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A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements

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• We introduce a fast and easy methodology to equilibrate CO₂ and brine in the liter range.
• Equilibration was reached in 60 minutes.
• This is an important step for CO₂ storage studies and experiments.
• Solubility of CO₂ in brine was measured using isothermal depressurization method.
• Comparing our solubility data with the literature shows its consistence.
A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements

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Abstract:

We introduce a fast, easy and reliable methodology, using a stirred reactor, to equilibrate carbon dioxide with brine and measure the solubility of carbon dioxide in the aqueous phase at high pressure (9MPa) and elevated temperature (33, 50 and 70°C) conditions at the litre scale. The solubility of carbon dioxide in brine was measured using an isothermal depressurization method and compared with data in the literature. This methodology can be used in petroleum engineering, carbon storage and chemical engineering applications.

Keywords: Equilibration of Brine/CO2, Solubility of CO2, CO2 Storage, supercritical CO2, dissolution trapping.

1. Introduction

Long term storage of carbon dioxide (CO2) in deep saline aquifers has been proposed to mitigate global warming [1]. Saline aquifers are abundant and geographically widespread with huge storage capacities [2-4]. The CO2 will likely be stored as a supercritical (sc) phase at depths of 800 m or more [2], which maximizes the stored mass of CO2.

When CO2 is injected into geological formations there are a number of trapping mechanisms which prevent its migration and subsequent escape to the atmosphere. These are: stratigraphic and structural trapping, geochemical trapping, solubility trapping, and capillary trapping [5]. These mechanisms are the subject of active research, and preparing an equilibrated mixture of carbon dioxide and brine is an important step for many of these experiments (see, for instance, [6-8]).

We present here a methodology with which CO2 can be rapidly equilibrated with brine at the litre-scale at high pressure and elevated temperature conditions representative of geological storage formations. This method could also be used to equilibrate other fluids if their viscosities are not too high, e.g. oils can be mixed with CO2 for petroleum engineering studies or CO2 can be mixed with other solvents (e.g. acetone, dichloromethane, diethyl ether, monoethanolamine, etc.) for chemical engineering applications.

In addition, the equilibrium solubility of CO2 in brine was measured with an accurate isothermal depressurization method. The results were consistent with literature data. Solubility data is crucial for assessing not only the effectiveness of solubility trapping but the equilibration methodology outlined is a crucial step in capillary trapping experiments which rely on immiscible phase displacements [6, 9].
2. Experimental Equipment and Conditions

2.1 Experimental Apparatus

An equilibration reactor (1200 mL C276 autoclave with gas entrainment stirrer – Parr Instruments Co., IL, USA) was used to establish equilibrium between the CO₂ and brine phases. High precision syringe pumps (Teledyne ISCO 1000D, Lincoln, NE, USA) maintained pressures with high accuracy. The brine composition we used was 5wt % NaCl and 1wt % KCl in deionized water. Figure 1 shows the experimental apparatus.

2.2 Experimental Procedure

2.2.1 Rapid establishment of CO₂/brine equilibrium

Three steps were developed to prepare brine saturated with CO₂ and CO₂ saturated with water vapour. During the first step scCO₂ was prepared in a syringe pump C, and a water heating jacket was used to heat the pump to the desired temperature (33°C, 50°C or 70°C). Pump C and all tubing were vacuumed for 20 min, then high pressure gaseous CO₂ (5MPa at 15°C) was transferred to pump C from a CO₂ cylinder by operating pump C in constant refill mode (the pump is driven by a stainless steel piston which was initially set to 0 ml volume which is driven back to full capacity, i.e. 1015 ml). When pump C was completely filled with CO₂ gas at the gas cylinder pressure, it was then pressurized to experimental pressure (9MPa); at these thermophysical conditions scCO₂ was generated.

During the second step, the reactor was heated to experimental conditions in an oil bath, then vacuumed and filled with de-aerated brine using a high precision syringe pump B. The reactor was then pressurized using pump B. The reactor is connected to the scCO₂ pump C operating at the same pressure, then 500 ml from the brine volume in the reactor were displaced by scCO₂ from pump C (pump was set to constant pressure mode) and withdrawing brine with pump B (pump was set to constant refill flow rate mode). The reactor is then isolated from pump B.

In the third step CO₂ and brine were brought to equilibrium inside the reactor by stirring with a stirrer at 200 rpm. The stirrer is a mixing shaft attached to a magnetic motor and has a gas entrainment design. It essentially pushes the lighter phase (scCO₂) into the bottom phase (brine) and generates a large surface area between the fluids by splitting the CO₂ into many small bubbles. This maximization of the contact surface and turbulent flow assured rapid equilibration.

The pressure was maintained constant during the dissolution process with pump C set to constant pressure mode. The pressure in the reactor was monitored using a pressure transducer (Rosemount 3051S pressure transmitter, Rosemount, USA) and pressure readings were logged on a computer. In addition the volume and pressure of pump C were logged to monitor scCO₂ volume balances.

Additional CO₂ was pumped into the vessel during the equilibration process because the CO₂ dissolved reducing the pressure. Equilibrium is reached if no more CO₂ is pumped into the reactor and no change in pump C volume is detected. Equilibration was completed in 60 minutes; however for subsequent experiments [6-8] the system was left overnight to stabilize.

2.3 Isothermal depressurization

The solubility of CO₂ in brine was measured in two steps by using the isothermal depressurization method.

In step 1 pump B was cleaned and vacuumed, then filled with de-aerated brine. The brine was pressurized to 9 MPa and the brine volume ($V_{B1}$) was noted. The pressure was reduced gradually to atmospheric pressure. The volume ($V_{B2}$) in pump B was recorded after depressurization to atmospheric pressure.
In step 2 pump B was emptied and vacuumed for 20 minutes, then a volume of CO₂ saturated brine \( V_{M1} \) – (same volume as for the pressurized de-aerated brine \( V_{B1} \) (equation 1)) - was transferred from the reactor to pump B by operating pump C in constant pressure mode and allowing CO₂ to displace some of the brine to pump B operating in constant refill mode.

\[
V_{M1} = V_{B1} \quad (1)
\]

This was conducted at constant pressure and temperature to prevent CO₂ separating out of solution during the transfer process. After the required amount of CO₂-saturated brine was transferred, pump B was isolated. Then the CO₂-saturated brine mixture in pump B was expanded at constant temperature (33°C, 50°C or 70°C) by reducing the applied pressure gradually. Starting with an operating pressure of 9 MPa, the pressure was reduced gradually until atmospheric pressure was reached. The volume \( V_{M2} \) in pump B was noted.

Dead volumes in the system were measured carefully and taken into account for volume balance calculations.

The isothermal expansion method is based on the concept that for a given volume of brine saturated with CO₂, the CO₂ is released if the pressure is reduced isothermally. If the volume of CO₂ saturated brine is known before depressurization \( V_{M1} \) and the total brine volume is known after depressurization \( V_{M2} \), then the amount of CO₂ that separated out of solution \( V_{CO2} \) can be calculated by subtracting the two volumes (equation 2). We can then calculate the solubility of CO₂ in brine at this condition.

\[
\text{Volume of CO₂ dissolved in the brine} \ (V_{CO2}) = V_{M2} - V_{M1} \quad (2)
\]

But to measure the solubility we have to consider two points to get an accurate measurement of solubility by using the isothermal depressurization method. First as the pressure is reduced, water vapor co-exists with CO₂ gas above the liquid phase. Second the brine volume will change with pressure reduction due to compressibility. Equation 2 is therefore modified:

\[
V_{CO2} + \Delta V_B + V_{WW} = V_{M2} - V_{M1} \quad (3)
\]

where \( V_{WW} \) is the volume of water vapour above the liquid phase and \( \Delta V_B \) is the change in brine volume with pressure due to compressibility.

So, step 1 was introduced to account for the compressibility of the brine and the amount of water vapour that will form on top of the liquid when the pressure is reduced. By isothermal depressurization of de-aerated brine we can know \( V_{B1} \) and \( V_{B2} \) and from equation 4 we can compute the sum of \( \Delta V_B \) and \( V_{WW} \)

\[
\Delta V_B + V_{WW} = V_{B2} - V_{B1} \quad (4)
\]

Two assumptions were made. The first was assuming that the effect of CO₂ presence on top of the liquid phase in step 2 on the amount of water vapour is negligible. Secondly we assumed that the CO₂ present in the brine will not change its compressibility. Substituting equation 4 into equation 3 results in

\[
V_{CO2} + V_{B2} - V_{B1} = V_{M2} - V_{M1} \quad (5)
\]

Rearranging equation 5 we get the actual amount of CO₂ dissolved in the brine at the given operating conditions,

\[
V_{CO2} = V_{B1} - V_{B2} + V_{M2} - V_{M1} \quad (6)
\]

Knowing the volume of CO₂ dissolved in the brine we can calculate the number of moles of CO₂ using the Peng–Robinson equation of state [10]. The density of brine was obtained from the literature [11]. At atmospheric pressure there is still some CO₂ dissolved in the brine; this has been calculated to be 0.0098 mole CO₂/ kg brine at 70 °C, 0.0162 mole CO₂/ kg brine at
50 °C, and 0.0239 mole CO₂/ kg brine at 33 °C based on literature models [12, 13] and was added to the total obtained solubility.

3. Results and Discussion

We tested the reactor for three thermophysical conditions (9 MPa/33°C, 9 MPa/50°C and 9 MPa/70°C) and measured CO₂ solubilities in brine for a range of pressures (9 MPa, 7.58 MPa, 3.44 MPa and 0.34 MPa) at three temperatures (33°C, 50°C and 70°C). Our results are displayed in Table 1.

A similar solubility measurement has been described in the literature [8], although the way we account for water vapor is different. In [14] the separated CO₂ gas from the equilibration mixture was bubbled through concentrated sulfuric acid solution to condense the water vapor. In [15, 16] water vapor in the gas phase was not considered.

CO₂ solubility in brine at 70°C and 9 MPa was measured three times to check experimental reproducibility (0.842 ± 0.0138) mole CO₂/kg brine). The low standard deviation (∼ 1.6%) demonstrates that the isothermal depressurization method is highly reproducible.

Our results are consistent with solubility data available in the literature (Table 2, Figures 2 and 3) [12, 14-27]. Only one brine of the same composition has been studied in the literature [22]; other data for similar brine compositions and operating conditions are also listed. It is interesting to note that a solution containing KCl will dissolve more CO₂ than a solution containing an equal concentration (wt.% NaCl [16]; so 6 wt.% NaCl solution will dissolve less CO₂ than a 5wt% NaCl/1wt.% KCl solution. In general at constant pressure and temperature the solubility decreases with increase in salinity (Figure 3).

4. Conclusions

A methodology to equilibrate brine with CO₂ at the litre-scale was presented. In two easy and fast steps we rapidly equilibrated supercritical CO₂ and brine at high pressure and elevated temperature. This method can be applied to a wide range of temperatures and pressures. We focus here on equilibrating brine and scCO₂ as this is most relevant for carbon storage studies [6, 9, 28]. However, we suggest that different fluids can also be saturated with CO₂ by using this method, e.g. in chemical engineering applications. Volumes in the liter range can be equilibrated in approximately one hour which is fast turn over compared with other mixing methods proposed.

The solubility of CO₂ in brine was measured by using the isothermal expansion method. This method has proven to be accurate and fast when compared to the available methods and data in the literature (Figures 2 and 3).

Acknowledgments

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**Figure 1**: Experimental apparatus for brine-CO$_2$ equilibrium.

**Figure 2**: Solubility data for CO$_2$ in brine with different salinities at CCS pressures (between 8.4-10.5 MPa) versus temperature – solid symbols are our measurements and open symbols are literature data: (▬) Nighswander et al. (1989) [14], (*) Li et al. (2004) [15], (◇) Y. Liua et al. (2010) [16], (x) Kiepe et al. (2002) [17], (Δ) Bando et al. (2003) [18], (○) Sabirzyanov et al. (2003), [19] (○) Koschel et al. (2006 [20], (+) Dodds et al (1956) [21], (X) M. Trusler, et.al. (to be published) [22], (●) Our measurements.
Figure 3: Solubility data for CO$_2$ in brine versus salinity at CCS temperatures (between 33-100°C) and pressures (between 8.4-10.5 MPa). Solid symbols are our measurements and open symbols are literature data (◊) $T=100^\circ$C and $p=10.20$ (±0.28) MPa [19, 20], (□) $T=80.1$ (±0.3) °C and $p = 9.51$ (±0.57) MPa [14,17], (Δ) $T=70^\circ$C and $p=9$ MPa [21, (▲)our measurement], (*) $T=59.5$ (±0.71) °C and $p = 10.19$ (±0.27) MPa [15, 18], (○) $T=50^\circ$C and $p = 9.5$ (±0.58) MPa [19-21], (●) our measurement], (+) $T=45^\circ$C and $p = 9.8$ (±0.86) MPa [16] (x) $T=40.3^\circ$C and $p = 8.47$ (±0.21) MPa [17].
Table 1: Solubility data for CO₂ dissolved in brine measured using the isothermal de-pressurization method. The salinity was constant with 0.856 moles NaCl and 0.134 moles of KCl per kilogram water.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Solubility of CO₂ (mole CO₂/kg brine)</th>
<th>Mole fraction of dissolved CO₂</th>
</tr>
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<tbody>
<tr>
<td>70</td>
<td>9</td>
<td>0.857</td>
<td>0.0159</td>
</tr>
<tr>
<td>70</td>
<td>9</td>
<td>0.836</td>
<td>0.0155</td>
</tr>
<tr>
<td>70</td>
<td>9</td>
<td>0.832</td>
<td>0.0154</td>
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<tr>
<td>70</td>
<td>7.58</td>
<td>0.78</td>
<td>0.0144</td>
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<tr>
<td>70</td>
<td>3.44</td>
<td>0.39</td>
<td>0.0073</td>
</tr>
<tr>
<td>70</td>
<td>0.34</td>
<td>0.045</td>
<td>0.0008</td>
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<tr>
<td>50</td>
<td>9</td>
<td>0.886</td>
<td>0.0164</td>
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<tr>
<td>33</td>
<td>9</td>
<td>1.015</td>
<td>0.0187</td>
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</table>

Table 2: Solubility data of CO₂ in water for different salinities and operating conditions from the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Salinity (wt. %)</th>
<th>Salinity (moles salt/kg brine)</th>
<th>Solubility of CO₂ (mole CO₂/kg brine)</th>
<th>Mole fraction of CO₂</th>
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<td>J. A. Nighswander, et al.</td>
<td>79.7</td>
<td>10.18</td>
<td>0</td>
<td>0</td>
<td>0.9376</td>
<td>0.0166</td>
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<td>(1989) [14]</td>
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<td>Z. Li, et al. (2004)</td>
<td>59</td>
<td>10.38</td>
<td>8.05% (Weyburn brine)</td>
<td>2.021 (Weyburn brine)</td>
<td>0.7666</td>
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<td>Y. Liu, et al. (2010)</td>
<td>45</td>
<td>10.09</td>
<td>10% (NaCl)</td>
<td>1.71 (NaCl)</td>
<td>0.7432</td>
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<td></td>
<td>45</td>
<td>10.09</td>
<td>10% (KCl)</td>
<td>1.34 (KCl)</td>
<td>0.893</td>
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<td></td>
<td>45</td>
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<td>5% (NaCl) &amp; 5% (KCl)</td>
<td>0.86 (NaCl) &amp; 0.67 (KCl)</td>
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<td>N. Akinfiev &amp; L. Diamond</td>
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