO₂ fugacity rather than PCO_2 . In pure water, CO₂ solubility increases with increasing CO₂ fugacity, but the increase is greater at lower temperatures (35 and 60°C) (Fig. 4) than at higher temperatures (100 and 140°C).

3.2 Salt solutions

CO₂ solubility was measured in 1.88 and 3.4 molal NaCl brines at 35, 70, 100 and 140°C (subset in Table 1 or full data set in supporting information) and in 0.1 and 1 molal CaCl₂, Na₂SO₄, and NaHCO₃ aqueous solutions at 60°C (Figs. 5a-c, respectively). For all individual salts, increasing molal ionic strength and increasing temperature reduced CO₂ solubility as predicted by theory and experiment. CO₂ solubility versus fugacity in one molal CaCl₂, Na₂SO₄, and NaHCO₃ solutions at 60°C are shown in Fig. 6. For each individual salt CO₂ solubility decreased with increasing ionic strength; however, ionic strength did not accurately predict which salt dissolved most or least. The three molal ionic strength Na₂SO₄ brine dissolved the least, (15% less CO₂ than the three molal ionic strength CaCl₂ brine), which agrees well with the results of Zhao (Zhao et al., 2015b).

4. Discussion

4.1 Ionic Strength

Simple molal ionic strength is calculated from the total analytical concentrations (C_T) of the electrolyte species assuming complete dissociation and no complexation in solution.

Complexation, however, is likely even in simple aqueous solutions. These complexes vary with ionic composition and temperature; different model databases yield different “true” ionic strengths (I_T) for the same water depending on which complexes are considered. With the exception of Pitzer, the model databases available for PhreeqC (Parkhurst, 1990) calculate a true ionic strength (ionic strength calculated with the consideration of complexes). The LLNL database differs slightly from the others because it considers the NaCl^0 and CaCl_2^0 neutral complexes. For this reason, the LLNL calculated I_T is used for this analysis. The CaCl_2 solution ($I_T = 2.71$) had 15% more dissolved CO_2 than Na_2SO_4 ($I_T = 1.98$). This suggests that complexation and I_T , at least as predicted by the databases, does not accurately account for differences in the solubility of CO_2 .

4.2 Water Activity

Another consideration regarding the salting out of CO_2 is the effect of ion dissolution on the water itself. Water activity, a_w , determined via Raoult’s Law by measuring the partial pressure of water ($P_{\text{H}_2\text{O}}$) over an aqueous solution of electrolytes, is a way to describe the effects of dissolved ions in solution. Dissolved ions decrease a_w by electrostricting water molecules (Robinson and Stokes, 2002) around them; this interaction decreases the concentration of available or free water. These waters of hydration are held with varying degrees of attraction strength and at various distances from the hydrating ion; the ion’s size, shape and charge

determine the degree of electrostriction, and how tightly each water is held. Smaller ions have tighter water shells than larger ions due to their higher charge density (Hribar et al., 2002). Electrolytes that form relatively stable solution complexes have a lower charge density and, therefore, a diminished capacity to complex free water; thus they may potentially decrease the salting out of CO₂.

Na⁺ and Ca²⁺ have similar ionic radii, 0.95 and 0.99 Å, respectively (Millero, 1969), but Ca²⁺ has twice the charge of Na⁺. As a result, Ca²⁺ holds more water molecules, holds them more tightly, and salts out more effectively than Na⁺ (hence the greater effect on ionic strength). Anions, however, such as Cl⁻ and SO₄²⁻ are more difficult to compare. Sulfate has roughly twice the charge density of Cl⁻, because of its double charge and an ionic radius that is only slightly larger than Cl⁻ (2.05 for SO₄²⁻ versus 1.81 Å for Cl⁻). Cl⁻ is spherical, but tetrahedral SO₄²⁻ has multiple possible centers for water electrostriction (Bush et al., 2007; Wan et al., 2012; Yacovitch et al., 2013). Solvated SO₄²⁻, (SO₄²⁻(H₂O)_n), forms hydrogen bonds with multiple water molecules (n=3-17); the most stable cluster is reported to be 12 (Wan et al., 2012; Wong and Williams, 2003). In contrast, for hydrated chloride (Cl(H₂O)_n), n≤6 (Powell et al., 1988).

CO₂ solubility (Table 1) versus a_w (Aseev, 1998) is shown in Fig. 7. Whereas CO₂ solubility generally decreases with decreasing a_w (R² = 0.74 at 6.7 MPa), significant deviations can be noted. Using the linear regression between CO₂ solubility and a_w to predict dissolved CO₂ in Na₂SO₄ (I=1.98) results in a 91% overestimate. For NaHCO₃ (I=0.098), it results in a 16% underestimate.

4.3 Electrostricted Water

A hydrated ion is generally described as having several shells of water molecules surrounding it. In the innermost shell, the ion interacts electrically with (electrostricts) the water and holds it so tightly that the water is incompressible. In the second shell the water molecules are somewhat ordered, but not incompressible. Outside of these shells, water molecules around the ion may be oriented, but they are shielded from the ionic charge (Hribar et al., 2002; Marcus, 1997; Millero, 1969). Hydration number describes the number of water molecules around the ion; silica solubility has been found to be linearly correlated with the hydration number of the cation of salts in solution (Marshall and Warakomski, 1980). In our study, CO₂ solubility was found to have a similar relationship; it was inversely correlated to the concentration of electrostricted water molecules:

$$h_a = \sum C_i n_i h_{comp} \quad 5$$

where n_i is ion stoichiometric coefficient, C_i is salt molal concentration, and h_{comp} is hydration number based on partial molar compressibility. Measured CO₂ solubility plotted against h_a at 60°C and 6.7 MPa fugacity (Fig. 8) yields a strong correlation ($R^2 = 0.96$) where CO₂ solubility decreases with increasing h_a . The same analysis performed at other fugacities (3 and 4.3 MPa) yields similarly strong correlations. This method of calculating the concentration of electrostricted water molecules and the use of h_a to predict dissolved CO₂ solubility is a unique aspect of this study. The dependence of CO₂ solubility on electrostricted water molecules encompasses a large ionic strength range of 0.1 to 3.4 molal and explains the behavior of 1 m CaCl₂ and 1 m Na₂SO₄, with h_a values of 14.3 and 17.0 mol/kgw, respectively. With a lower concentration of electrostricted water CaCl₂ has more free water for CO₂ dissolution. This relationship is further supported by experiments demonstrating that Na₂SO₄ causes a greater

1 decrease in seawater compressibility than CaCl_2 (Duedall, 1977). This lower compressibility
2 indicates a greater degree of water electrostriction, which is consistent with the calculated h_a .

3 The choice of source for hydration number is important; reported hydration numbers vary
4 depending on the method of determination (Marcus, 1997; Marcus, 2006; Ohtaki, 2001; Ohtaki
5 and Radnai, 1993; Varma and Rempe, 2006; Zavitsas, 2001). In spite of inconsistencies between
6 methods, reported values from a single method of determination are usually considered internally
7 consistent. For this study hydration numbers based on partial molar compressibility (h_{comp}) come
8 from a single source (Marcus, 1997). Hydration numbers used in this study are as follows: 3.3
9 for Na^+ , 8.9 for Ca^{2+} , 10.4 for SO_4^{2-} , 2.7 for Cl^- , 1.7 for HCO_3^- , 8.9 for Mg^{2+} , and 2.3 for K^+ .
10 Hydration number based on partial molar compressibility describes primary hydration or
11 hydration of the first shell, which allows its use to estimate the molal concentration of tightly
12 electrostricted water (Table 1) and free water. CO_2 , on the other hand, requires a much greater
13 number of water molecules for its solvation. Although we found no reports on the specific cage
14 structure around CO_2 at sequestration reservoir conditions, under the conditions in which a CO_2
15 clathrate forms, a typical S1 hydrate structure contains 46 water molecules per CO_2 (Sloan,
16 2008), suggesting the potential for competition between CO_2 and ions for free water.

17 Our calculation of electrostricted water (eq. 5) assumes that hydration number is an additive
18 property between ions. However, some evidence exists that ions are cooperative, rather than
19 additive and that the number of water molecules interacting with a cation and anion in close
20 proximity is greater than the sum of the water molecules interacting with each ion individually.
21 Cooperativity, however, occurs only in secondary hydration shells or outside of shells (Tielrooij
22 et al., 2010). Since cooperativity does not occur in primary hydration shells it does not affect our
23 calculation of electrostricted water concentration because h_{comp} accounts only for water

1 molecules in the primary hydration shell (Marcus, 1997). Cooperativity, therefore, is not
2 significant in predicting CO₂ solubility.

3 While the correlation is quite good in Fig. 8, there is some scatter around our linear equation
4 fit line. Some scatter is due to the reported measurement uncertainty and temperature variation.
5 The correlation analysis was performed on data at 60°C, but actual temperatures were $59.1 \pm$
6 2.9°C (Table 1) resulting in estimated errors of up to 2.5%, which could represent up to 50% of
7 the scatter. It is also possible that hydration number is not constant at high electrolyte
8 concentration due to the formation of ion pairs (Marcus, 2014) which have a lower charge
9 density. Ion association and complexation also increase with increasing temperature and
10 decreasing pressure (Hnedkovsky, Wood et al. 2005; Zimmerman, Arcis et al. 2012). In a 1 m
11 Na₂SO₄ brine, the concentration of NaSO₄⁻ was estimated to increase 1.3% from atmospheric
12 conditions to 60°C and 10 MPa and 1.4% at 100°C and 40 MPa pressure, resulting in < 1%
13 change in CO₂ solubility.

14 4.4 Thermodynamic analysis

15 As the concentration of electrostricted water increases, the likelihood increases that
16 solvation of a CO₂ molecule will require the extraction of water from the primary shell around an
17 ion. This extraction requires energy, ΔG_{hydr} , which is comprised of enthalpy (ΔH_{hydr}) and
18 entropy (ΔS_{hydr}) components. A higher $-\Delta H_{\text{hydr}}$ indicates that more energy is released upon ion
19 hydration; this creates a greater energy barrier to remove a water molecule from the primary
20 ionic hydration shell for CO₂ solvation. A strong correlation ($R^2 = 0.92$) between CO₂ solubility
21 and ΔH_{hydr} (Fig. 9) at 6.7 MPa and 60°C shows that the enthalpy of hydration of the ion affects
22 CO₂ solubility.

Another factor, system entropy, may also control CO₂ solubility. Pure water is structured as a network of hydrogen bonds (H-bonds); each water molecule participates in a number of H-bonds. For ice, the average number is four and for dilute water vapor it is zero (Marcus and Ben-Naim, 1985). The number of H-bonds in water is between four and zero and temperature dependent. Decreased entropy corresponds to more highly structured water or an increased number of H-bonds in which a water molecule participates. Dissolution of a non-polar gas such as CO₂ in water causes a decrease in entropy because structuring is required to cage around CO₂ (Ben-Naim, 2009; Frank and Wen, 1957; Robinson and Stokes, 2002). In contrast, the hydration of most dissolved ions causes increased entropy, because while hydration structures the water molecules in the inner shell, the overall average number of H-bonds in which a water molecule participates often decreases (Marcus, 1997). These opposing entropic forces may mean that entropy is another control on CO₂ solubility. CO₂ solubility versus ΔS_{hydr} at 6.7 MPa and 60°C is plotted in Fig. 10. This strong correlation ($R^2 = 0.95$) shows that entropy changes during ion solvation affect the amount of CO₂ that will dissolve.

4.5 Prediction of CO₂ solubility in mixed brines

CO₂ solubility was predicted at 60°C and 6.7 MPa fugacity using the linear regression of CO₂ solubility versus h_a and ΔH_{hydr} in three mixed brines: Bravo Dome (this study), a 10 wt% mix (1:1:1) NaCl + KCl + CaCl₂ (Liu et al., 2011) and the Mt Simon brine, which is a Na⁺, Ca²⁺, Cl⁻ type brine with minor amounts of Mg²⁺, K⁺, Sr²⁺, and Br⁻ ($I=1.712$) (Zhao et al., 2015a). For the latter two data sets, linear interpolation was used to determine CO₂ solubility at 60°C. The models based on h_a , ΔH_{hydr} , and ΔS_{hydr} predicted CO₂ solubility for the Bravo Dome solution to within 1, 3 and 1%, respectively. For both the Mt. Simon and mixed NaCl+KCl+CaCl₂ (Liu et al., 2011) brines, all three linear correlation models predicted CO₂ solubility to < 10%, with the

linear regression model of CO₂ solubility versus ΔH_{hydr} yielding the most accurate prediction of <5%.

This type of model may not account for reactions and complex formation that occur in response to CO₂ injection. Bicarbonate in brine can cause inaccurate model predictions (Newell et al., 2008) due to buffering, because it consumes CO₂ and maintains pH higher than it would be in the absence of bicarbonate. Divalent ions: Mg²⁺, Ca²⁺, and SO₄²⁻ can also form complexes that reduce h_a and may reduce the salting out potential. Multiple studies have determined that numerous complexes may form (NaSO₄⁻, NaHSO₄⁰, MgSO₄⁰, CaSO₄⁰, MgCO₃⁰, CaCO₃⁰, NaHCO₃⁰, CaHCO₃⁺ and MgHCO₃⁺) in low pressure, low temperature solutions (Duedall, 1977; Fisher, 1975; Kester and Pytkowicz, 1970, 1975; Pytkowicz and Hawley, 1974). However, under high PCO_2 pH will drop to near or below 5, making the CO₃²⁻ concentration negligible. In addition, Cl⁻ complexes may be important due to their high concentrations in formation water. Organic acid anions also form complexes with cations when concentrations are sufficiently high. Complex concentration changes may result in slight deviations from these model predictions. In spite of this, the regression models predicted CO₂ solubility in three mixed brines reasonably well.

5. Conclusions

In this study we measured CO₂ solubility in simple and mixed salt solutions at high PCO_2 and used the data to provide insight into the mechanisms of CO₂ salting out. While CO₂ solubility decreases with increasing ionic strength, the physical relationship varies with salt type due to changes in the concentration of electrostricted water molecules (h_a), amount of energy required to remove water from around the ion (ΔH_{hydr}), and degree to which the water is ordered

(ΔS_{hydr}). Linear regressions of dissolved CO_2 versus the concentration of electrostricted water, ΔH_{hydr} , and ΔS_{hydr} resulted in strong correlations that predicted CO_2 solubility in three mixed brines to within 10%. While the regression models used in this paper are effective for specific temperatures and fugacities, they suggest that a simple accounting of water molecules can guide predictions on CO_2 solubility in mixed, complicated reservoirs. In cases of limited free water molecules, it is important to evaluate the energy required to extract water from the primary hydration shell of an ion.

ASSOCIATED CONTENT

Supporting Information. Experimental apparatus and expansion chamber diagrams. Complete tabulated data set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written with contributions from all authors. Kimberly Gilbert designed the experimental system, performed approximately half of the CO_2 solubility measurements and wrote the paper. Philip Bennett provided valuable guidance and extensive paper editing. Tongwei Zhang and Katherine Romanack performed the second half of the solubility measurements. Will Wolfe helped with the design and implementation of the experimental

apparatus. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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Figure 1. CO₂ fugacity versus PCO_2 generated from Duan and Sun, 2003.

Figure 2. Measured CO₂ solubility in pure water at 60°C versus PCO_2 compared with data from Liu, et al. 2011.

Figure 3. Measured CO₂ solubility in pure water at 60°C versus CO₂ fugacity compared with data from Liu, et al. 2011., and models using (Duan and Sun, 2003) and the PhreeqC database in PhreeqC.

Figures 4. Measured CO₂ solubility in pure water versus CO₂ fugacity at 35, 60, 100 and 140°C.

Figures 5a-c. Measured CO₂ solubility in a) CaCl₂, b) Na₂SO₄ and c) NaHCO₃ solutions versus CO₂ fugacity at 30°C and 60°C at various ionic strengths.

Figures 6. Measured CO₂ solubility in CaCl₂, Na₂SO₄, NaHCO₃ solutions and water versus CO₂ fugacity at high ionic strength solutions at 60°C.

Figure 7. Measured CO₂ solubility versus a_w at 60°C and a fugacity of 6.7 MPa.

Figure 8. Measured CO₂ solubility versus concentration of electrostricted water (h_a) with the correlation line at 60°C and a fugacity of 6.7 MPa.

Figure 9. Measured CO₂ solubility versus CO₂ enthalpy of hydration (Marcus, 1997) at 60°C and a CO₂ fugacity of 6.7 MPa.

Figure 10. Measured CO₂ solubility versus CO₂ entropy of hydration (Marcus, 1997) at 60°C and a CO₂ fugacity of 6.7 MPa.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 5c

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10