

Modelling CO₂ solubility in pure water and NaCl-type waters from 0 to 300 °C and from 1 to 300 bar Application to the Utsira Formation at Sleipner

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Abstract

The goal of this study is to better quantify the solubility of CO₂ in brines. New experimental data on the solubility of CO₂ in a mixed salt solution at CO₂ sequestration pressure and temperature conditions are presented. A thermodynamic model for calculation of the phase equilibria of CO₂–H₂O–NaCl system is briefly described; notably, the solubility of the carbon dioxide in the aqueous phase. This model was used to check its validity by comparing the calculation results with new experimental measurements, available experimental observations and other models CO₂ solubility results. Comparison with experimental data indicates that the model can predict accurately CO₂ solubility in pure water and in aqueous NaCl solutions of ionic strengths up to 3 molal from 0 to 300 °C and from 1 to 300 bar. This model has been applied to CO₂ storage at Sleipner, North Sea. The salinity of the porewater within the Utsira Formation (the CO₂ host formation) is approximately the same as seawater. Predicted CO₂ solubility is in good agreement with new experimental measurements.

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1. Introduction

As the main contributor to the greenhouse effect, the impact of atmospheric CO₂ on climate has

recently received much attention. The burning of fossil fuels and other anthropogenic activity have caused a dramatic increase in the concentration of atmospheric CO₂ when compared to its value recorded in ice cores during the last 400,000 years (Houghton et al., 1996; IPCC, 2001). Capture of CO₂ from large point sources (e.g. power stations) and its storage in deep geologic formations has been considered as a means to mitigate global warming

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(Omerod, 1994). Among proposed sequestration strategies, injection into saline aquifers represents one of the most promising alternatives. There are a very large number of underground, brine-filled strata that could potentially be used to store CO₂. Indeed, storage potential estimates for just the rocks beneath the North Sea, suggest that they have the capacity to store over 700 years of current European CO₂ emissions from thermal power generation (Holloway et al., 1996). Over time, CO₂ will dissolve in the interstitial solution of the aquifer and in some formations it would slowly react with minerals to form carbonates, which would lock up the CO₂ permanently. Suitable aquifers would have also a cap rock of low permeability to minimise CO₂ leakage.

The Sleipner project is the world's first commercial-scale storage CO₂ project. When injection began in 1996, it marked the first instance of CO₂ being stored in a geological formation because of climate-change considerations (Backlid et al., 1996). Sleipner is a natural gas field which has about 9% CO₂ as an impurity in the gas. This is separated from the methane at the surface, and then stored deep underground rather than being emitted to the atmosphere. Since 1996, nearly a million tons per year of CO₂ has been injected into the large, deep, late Miocene Utsira saline aquifer. The sand-rich Utsira Formation extends under a broad area of the North Sea, and at Sleipner has a thickness of about 200 m and a minimum depth of about 800 m. The 'bubble' of injected CO₂ is being monitored by repeated seismic surveys. Interpretation of the geophysical data and reservoir simulations have been undertaken as part of a European R&D project (SACS, and its follow-on projects SACS2 and CO2STORE) which are led by the operating company Statoil. During underground storage operations in deep reservoirs, the CO₂ can be trapped in three main ways (with descriptors from Bachu et al., 1994): as 'free' CO₂, most likely as a supercritical phase (physical trapping); dissolved in formation water (hydrodynamic trapping); and precipitated in carbonate phases such as calcite (mineral trapping). During the early stages of storage, physical trapping is likely to be the most dominant trapping mechanism. However, over time, hydrodynamic trapping and eventually mineral trapping will make signifi-

cant contributions to the long-term containment of CO₂ (Pruess and Garcia, 2002).

The present study focuses on hydrodynamic trapping, in particular the quantity of CO₂ that can dissolve in formation water. At equilibrium, this will be governed by in situ pressure and temperature, and the composition of formation water. Within a CO₂ storage system these will vary depending the exact position within the aquifer. For example, at the injection point at Sleipner these conditions are 37 °C, 100 bar, and a porewater of approximately seawater salinity (Gregersen et al., 1998). However, at the top of the Utsira Formation pressures and temperatures will be slightly less.

Knowledge of the solubility in the CO₂–H₂O–salts system enhances the accuracy of storage calculations. There have been many experimental studies on the solubility of CO₂ in pure water and in aqueous NaCl solutions. The solubility was investigated quantitatively with some variable parameters, i.e., pressure, temperature and salinity. However, few knowledge is available on the CO₂ solubility in mixed salt solutions at CO₂ sequestration temperature and pressure conditions. This study used CO₂ solubility data from two sources; new data generated under Sleipner-specific conditions, and pre-existing data obtained from the literature. First, this paper describes the new CO₂ solubility data generated under Sleipner-specific conditions. The new measurements were made using a synthetic Utsira Formation water. The experimental conditions chosen were between 18 and 80 °C and between 80 and 120 bar, with most data generated at 37 °C and 100 bar—in situ temperature and pressure at the injection point in the Utsira formation at Sleipner.

Due to the in situ conditions and the nature of the fluid (saline) in which CO₂ is likely to be injected, modelling CO₂ solubility requires taking into account salinity effects in aqueous solutions as well as the non-ideal behaviour of the CO₂ gaseous phase. After a short presentation of the thermodynamic model for the solubility of carbon dioxide, the second part of this paper is devoted to a comparison of calculation results with experimental data and other models. On the basis of these results, we finally propose a quantification of the dissolved CO₂ that might be stored in the Utsira Sand at the relevant conditions.

2. Materials and methods

2.1. Experimental

The CO₂ used in this study was high purity (99.99%) liquid CO₂ (Air Products, 4.5 Grade). This liquid CO₂ was obtained in a cylinder fitted with a dip tube and pressurised with 2000 psi (approximately 140 bar) of helium. However, the actual experimental pressures were controlled by ISCO syringe pumps, which were run under ‘constant pressure’ mode. For experiments below 31.1 °C, the pressure was sufficient for the CO₂ to be liquid. However, above this temperature (i.e. for most of the experiments) the CO₂ was a supercritical fluid.

At the start of the experimental programme it was decided to make up a single, 25 l stock solution of synthetic Utsira porewater (SUP), and that this would be used for all the experiments. This solution was based upon the only analysis of the Utsira

Table 1

Composition of Oseberg, Brage and SUP porewaters (units are mg l⁻¹ except for TIC and TOC which are mol l⁻¹)

Analyte	Oseberg porewater from Gregersen et al. (1998)	Average Brage analyses conducted at BGS	Average synthetic Utsira porewater starting solution
pH (≈ 20 °C)	7.1	7.65	7.77
Li	–	1.77	–
Na	10,392	9934	10,306
K	208	317	225
Mg	630	664	633
Ca	426	412	432
Sr	10	9.65	10
Ba	0.5	6.17	0.31
Mn	–	<0.02	–
Total Fe	2	0.28	1.21
Al	–	<0.1	0.35
Total P	–	<0.1	–
Total S	–	<2.5	1.05
Si	–	23.7	0.58
SiO ₂	–	50.7	1.23
Cl	18,482	18,921	18,659
Br	–	71.5	<2.00
NO ₃	–	8.4	–
SO ₄	ND	<60	<2.00
HCO ₃	707	842	386
TIC (CO ₃ ²⁻)	–	0.003	–
TOC	–	<0.0003	–

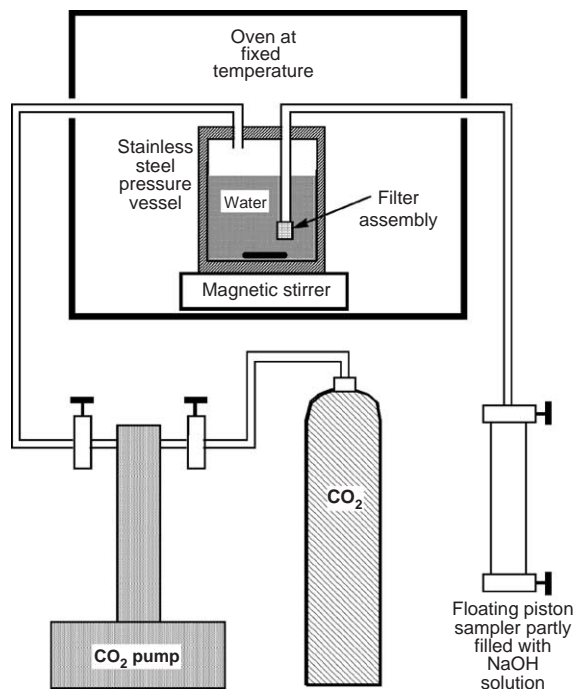


Fig. 1. Schematic representation of equipment used for CO₂ solubility studies.

porewater available at the start of the study—from the Oseberg field some 200 km north of Sleipner (Gregersen et al., 1998). This synthetic porewater was close to seawater composition. Three analyses of the initial solution were made, and these averaged to give a representative composition (Table 1) of the starting fluid for the experiments. Subsequently, samples of Utsira porewater from the Brage field (close to the Oseberg field) were obtained. In terms of major element compositions, both porewaters are very similar. Although this does not necessarily mean that the porewater is of broadly uniform composition throughout the Utsira Formation, this assumption is made given the very limited data available.

A schematic diagram of the ‘batch’ apparatus is shown in Fig. 1. The equipment consists of a stainless steel pressure vessel with Viton O-ring pressure seals, containing a PTFE (polytetrafluoroethylene) sample container. Two sizes of otherwise identical pressure vessels were used in this study, having volumes of either 100 ml or 150 ml. During assembly, a sample of synthetic Utsira porewater was

placed into the PTFE container (filled to approximately 2/3 full), together with a magnetic stirrer bead. The top of the pressure vessel was then securely tightened down, and pressure tubing connected. The whole assembly was then placed on top of a magnetic stirrer inside a Gallenkamp PlusII fan-assisted oven that could be maintained to within ± 0.5 °C. Although the base of the stainless steel pressure vessel was in the order of 1 cm thick, it still allowed for good ‘coupling’ between the magnetic stirrer and the stirrer bead. Consequently, the aqueous solution was well mixed and was in good contact with the overlying CO₂. A known pressure of CO₂ was then admitted to the reactor using a high pressure ISCO 260D syringe pump. This pump was set to ‘constant pressure’ mode such that it automatically injected or withdrew CO₂ as necessary. This minimised the impact of any leaks of CO₂ from the reactors or pipework. The system was left for at least 24 h before any samples were taken.

A sample of the CO₂-rich aqueous phase was then removed (still at pressure) and reacted with 4 M NaOH solution to preserve any dissolved carbon species. Analyses of the alkaline preserved samples were performed by potentiometric titration. Either 0.01 mol l⁻¹ (0.02 N) or 0.5 mol l⁻¹ (1 N) sulphuric acid was used as titrant against 2.0 ml or 1.0 ml of samples of pH less than 10 and greater than 11.5 respectively. The pH of the analytical sample was monitored as a function of volume of titrant added and the titration was allowed to proceed until a pH of less than 2 was achieved. Two quality control standards were used. For the samples of pH greater than 11.5, a quality control standard containing 2 mol l⁻¹ of hydroxyl ions and 0.5 mol l⁻¹ of carbonate ions was prepared by dissolving 40.00 g of BDH AnalAR[®] sodium hydroxide and 26.4472 g of BDH AnalAR[®] sodium carbonate in 500 ml of deionised water. For the samples of pH less than 10, a quality control standard containing 200 mg l⁻¹ bicarbonate was prepared by dissolving 0.2754 g of BDH AnalAR[®] grade sodium bicarbonate in 1000 ml of deionised water. The relevant QC standards were analysed at the start and finish of the analytical run and after not more than every ten samples.

The ‘raw’ analytical data for the experimental solution/NaOH solution mixture reported CO₃²⁻ concentrations in mg l⁻¹. However, these values need to

be corrected for dilution due to the NaOH. The dilution factor was calculated by assuming that all Cl⁻ was derived from the SUP. By knowing the starting and final Cl⁻ concentration, the dilution factor could be calculated. It was assumed that the experimental solutions behaved in a similar way to pure water, with depressurising and cooling resulting in volume changes of less than 1% (assuming no degassing). This change is considered relatively small compared to uncertainties introduced by the sampling or analytical processes. Consequently, compressibility and expansivity corrections have not been applied to the results. Further details are provided in an internal report of the British Geological Survey (Rochelle and Moore, 2002).

The errors assumed for the data were set at ± 0.05 mol.l⁻¹ (2200 mg l⁻¹ as CO₂). These are much larger than the analytical errors, but were set so as to account for ‘equipment handling’ variations during sampling. Larger variations caused by obvious sampling problems (as noted above) were apparent from trends in the data, and caused rejection of suspect data.

Various degrees of ‘scatter’ were found in the data. Overly high solubility values were disregarded as these resulted from breakthrough of ‘free’ CO₂ into the sampling tube (often after several samples had already been taken and the water–CO₂ interface was relatively low in the vessel). In general, there was also a hint of this when pressure connectors were de-coupled after the sample was taken. However, it was also possible to get apparently reduced concentrations of dissolved CO₂—as a result of pressure reduction and degassing during sampling. Although care was taken to minimise reductions in pressure, these could occur when opening valves to equilibrate pressures in the sampling line, or too fast a sampling flow rate through the in-line filter. It was relatively difficult to identify if significant pressure reductions occurred during sampling (compared to the cases where CO₂ breakthrough occurred). In an attempt to combat such artefacts, several samples were taken at a particular pressure and temperature. The upper bound of the measured CO₂ concentrations was taken as being more representative of actual CO₂ solubility. A summary of measured CO₂ solubility in synthetic Utsira porewater is given in Table 2.

Table 2
Summary of CO₂ solubility experiments in synthetic Utsira pore-water (SUP)

Temperature (°C)	Pressure (bar)	CO ₂ solubility (mol kg ⁻¹ H ₂ O)
18	100	1.364
18	100	1.259
35	100	1.020
37	80	1.005
37	80	1.020
37	80	1.000
37	80	1.000
37	80	0.954
37	90	1.020
37	100	0.959
37	100	1.072
37	100	1.087
37	100	1.085
37	110	1.100
37	120	1.072
37	120	1.183
37	120	1.152
37	120	1.121
50	80	0.903
50	80	0.936
50	100	0.956
50	120	1.105
50	120	1.085
70	80	0.691
70	80	0.671
70	90	0.690
70	100	0.710
70	100	0.689
70	100	0.731
70	100	0.744
70	110	0.862
70	120	0.814
70	120	0.890
80	100	0.744
80	100	0.814

2.2. Thermodynamics

The phase equilibrium is calculated using equality rule of the fugacities:

$$f_i^v = f_i^{\text{aq}} \quad (1)$$

While for an ideal gas, the fugacity value in the vapour phase will be equal to that of the partial pressure (in bar), in reality the non-ideal behaviour should be corrected by a function depending on the

pressure, the temperature, and the molar fraction of the considered species in the vapour phase, according to the following equation:

$$f_i^v = \phi_i x_i P \quad (2)$$

The calculation of gas fugacity necessitates first to evaluate the molar volume which depends on the vapour phase composition, the pressure, and the temperature. The gas fugacity is calculated using the Peng and Robinson (1976, 1980) Equation Of State (EOS). This EOS permit to calculate the molar volume of a pure or mixed vapour phase as well as the fugacity coefficient of each gas.

Similarly, the fugacity value in the aqueous phase depends on the pressure, the temperature, and the solution composition. For the aqueous phase, the fugacity is calculated using a different method for water and for other components. For the solvent, the fugacity is calculated using its vapour pressure (Dhima et al., 1998):

$$f_{\text{H}_2\text{O}}^{\text{aq}} = a_{\text{H}_2\text{O}} \cdot P_{\text{H}_2\text{O}}^{\text{sat}} \cdot \exp\left(\frac{\bar{V}_{\text{H}_2\text{O}}^{\text{aq}}}{RT} [P - P_{\text{H}_2\text{O}}^{\text{sat}}]\right) \quad (3)$$

The water activity, a_i (dimensionless), is calculated using the expression given by Helgeson (1969):

$$\ln a_{\text{H}_2\text{O}} = -0.03603 \cdot I \cdot \Theta_{\text{NaCl}} \quad (4)$$

where Θ_{NaCl} is the osmotic coefficient as evaluated by Helgeson (1969) and I is the true ionic strength of the solution, i.e. the nominal or stoichiometric ionic strength corrected for the fact the NaCl is not completely dissociated (Helgeson et al., 1981). The saturated molar volume of the liquid water, $\bar{V}_{\text{H}_2\text{O}}^{\text{aq}}$ is considered independent of pressure, and is calculated using the expression given by Saul and Wagner (1987). The water vapour pressure, $P_{\text{H}_2\text{O}}^{\text{sat}}$ (in bar) is also determined as suggested by Saul and Wagner (1987). Since there are no vapour composition measurements for the CO₂–H₂O–NaCl system in the temperature range of this study, we assume that water vapour pressure of the mixtures is the same as pure water saturation pressure.

For the fugacity of the dissolved CO₂ in the aqueous phase, we use Henry's law approach (Prausnitz et al., 1986), with the Krichevsky and

Kasarnovsky (1935) correction for high pressure conditions:

$$f_{\text{CO}_2}^{\text{aq}} = m_{\text{CO}_2} \gamma_{\text{CO}_2} K_{\text{CO}_2}^{\text{H}}(T, P_{\text{H}_2\text{O}}^{\text{sat}}) \times \exp\left(\frac{\bar{V}_{\text{CO}_2}^{\infty}}{RT} [P - P_{\text{H}_2\text{O}}^{\text{sat}}]\right) \quad (5)$$

where $K_{\text{CO}_2}^{\text{H}}(T, P_{\text{H}_2\text{O}}^{\text{sat}})$ is the Henry's constant of the reaction $\text{CO}_{2,\text{aq}} \leftrightarrow \text{CO}_{2,\text{gas}}$. The values of Henry's constant for carbon dioxide were evaluated by Helgeson (1969) for the temperature range from 0 °C to 300 °C at saturation pressure of water. The partial molar volume at infinite dilution $\bar{V}_{\text{CO}_2}^{\infty}(T)$ is calculated as suggested by Dhima et al. (1998), using an improvement of the Lyckman et al. (1965) equation. Estimating the activity of aqueous species requires the calculation of their activity coefficient integrating the effect of salinity and temperature. Neutral species may also behave in a non-ideal manner, exhibiting activity coefficients that deviate from unity. The temperature and salinity dependence of activity coefficient for dissolved gases such as CO_2 is represented using the correlation developed in Helgeson (1969):

$$\ln \gamma_{\text{CO}_2} = \sigma_{\text{CO}_2}(T) \cdot I \quad (6)$$

where $\sigma_{\text{CO}_2}(T)$ is a fitting parameter called the salting coefficient. Helgeson (1969) has determined $\sigma_{\text{CO}_2}(T)$ by using experimental data.

Finally, combining Eqs. (1), (2) and (5) leads to the following formulation for CO_2 solubility in a saline solution:

$$m_{\text{CO}_2} = \frac{\varphi_{\text{CO}_2} x_{\text{CO}_2} P}{\gamma_{\text{CO}_2} K_{\text{CO}_2}^{\text{H}}(T, P_{\text{H}_2\text{O}}^{\text{sat}}) \exp\left(\frac{\bar{V}_{\text{CO}_2}^{\infty}}{RT} [P - P_{\text{H}_2\text{O}}^{\text{sat}}]\right)} \quad (7)$$

Although we use this simple semi-empirical model to describe the CO_2 solubilities at conditions relevant to the CO_2 storage in the Northern Sea, several other more sophisticated models on CO_2 solubility have been published. Based on two modified EOS of Peng–Robinson for each of the phases (liquid and vapour), Soreide and Whitson (1992) presented a model (SW model) to predict phase equilibrium of CO_2 and water/NaCl solution mixtures. More recently, Duan and Sun (2003) presented an empirical model (Duan model)

based on a specific interaction theory for the liquid phase (Pitzer, 1973) and a highly accurate equation of state for the vapour phase (Duan et al. 1992). This model is intended to calculate CO_2 solubility in pure water and aqueous NaCl solutions for temperatures from 0 to 260 °C and for pressures from 0 to 2000 bar and for ionic strength from 0 to 4.3 molal. Because of the scarcity of CO_2 solubility data for electrolyte systems other than NaCl, especially at high temperatures, the model proposed by Duan and Sun (2003) fitted to experimental measurements in the CO_2 –NaCl– H_2O system. Nevertheless, with this specific interaction approach, this model is able to predict CO_2 solubility in other systems, such as CO_2 – H_2O – CaCl_2 and CO_2 –seawater, without fitting experimental data from these systems.

3. Results and discussion

It is difficult to compare directly the CO_2 –synthetic Utsira porewater dataset produced in this study with other data, as little previous experimental data could be found for the pressure, temperature and salinity of interest. The more significant investigations of CO_2 solubility in water and in aqueous NaCl solutions are listed in Table 3. The most extensive studies of CO_2 solubility in pure water are those of Wiebe and Gaddy (1939, 1940) below 100 °C and Takenouchi and Kennedy (1964) above 110 °C, from 50 to 350 °C and from 100 to 3500 bar. Natural porewaters within potential CO_2 host formations are likely to be in the range of 40–150 °C with NaCl concentrations up to and exceeding 3 molal. CO_2 solubility has been tested over a wide range of NaCl concentrations from 25 °C to 250 °C. The most extensive studies are those of Drummond (1981), Nighswander et al. (1989), Nicolaisen (1994) and Rumpf et al. (1994). However, we note the general lack of experimental measurements of CO_2 solubility in NaCl solutions at high pressures ($100 < P < 300$ bar), moderate temperatures ($40 < T < 120$ °C) and in high ionic strength (up to 3 m) solutions. CO_2 solubility data in aqueous solutions containing salts other than NaCl at elevated pressures are very limited. The most significant investigations are listed in Table 4. The most extensive studies of experimental CO_2 solubility data in aqueous CaCl_2 solutions are those of Prutton and Savage (1945),

Table 3

Temperature, pressure and salinity conditions range of experimental data on the carbon dioxide solubility in pure water and in NaCl solutions

Aqueous solution	Salt molality (mol kg ⁻¹ H ₂ O)	Temperature (°C)	Pressure (bar)	Authors
Pure water	0	12–100	30–800	Wiebe and Gaddy (1939, 1940)
Pure water	0	101–120	30–700	Prutton and Savage (1945)
Pure water	0	71	100–1000	Dhima et al., (1998)
Pure water	0	15–260	6.9–202.7	Gillepsie and Wilson (1982)
Pure water	0	110–260	100–700	Takenouchi and Kennedy (1964)
Pure water	0	250–350	200–3500	Toedheide and Franck (1963)
Pure water	0	100–200	3–80	Müller et al. (1988)
Pure water	0	200–330	98–490	Malinin (1959)
NaCl solution	0–2	172–330	16–93	Ellis and Golding (1963)
NaCl solution	0–6	50–400	30–266	Drummond (1981)
NaCl solution	0–6	40–160	1–100	Rumpf et al. (1994)
NaCl solution	0–3	0–25	1	Harned and Davis (1943)
NaCl solution	0–6	25–150	48	Malinin and Kurovskaya (1975)
NaCl solution	0–4	25–75	48	Malinin and Savalyeva (1972)
NaCl solution	0.1–4	0–40	1	Markham and Kobe (1941)
NaCl solution	0–6	40–160	2–96	Nicolaisen (1994)
NaCl solution	0–0.2	80–200	1–100	Nighswander et al. (1989)
NaCl solution	0–3	25	1	Onda et al. (1970)
NaCl solution	1–4.3	135–527	30–2800	Gehrig (1980)
NaCl solution	0–4.3	150–250	100–1400	Takenouchi and Kennedy (1965)
NaCl solution	0.4–5.1	15–35	1	Yasunishi and Yoshida (1979)

from 75 to 120 °C and from 15 to 885 bar with molality up to 3.9 m. For seawater salinity (approximately the same as the Utsira porewater), data are available at lower temperatures more applicable to oceanic disposal of liquid CO₂ (e.g. Teng and Yamasaki, 1998), and at atmospheric pressure (Murray and Riley, 1971). Higher temperature data are limited to relatively simple solutions, with most of the

data being above seawater salinity (e.g. Ellis and Golding, 1963; Takenouchi and Kennedy, 1965). However, a somewhat limited indirect comparison is possible. Fig. 2 shows a comparison between literature data for CO₂ solubility in seawater (having approximately the same salinity as the synthetic Utsira porewater) and the experimental result at 18 °C in SUP. We can see the accuracy between new exper-

Table 4

Temperature, pressure and salinity conditions range of experimental data on the carbon dioxide solubility in simple aqueous electrolyte solutions others than aqueous NaCl solutions

Salt	Salt molality (mol kg ⁻¹ H ₂ O)	Temperature (°C)	Pressure (bar)	Authors
Na ₂ SO ₄	0.2–2.0	25–40	1	Markham and Kobe (1941)
	1.0–2.0	40–160	0.1–98	Rumpf and Maurer (1993)
	0.2–2.3	15–35	1	Yasunishi and Yoshida (1979)
CaCl ₂	0.0–7.0	100–150	48	Malinin and Kurovskaya (1975)
	0.4–3.4	25–75	48	Malinin and Savalyeva (1972)
	0.0–3.9	75–120	15–885	Prutton and Savage (1945)
	0.2–4.6	25–35	1	Yasunishi and Yoshida (1979)
AlCl ₃	0.4–2.6	25	1	Yasunishi and Yoshida (1979)
BaCl ₂	0.1–1.5	25	1	Yasunishi and Yoshida (1979)
K ₂ SO ₄	0.1–0.4	25	1	Yasunishi and Yoshida (1979)
KCl	0.1–4.0	0–40	1	Markham and Kobe (1941)
	0.4–4.1	25–35	1	Yasunishi and Yoshida (1979)
MgCl ₂	0.1–3.9	15–35	1	Yasunishi and Yoshida (1979)
MgSO ₄	0.1–2.3	25	1	Yasunishi and Yoshida (1979)
	0.5–2.0	0–40	1	Markham and Kobe (1941)

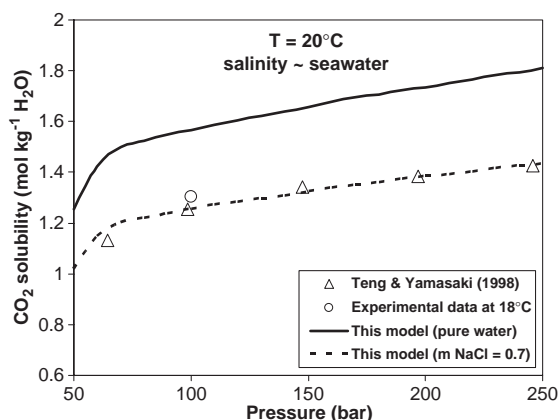


Fig. 2. Liquid CO₂ solubility in seawater as a function of pressure. Model calculation compared to experimental data for 20 °C.

imental data at 18 °C and those of [Teng and Yamasaki \(1998\)](#); CO₂ solubility at 18 °C is slightly higher than solubility at 20 °C in a solution of the same salinity). All these data show CO₂ solubility to be less than for pure water under similar conditions.

The composition of various co-existing CO₂-rich gas phases and aqueous solutions, at equilibrium, was calculated according to the thermodynamic model presented above.

An initial series of calculations is intended to show the accuracy of this model in reproducing CO₂ solubility in a mixed electrolyte aqueous solution (SUP). To compare the modelling results with

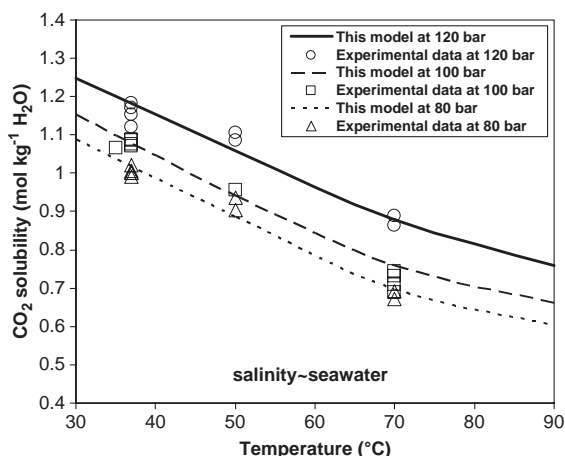


Fig. 3. CO₂ solubility in SUP as a function of temperature calculated for 80, 100 and 120 bar. Dots are experimental results.

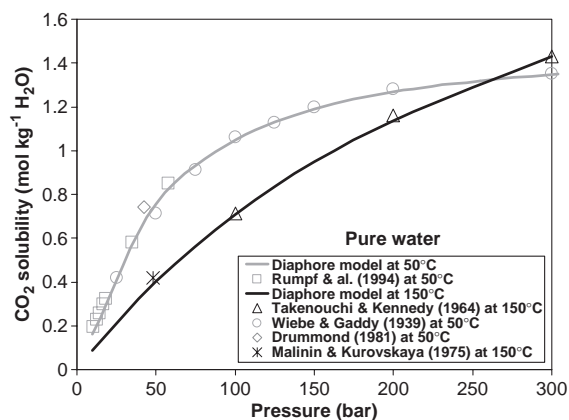


Fig. 4. CO₂ solubility as a function of pressure in pure water. Model calculations compared to experimental data for 50 and 150 °C.

experimental data reported in [Table 2](#), the CO₂ solubilities have been expressed in terms of molality (mol kg⁻¹ H₂O) and these are plotted in [Fig. 3](#). As shown in [Fig. 3](#), CO₂ solubility in the synthetic Utsira porewater (SUP) decreases with increasing temperature. From the comparison between the experimental data and calculated results at 80, 100 and 120 bar, it can be seen that CO₂ solubility in SUP shows a slight increase with increasing pressure (at 50 °C, CO₂ solubility is ~15% lower at 80 bar than at 120 bar). It may be concluded that most experimental data on the solubility of CO₂ in SUP can be represented by the model adequately, and are within or close to experimental uncertainty (about 7%).

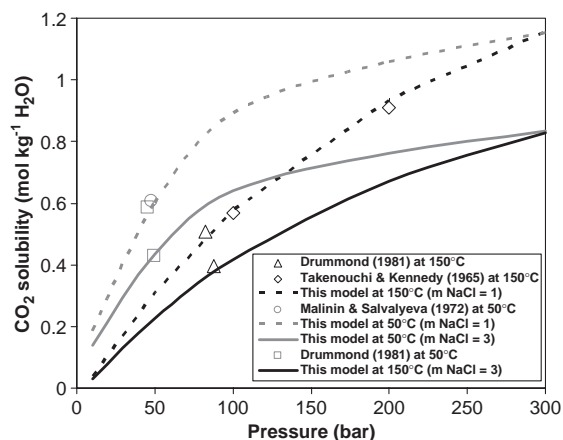


Fig. 5. CO₂ solubility as a function of pressure in NaCl solutions of 1 and 3 m. Model calculations compared to experimental data for 50 and 150 °C.

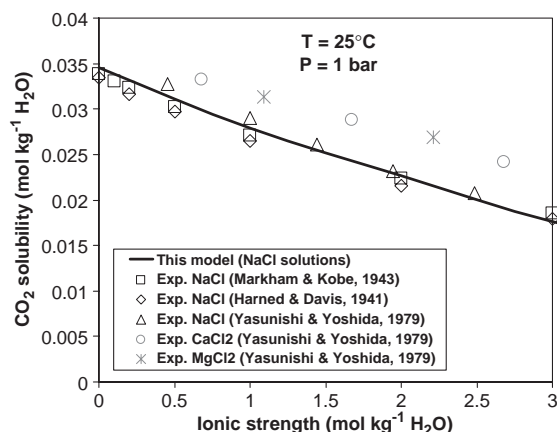


Fig. 6. CO_2 solubility as a function of ionic strength (both in $\text{mol kg}^{-1} \text{H}_2\text{O}$). Model calculation compared to experimental data for 25 °C.

Figs. 4 and 5 show the agreement between the literature data and our model. In order to evaluate the accuracy of the model in reproducing CO_2 solubility in pure water and NaCl solutions at high temperature, we performed a series of calculation at 150 °C for pressures ranging from 1 to 300 bar. The calculation results presented on Figs. 4 and 5 can be favourably compared to the measurements carried out by Takenouchi and Kennedy (1964, 1965). As shown in Fig. 4, the solubility of CO_2 in pure water increases with an increase in pressure. It varies in a more complex way with temperature. At lower pressures (<100 bar), CO_2 solubility decreases with increasing temperature. However, at higher pressures (>100 bar), the relationship with increasing temperature changes over, such that at 250 bar CO_2 solubility actually increases with increasing temperature. For example, the range of CO_2 solubility in pure water is from approximately $0.75 \text{ mol kg}^{-1} \text{H}_2\text{O}$ at 50 °C and 50 bar to approximately $1.15 \text{ mol kg}^{-1} \text{H}_2\text{O}$ at 150 °C and 200 bar.

The results in Fig. 5 indicate a systematic decrease in the solubility of CO_2 with increasing ionic strength. For a 3 molal NaCl solution this equates to an approximately twofold reduction relative to pure water at 50 °C and 100 bar. Fig. 6 also shows a satisfying agreement between calculated CO_2 solubility and experimental measurements in NaCl for electrolyte concentrations as high as 3 molal at 1 bar and 25 °C, corroborating the validity of the activity

coefficient calculation at standard conditions. Another important aspect pointed out by the results of Fig. 6 is the variability of CO_2 solubility according to the nature of the electrolyte. The solubility of CO_2 in CaCl_2 or MgCl_2 solutions shows a pattern similar to that expected in NaCl solution—experimental measurements showing elevated solubility relative to NaCl solutions of equivalent ionic strength. Both of these divalent salts appear to show the same increase in solubility relative to NaCl solutions of equivalent ionic strength. Maybe, because Ca^{2+} and Mg^{2+} tend to form ion pairs very easily with the anions present in solution, the salting-out effect on the solubility of CO_2 in CaCl_2 or MgCl_2 solutions is lower than in NaCl solutions of equivalent ionic strength. Thus, a calculation performed with equivalent-NaCl solutions of the same ionic strength, shows that this approximated method systematically underestimates the CO_2 solubility in aqueous CaCl_2 solutions (Figs. 6 and 7). The relative error induced by NaCl approximation (Fig. 6) becomes significantly high for higher ionic strength (above 5% and up to 20%). On the basis of the experimental data from Prutton and Savage (1945), we carried out other CO_2 solubility calculations in 1.01 m CaCl_2 solutions for moderate temperature (101 °C). The results presented on Fig. 7 globally confirm that the error induced by the equivalent-NaCl approximation has a relatively high impact on the CO_2 solubility value (less than 20%) for the aqueous CaCl_2 solution considered. Consequently,

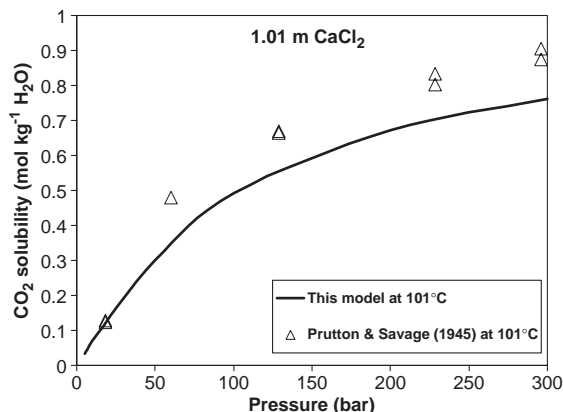


Fig. 7. CO_2 solubility as a function of pressure in aqueous CaCl_2 solution of 1.01 m. Model calculations compared to experimental data for 75.5 and 101 °C.

these results show that the use of a simplified equivalent-NaCl approach may be acceptable only for NaCl-type waters.

Fig. 8a and b show a good agreement between the results of the calculations performed with Duan model and the experimental measurements on the whole pressure range. In contrast, an important discrepancy between experimental and SW results (20% at 150 °C and 200 bar in 1 molal NaCl solution) is observed. The SW model overestimates CO₂ solubility in pure water and in NaCl solutions (by more than 20% at 50 °C in 2 molal NaCl solution) at high pressures (>100 bar).

The results achieved up to now let us think that our model notably improve CO₂ solubility prediction—at least for pure water and aqueous NaCl solutions (0–3

m NaCl, 0–300 °C, 1–300 bar). This range of temperature, pressure and salinity is likely to encompass a very large proportion of subsurface environments that might be considered for the deep underground storage of CO₂.

4. Geochemical implications

Assuming non-reactive aquifer conditions, the ultimate CO₂ sequestration capacity in solution of an aquifer is defined as the total amount of CO₂ that can theoretically dissolve to saturation in the formation water of this aquifer and be permanently trapped in a state of equilibrium (Bachu and Adams, 2003). To calculate the ultimate CO₂ sequestration capacity in solution, there is need to know the pore volume of the aquifer, the formation water density and the maximum CO₂ content at saturation (functions of temperature, pressure and salinity of the formation water). The Utsira sand covers an area of more than 26,000 km² and ranges in depth from about 550 to 1500 m (Chadwick et al., 2000). It occupies two distinct depositional basins, which are likely to be in poor hydraulic contact. The maximum reservoir thickness is about 300 m and the estimated pore volume of the reservoir (excluding stratigraphically different, but possibly linked sand units) is 55.10¹⁰ m³. By using new data, our model, and correlations given by Batzle and Wang (1992) to calculate the Utsira porewater density, it is possible to estimate the ultimate CO₂ sequestration capacity in solution of the Utsira sand at relevant conditions. For the following calculation, we assumed constant in situ pressure and temperature conditions of 37°C and 100 bar—in situ temperature and pressure at the injection point in the Utsira formation at Sleipner. Considering only the region of 26,000 km² (Utsira sand) where the injected CO₂ would be a dense fluid (liquid or supercritical), the ultimate capacity of the Utsira sand to sequester CO₂ in solution in formation water is calculated to be 22 Gt CO₂.

It is noteworthy that the Utsira Formation (approximately 800 m deep) is at the shallower end of the likely range of CO₂ storage depths. Porewaters within deeper aquifers or associated with hydrocarbon fields (Abbotts, 1991) could be significantly more saline than the synthetic porewaters used in

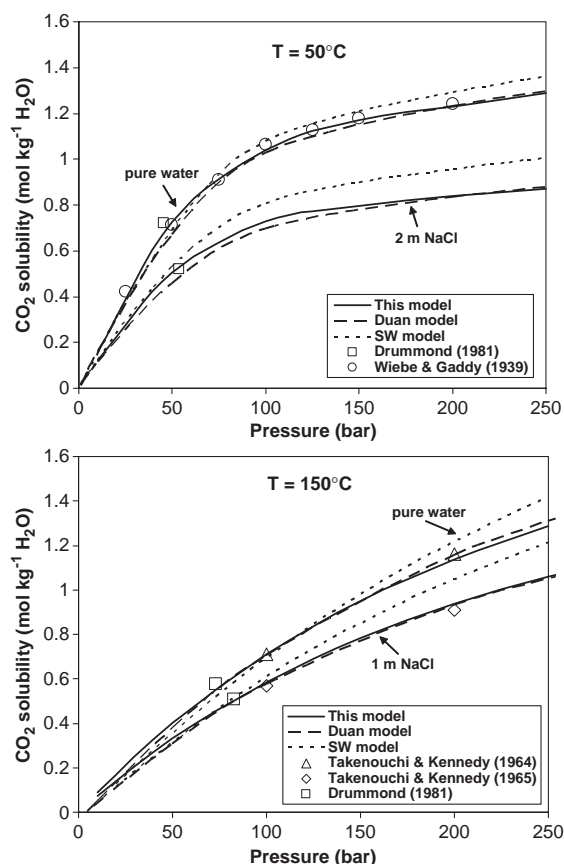


Fig. 8. (a) CO₂ solubility as a function of pressure calculated for 50 °C. SW and Duan models compared to this model. (b) CO₂ solubility as a function of pressure calculated for 150 °C. SW and Duan models compared to this model.

these experiments. The effect of higher salinity would be to lower the concentration of dissolved CO₂ in solution and hence possibly reduce the amount of CO₂–rock reaction. Conversely however, deeper aquifers may be warmer, which would tend to increase the rate of mineral reactions which might ‘consume’ CO₂. The overall effect of competing processes such as these will be site-specific therefore, and this should be considered during initial investigations of potential storage sites. This work highlights the need for long-term field and laboratory experiments to test geochemical aspects of CO₂ sequestration.

5. Conclusion

This work provides measurements of the solubility of CO₂ within the Utsira formation at Sleipner. It allows comparison of the results with extrapolations from previous experimental data. Finally, it validates a modelling approach for use in a limited range of temperature, pressure and salinity. The model can predict CO₂ solubility in brines dominated by NaCl for temperatures from 0 to 300 °C and for pressures from 1–300 bar, and for ionic strengths up to 3 molal. This model is able to predict CO₂ solubility in more complex brines such as saline Utsira porewater with good accuracy. These results will contribute to further our understanding of the reactive behavior of the supercritical CO₂ under physical–chemical conditions relevant to geologic storage and sequestration.

Notation

T	Absolute temperature (Kelvin)
P	Total pressure (bar); $=P_{\text{CO}_2}+P_{\text{H}_2\text{O}}^{\text{sat}}$
x	Mole fraction in vapour phase
R	Universal gas constant ($=0.08314467 \text{ bar mol}^{-1} \text{ K}^{-1}$)
m	Molality in the aqueous phase ($\text{mol kg}^{-1} \text{ H}_2\text{O}$)
φ	Fugacity coefficient in the vapour phase
γ	Activity coefficient in the aqueous phase
f	Fugacity (bar)
\bar{V}	Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
K^{H}	Henry’s constant of dissolved gas ($\text{bar mol}^{-1} \text{ kg H}_2\text{O}$)

I Ionic strength of the aqueous solution ($\text{mol kg}^{-1} \text{ H}_2\text{O}$)

Superscripts

v	Vapour
aq	Aqueous solution
∞	Infinite dilution state

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