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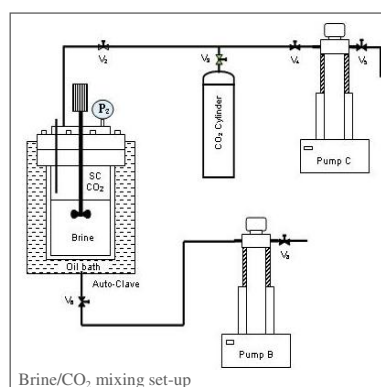
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A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements

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- We introduce a fast and easy methodology to equilibrate CO<sub>2</sub> and brine in the liter range.
- Equilibration was reached in 60 minutes.
- This is an important step for CO<sub>2</sub> storage studies and experiments.
- Solubility of CO<sub>2</sub> in brine was measured using isothermal depressurization method.
- Comparing our solubility data with the literature shows its consistence.

Accepted Manuscript

# 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/CO<sub>2</sub>, Solubility of CO<sub>2</sub>, CO<sub>2</sub> Storage, supercritical CO<sub>2</sub>, dissolution trapping.

## **1. Introduction**

Long term storage of carbon dioxide (CO<sub>2</sub>) 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 CO<sub>2</sub> will likely be stored as a supercritical (sc) phase at depths of 800 m or more [2], which maximizes the stored mass of CO<sub>2</sub>.

When CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> for petroleum engineering studies or CO<sub>2</sub> can be mixed with other solvents (e.g. acetone, dichloromethane, diethyl ether, monoethanolamine, etc.) for chemical engineering applications.

In addition, the equilibrium solubility of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>/brine equilibrium**

Three steps were developed to prepare brine saturated with CO<sub>2</sub> and CO<sub>2</sub> saturated with water vapour. During the first step scCO<sub>2</sub> 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 CO<sub>2</sub> (5MPa at 15°C) was transferred to pump C from a CO<sub>2</sub> 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 CO<sub>2</sub> gas at the gas cylinder pressure, it was then pressurized to experimental pressure (9MPa); at these thermophysical conditions scCO<sub>2</sub> 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 up to our experimental condition using pump B. The reactor is connected to the scCO<sub>2</sub> pump C operating at the same pressure, then 500 ml from the brine volume in the reactor were displaced by scCO<sub>2</sub> 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 CO<sub>2</sub> 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 entrapment design. It essentially pushes the lighter phase (scCO<sub>2</sub>) into the bottom phase (brine) and generates a large surface area between the fluids by splitting the CO<sub>2</sub> 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 scCO<sub>2</sub> volume balances.

Additional CO<sub>2</sub> was pumped into the vessel during the equilibration process because the CO<sub>2</sub> dissolved reducing the pressure. Equilibrium is reached if no more CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> separating out of solution during the transfer process. After the required amount of CO<sub>2</sub> saturated brine was transferred, pump B was isolated. Then the CO<sub>2</sub>-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 CO<sub>2</sub>, the CO<sub>2</sub> is released if the pressure is reduced isothermally. If the volume of CO<sub>2</sub> saturated brine is known before depressurization ( $V_{M1}$ ) and the total brine volume is known after depressurization ( $V_{M2}$ ), then the amount of CO<sub>2</sub> that separated out of solution ( $V_{CO2}$ ) can be calculated by subtracting the two volumes (*equation 2*). We can then calculate the solubility of CO<sub>2</sub> in brine at this condition.

$$\text{Volume of CO}_2 \text{ dissolved in the brine } (V_{CO2}) = V_{M2} - V_{M1} \quad (2)$$

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 CO<sub>2</sub> gas above the liquid phase. Second the brine volume will change with pressure reduction due to compressibility. Equation 2 is therefore modified:

$$V_{CO2} + \Delta V_B + V_{WV} = V_{M2} - V_{M1} \quad (3)$$

where  $V_{WV}$  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  $V_{WV}$

$$\Delta V_B + V_{WV} = V_{B2} - V_{B1} \quad (4)$$

Two assumptions were made. The first was assuming that the effect of CO<sub>2</sub> presence on top of the liquid phase in *step 2* on the amount of water vapour is negligible. Secondly we assumed that the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> dissolved in the brine we can calculate the number of moles of CO<sub>2</sub> 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 CO<sub>2</sub> dissolved in the brine; this has been calculated to be 0.0098 mole CO<sub>2</sub>/ kg brine at 70 °C, 0.0162 mole CO<sub>2</sub>/ kg brine at

50 °C, and 0.0239 mole CO<sub>2</sub>/ 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

CO<sub>2</sub> solubility in brine at 70°C and 9 MPa was measured three times to check experimental reproducibility (0.842 ± 0.0138) mole CO<sub>2</sub>/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 CO<sub>2</sub> than a solution containing an equal concentration (wt.%) NaCl [16]; so 6 wt.% NaCl solution will dissolve less CO<sub>2</sub> 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 CO<sub>2</sub> at the litre-scale was presented. In two easy and fast steps we rapidly equilibrated supercritical CO<sub>2</sub> 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 scCO<sub>2</sub> as this is most relevant for carbon storage studies [6, 9, 28]. However, we suggest that different fluids can also be saturated with CO<sub>2</sub> 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 CO<sub>2</sub> 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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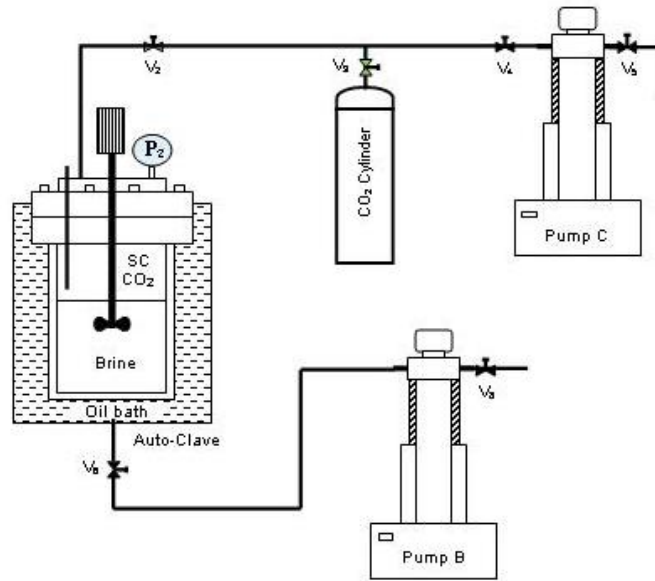
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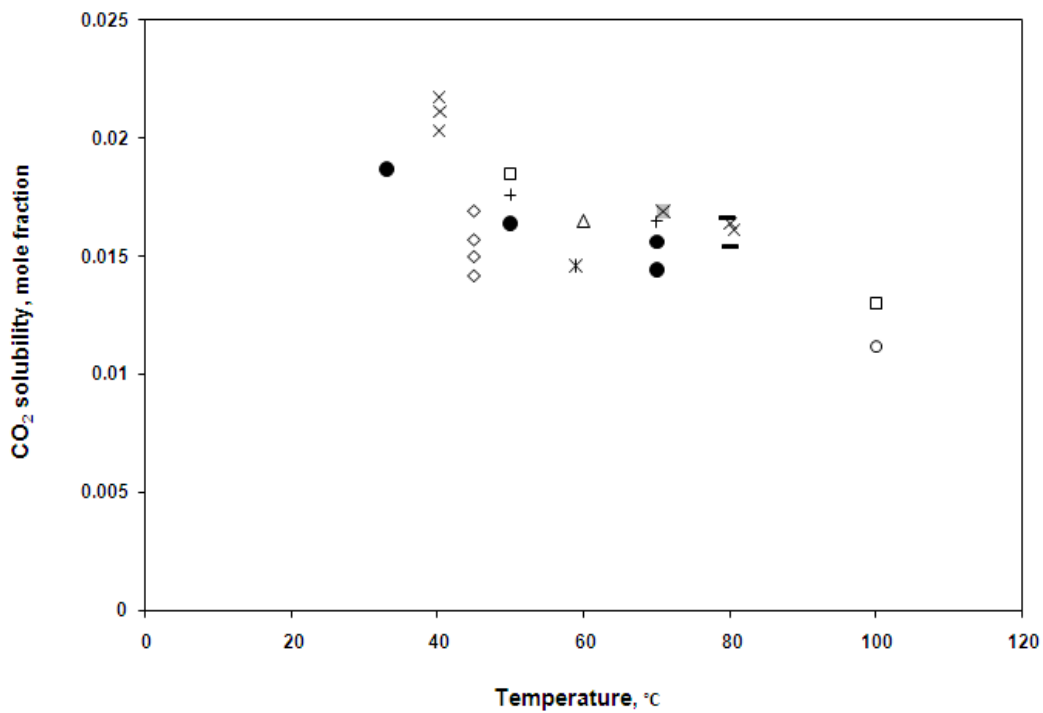


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**Figure 1:** Experimental apparatus for brine-CO<sub>2</sub> equilibrium.



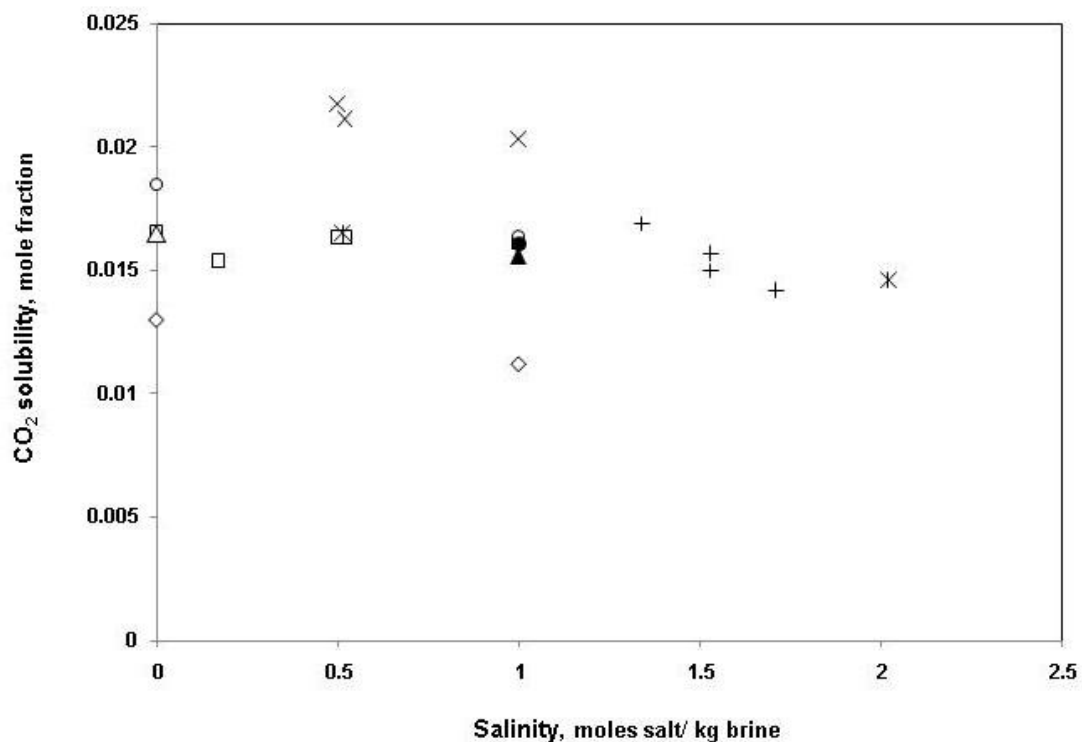
**Figure 2:** Solubility data for CO<sub>2</sub> in brine with different salinities at CCS pressures (between 8.4-10.5 MPa)

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<sub>2</sub> 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 ( $\diamond$ ) T= 100°C and p= 10.20 ( $\pm$ 0.28) MPa [19, 20], ( $\square$ ) T= 80.1 ( $\pm$ 0.3) °C and p = 9.51 ( $\pm$ 0.57) MPa [14,17], ( $\Delta$ ) T= 70°C and p= 9 MPa [21, ( $\blacktriangle$ )our measurement], ( $*$ ) T= 59.5 ( $\pm$ 0.71) °C and p = 10.19 ( $\pm$ 0.27) MPa [15, 18], ( $\circ$ ) T= 50°C and p = 9.5 ( $\pm$ 0.58) MPa [19-21, ( $\bullet$ ) our measurement], (+) T= 45°C and p= 9.8 ( $\pm$ 0.86) MPa [16] (x) T= 40.3°C and p = 8.47 ( $\pm$ 0.21) MPa [17].

**Table 1:** Solubility data for CO<sub>2</sub> 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.

T (°C)	P (MPa)	Solubility of CO <sub>2</sub> (mole CO <sub>2</sub> / kg brine)	Mole fraction of dissolved CO <sub>2</sub>
70	9	0.857	0.0159
70	9	0.836	0.0155
70	9	0.832	0.0154
70	7.58	0.78	0.0144
70	3.44	0.39	0.0073
70	0.34	0.045	0.0008
50	9	0.886	0.0164
33	9	1.015	0.0187

**Table 2:** Solubility data of CO<sub>2</sub> in water for different salinities and operating conditions from the literature.

Reference	T (°C)	P (MPa)	Salinity (wt. %)	Salinity (moles salt/ kg brine)	Solubility of CO <sub>2</sub> (mole CO <sub>2</sub> / kg brine)	Mole fraction of CO <sub>2</sub>
<b>Experimental data</b>						
J. A. Nighswander, et.al. (1989) [14]	79.7 80.1	10.18 9.94	0 1% (NaCl)	0 0.171 (NaCl)	0.9376 0.8631	0.0166 0.0154
Z. Li, et.al. (2004) [15]	59	10.38	8.05% (Weyburn brine)	2.021 (Weyburn brine)	0.7666	0.0146
Y. Liua, et.al.(2010) [16]	45	10.09	10% (NaCl)	1.71 (NaCl)	0.7432	0.0142
	45	10.09	10 % (KCl)	1.34 (KCl)	0.893	0.0169
	45	10.58	5 % (NaCl)& 5% (KCl)	0.86 (NaCl)& 0.67(KCl)	0.825	0.0157
	45	8.59	5 % (NaCl)& 5% (KCl)	0.86 (NaCl)& 0.67(KCl)	0.784	0.0150
J. Kiepe, et.al. (2002) [17]	40.38	8.43	3 % (NaCl)	0.52 (NaCl)	1.1738	0.02112
	80.08	9.24	3 % (NaCl)	0.52 (NaCl)	0.9048	0.01636
	40.31	8.28	3.7 % (KCl)	0.5 (KCl)	1.2000	0.02174
	80.08	8.74	3.7 % (KCl)	0.5 (KCl)	0.8981	0.01636
	40.31	8.7	7.5 % (KCl)	1 (KCl)	1.0862	0.02031
	80.55	9.45	7.5 % (KCl)	1 (KCl)	0.8574	0.0161
S. Bando, et.al. (2003) [18]	60	10	3 % (NaCl)	0.514 (NaCl)	0.9127	0.0165
R. Sabirzyanov, et.al. (2003) [19]	50 100	10 10	0 0	0 0	1.0471 0.7317	0.0185 0.013
D. Koschel, et.al. (2006) [20]	50.1 100.1	10 10.4	5.8% (NaCl) 5.8% (NaCl)	1 (NaCl) 1 (NaCl)	0.8891 0.6040	0.0164 0.0112
W. Dodds, et.al. (1956) [21]	70 50	9 9	0 0	0 0	0.9320 0.9953	0.0165 0.0176
M. Trusler, et.al. (to be published) [22]	70.9	13.69	5% (NaCl)& 1% (KCl)	0.86 (NaCl)& 0.13 (KCl)	0.9147	0.0169
<b>Theoretical data</b>						
N. Akinfiev & L. Diamond (2010) [23]	70	9	5.8% (NaCl)	1	0.75	0.0138
N. Darwish, N. Hilal (2010) [24]	50	9	5.8% (NaCl)	1	0.9	0.0166
N. Spycher & K. Pruess (2010) [25]	50	9	5.8% (NaCl)	1	0.9	0.0166
	90	9	5.8% (NaCl)	1	0.7	0.0129
X. Ji, et.al. (2005) [26]	60.15	9	3 % (NaCl)	0.5292	0.9033	0.0163
	80.15	9	3 % (NaCl)	0.52	0.8460	0.0153
N. Spycher & K. Pruess (2005) [27]	60	9	3 % (NaCl)	0.5	0.85	0.0154
Z. Duan & R. Sun (2003) [12]	60.15	10	5.8% (NaCl)	1	0.8405	0.0155