An Equation of State for thermodynamic equilibrium of gas mixtures and brines to allow simulation of the effects of impurities in subsurface CO2 storage

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ABSTRACT

Comprehensive understanding and prediction of chemical and reactive processes during and following injection of CO2 in depleted gas reservoirs and saline aquifers is important for the assessment of the performance and impacts of planned and existing Carbon Capture and Storage (CCS) projects. Over the last decade significant improvements have been made in numerical modelling of the complex, coupled processes involved. Among the many remaining issues where progress is still called for, is the consistent simulation of impacts of gas mixtures. In particular the presence of ‘impurities’ or ‘co-contaminants’ in the injected CO2 stream that are retained from the original flue-gases, such as H2S and SO2, have the potential, upon dissolution in the pore water, to alter aqueous and water–mineral reactions. Moreover, presence of these and other injected or in situ gases (e.g. CH4) affect CO2 solubility and thermodynamic properties of the fluid and gas phases, which, in turn, impact transport processes.

As an important step towards evaluation of the impact of gas mixtures on these processes, a new Equation of State (EOS) has been developed which allows accurate and efficient modelling of thermodynamic equilibrium of gas mixtures and brines over a large range of pressure, temperature and salinity conditions. Presently the new EOS includes CO2, SO2, H2S, CH4 and N2. This model is based on equating the chemical potentials in the system, using the Peng–Robinson EOS to calculate the fugacity of the gas phase. The model performs favourably with respect to existing EOS’s and experimental data for single gas systems and accurately reproduces available data sets for gas mixtures. Preliminary analysis shows, amongst others, that CO2 solubility is most sensitive to CH4 admixture and least sensitive to the presence of SO2 in the injected gas.

1. Introduction

There is broad consensus that anthropogenic emission of carbon dioxide (CO2) into the atmosphere is an important driver of global warming and regional climate change and that the current trend of increasing CO2 emissions should be reversed (IPCC, 2007). Carbon dioxide capture and storage (CCS) is a significant component of the portfolio of mitigation technologies required to achieve such reversal (Smith et al., 2009). CCS generally involves capture of CO2 at major stationary sources such as power plants and injection in underground geological structures such as saline aquifers, depleted hydrocarbon reservoirs, or producing hydrocarbon reservoirs to enhance oil or gas recovery. Depths greater than 800 m are generally needed for aquifers to allow CO2 to be sequestered in supercritical and hence, fairly dense state (Bachu and Adams, 2003). While demonstration projects for storage in depleted gas/oil reservoirs have started only recently, the number of aquifer storage pilots conducted on various continents is progressively growing since first injection in a saline aquifer overlying the Sleipner field in the North Sea began in 1996 (AAAS, 2009; http://www.globalccsinstitute.com).

Coeval with these developments, efforts are ongoing to study the processes and factors that control the injectivity, containment, and long-term safety of geological storage. Numerical models play an important role in these efforts and are essential, together with experimental studies, to help develop a comprehensive understanding of the complex, coupled physico-chemical processes at play in subsurface storage. Over the last decades, capabilities of these numerical simulators have been progressively improving and they have been used to clarify key system behaviours such as the role of heterogeneity and density influences on spreading of CO2 (Bachu, 2008), the pressure response of aquifers (Birkholzer et al., 2009), the thermal response of depleted gas reservoirs (Oldenburg et al., 2009), and CO2–brine–mineral chemical reactions (White et al., 2005; André et al., 2007; Gaus, 2010).

While simulation of injection of pure, dry CO2 and its interaction with aquifer/reservoir constituents is well developed, capabilities to investigate presence and impacts of other (gaseous...
components than CO₂ are still limited. These additional components can either be so-called impurities or co-contaminants (SO₂, H₂S, N₂, NO₃) retained from the original flue-gases from which CO₂ was separated, or pre-injection in situ gases in the reservoir (Ghaderi et al., 2011) or aqurer, notably methane (CH₄). Evaluation of the impacts of the presence of such components is important because they modify dynamical and thermal properties (viscosity, density, Joule–Thomson coefficient) of the gas/liquid streams, chemical partitioning among the CO₂-rich phase and brine, and brine mineral reactions (Jacquemet et al., 2009; Gaus, 2010). Moreover, knowledge of the consequences of impurities in the CO₂ stream is of particular interest as high-level purification of CO₂ is costly and injection of co-contaminants with the CO₂ may therefore reduce the front-end processing costs of CCS (Knauss et al., 2005).

Simplified approaches to evaluate the impacts of additional gases have been used in a couple of studies. Gunter et al. (2000) performed batch-type modelling (without transport) of geochemical interaction of carbonate minerals with brine containing dissolved H₂S and H₂SO₄ (latter can be considered to be derived from SO₂–brine system). However, CO₂ was not included and concentrations of the acid gases were not obtained from solubility calculations. Knauss et al. (2005) used a more comprehensive approach involving 1D transport modelling, simulating the response of an aquifer to injection of a brine pre-equilibrated with imposed fugacities of CO₂, H₂S and SO₂. Here, the separate non-aqueous (gas-mixture) phase was not considered in transport and simplifications were involved regarding activity calculations. Xu et al. (2007) further improved on this by simulating injection of pure CO₂ together with an H₂S and SO₂ equilibrated brine. In their simulations the EC02N module (Equation of State) of the TOUGH2 code (Pruess et al., 2004) handles equilibrium calculations of the CO₂–H₂O–NaCl system during transport. However, presence of non-aqueous H₂S and SO₂ in the CO₂-stream could not be modelled explicitly.

To further extend simulation-capabilities for analysing the impacts of associated gases in subsurface CO₂ storage, there is a need for efficient and accurate equations of state (EOS) that model the thermodynamic equilibrium of a large suite of gas mixtures and brines with a wide range of composition (Jacquemet et al., 2009). Some authors such as Zhang et al. (2011) have used a modified version of the TMVOC simulator of the TOUGH2 family to model the fate and transport of co-injected H₂S with CO₂ in deep saline formations. Battistelli and Marcolini (2009) recently took an important step by presenting an EOS module (TMGAS) for the TOUGH2 reservoir simulator (Pruess et al., 1999) that handles mixtures of several inorganic gases and hydrocarbons. They showed TMGAS reproduces density, viscosity and specific enthalpy data for several binary gas mixtures and does well in predicting solubility of several pure gases (CH₄, CO₂, H₂S) in brine and in predicting water content of pure CO₂. Moreover, they demonstrated injection of a H₂S–CO₂ mixture in a hydrocarbon reservoir containing methane does alter behaviour compared to pure CO₂ system modelling. Battistelli et al. (2011) have used TMGAS-TOUGHEACT to model the injection of an acid gas mixture (CO₂ + H₂S + CH₄) into a high-pressure undersaturated sour oil reservoir. Geloni et al. (2011) have used the same software to analyse the effect of CO₂ + CH₄ in rock and cement and caprock across the wellbore in an exploited hydrocarbon reservoir. Unfortunately, TMGAS still is proprietary software. Moreover, not all details of the EOS appear to have been disclosed in publication(s), which makes it not easily available or reproducible for broader academic investigations in CCS.

In this paper, we present a new or alternative Equation of State (EOS) which, similar to TMGAS, allows accurate and efficient modelling of thermodynamic equilibrium of gas mixtures and brines over a large range of pressure (up to 600 bar), temperature (up to 110 °C) and salinity (up to 6 mol NaCl). Presently the model includes CO₂, SO₂, H₂S, CH₄ and N₂, but the suite of gases can be readily extended. Non-NaCl brines can be handled and activity of aqueous species is based on the Pitzer formalism for high ionic strength. In the following we first present the EOS in detail. Then we show that the model performs favourably with respect to existing EOS’s and experimental data for single gas systems and accurately reproduces available data sets for gas mixtures. Focus is on solubility of impurities and special attention is paid to SO₂ which is likely to have prominent geochemical impacts (Knauss et al., 2005; Xu et al., 2007). Finally, we illustrate that CO₂ solubility is most sensitive to CH₄ admixture and least sensitive to the presence of SO₂ in the injected gas mixture.

2. Thermodynamic model

The model describes thermodynamic equilibrium between a non-aqueous phase (NaClP), basically a multi-component mixture that can be in gas, supercritical or condensed conditions, and an aqueous phase (aqP), that may include dissolved hydrocarbons (here methane) and gases in addition to water and dissolved solids. The EOS does not include solid/minerals as a separate phase.

2.1. Equilibrium between AqP and NaClP

Thermodynamic equilibrium implies that the chemical potential of each component in the AqP and the NaClP are equal. For the NaClP phase we use

\[ \mu_{\text{NaClP}}(T, P) = \mu_{\text{aqP}}^0(T, P) + RT \ln(f), \]
where $\mu$ is chemical potential and $\mu^0$ is chemical potential at reference temperature, $R$ is the gas constant, $T$ is temperature, $P$ is pressure, and $f$ is fugacity which is equal to

$$f = P\phi y.$$  \hspace{1cm} (2)

where $\phi$ is the fugacity coefficient, $y$ is the mole fraction of the component in the NaqP and $P$ is total pressure.

The chemical potential of the AqP is written in terms of activity $a$ rather than fugacity.

$$\mu_{AqP}(T, P) = \mu_{AqP}^0(T, P) + RT \ln(a).$$ \hspace{1cm} (3)

Equating the two chemical potentials gives

$$\frac{\mu_{NaqP}^0(T, P) - \mu_{AqP}^0(T, P)}{RT} = \ln\left(\frac{a}{P\phi y}\right).$$ \hspace{1cm} (4)

In terms of equilibrium constant $K^0$ this reads

$$\frac{\mu_{NaqP}^0(T, P) - \mu_{AqP}^0(T, P)}{RT} = \ln(K^0).$$ \hspace{1cm} (5)

By using $k_H = Nw/K^0$ (Prausnitz et al., 1986) Eqs. (4) and (5) yield

$$Nw = \frac{a}{P\phi y} k_H \chi.$$ \hspace{1cm} (6)

where $Nw$ is the number of moles per kilogram of water (55.508) and $k_H$ is Henry’s constant. We further use $a = Nw \chi$, which is reasonable because the solubility of the gas species is small (Spycher and Pruss, 2005). The effect of salt is accounted for in the activity coefficient of the gas species, $\gamma$ (Eq. (26)). Therefore the final equation for dissolved gas yields (Akinfiev and Diamond, 2003; Zirrahi et al., 2012).

$$P\phi y = k_H \chi$$ \hspace{1cm} (7)

Hence, for each gas we have

$$\langle P\phi y \rangle_{NaqP} = \langle k_H \gamma \chi \rangle_{NaqP}$$ \hspace{1cm} (8)

where subscript $i$ denotes individual gases like CO$_2$, SO$_2$, N$_2$, H$_2$S, CH$_4$ except water. Similar to Battistelli and Marcolini (2009), we ignore binary interaction between different dissolved gases in the aqueous phase. Therefore, the activity coefficient in Eq. (8) for individual gas species does not depend on presence of other gases. This assumption is an important one in the present EOS since it allows use of a rather simple, non-iterative solving method.

Since the EOS should be able to quantify thermodynamic equilibrium between gas mixtures and brine, water is an important system component. For equilibrium between H$_2$O in the AqP and the NaqP we follow the approach of Spycher et al. (2003):

$$\text{H}_2\text{O}(1) \leftrightarrow \text{H}_2\text{O}(g)$$ \hspace{1cm} (9)

$$K_{H_2O} = \frac{f_{H_2O(1)}}{a_{H_2O(1)}}$$ \hspace{1cm} (10)

where $K$ is Spycher’s true equilibrium constant, $f$ is the fugacity of NaqP water, and $a$ is the activity of AqP water. The equilibrium constant of water is a function of temperature and pressure as given by Eq. (11)

$$K_{H2O}(T, P) = K_{H2O}^0(T, P_0) \exp \left(\frac{(P - P_0) V_{H2O}}{RT}\right)$$ \hspace{1cm} (11)

where $T$ is temperature in $K$; $V_{H2O}$ is the average partial molar volume of the water in the AqP over the pressure interval from $P$ to $P_0$ which is equal to 18.1; $P_0$ is a reference pressure, which is assumed to be 1 bar. The equilibrium constant at reference pressure $K_{H2O}^0(T, P_0)$ is obtained from

$$\log(K_{H2O}^0) = -2.209 + 3.097 \times 10^{-2} \theta - 1.098 \times 10^{-4} \theta^2 + 2.048 \times 10^{-7} \theta^3,$$ \hspace{1cm} (12)

where $\theta$ is temperature in °C (Spycher et al., 2003). By combining (10), (11) and (2) we obtain

$$y_{H2O} = \frac{k_{H2O}^0 \phi_{H2O}}{P_0} \exp \left[\frac{(P - P_0) V_{H2O}}{RT}\right]$$ \hspace{1cm} (13)

At the range of consideration for pressure and temperature (5–110 °C), the solubility of gases in water is low, and the activity of the water component can be approximated by its mole fraction in the liquid phase. Therefore, in Eq. (13) the effect of dissolved salt is accounted for in the activity of water. Using these considerations yields

$$K_{H2O}^0 \exp \left[\frac{(P - P_0) V_{H2O}}{RT}\right] x_{H2O} = \phi_{H2O} P y_{H2O}$$ \hspace{1cm} (14)

Eq. (14) is used in the model for equilibrium of H$_2$O in the system. For the full set of equilibrium equations, Eq. (14) is combined with Eq. (8).

2.2. Non aqueous phase

In Eqs. (8) and (14) the fugacity coefficient must be derived from PVT or PVT-X properties of brines and different gas mixtures by utilizing an Equation of State. There are many EOS’s in the literature. Some authors such as Duan and Sun (2003) and Duan and Mao (2006) used a virial like Equation of State. However, the complexity of the equation makes it not very practical for our aims. Cubic equations in volume were developed and improved over the last century. Redlich and Kwong (1949) (RK) and Peng and Robinson (1976) (PR) are well-known examples. Other examples are the equations of Schmidt and Wenzel (1980) and Soave Redlich−Kwong (1972) which basically are modifications of the Van der Waals EOS. Still other studies used a modified form of RK to represent the properties of gas mixtures such as CO$_2$−H$_2$O (Spycher et al., 2003; King et al., 1992; Zirrahi et al., 2010; Hassanzadeh et al., 2008). Similar to Battistelli and Marcolini (2009), we use the classical Peng−Robinson (1976) EOS. Although the PR EOS is more elaborate than, for instance, RK, it has the advantage that it has greater accuracy around the liquid−vapour boundary.

In our model, the calculation of the fugacity coefficient in the non aqueous phase is as follows. The compressibility factor obeys

$$Z^2 - (1 - B)Z + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0$$ \hspace{1cm} (15)

Parameters $A$ and $B$ are a function of pressure and temperature and are defined as follows:

$$A = \frac{a(T)P}{(RT)^2}$$ \hspace{1cm} (16)

$$B = \frac{bP}{RT}$$ \hspace{1cm} (17)

where

$$a(T) = 0.45724 \frac{R^2 T^2}{P_c} - a(T)$$ \hspace{1cm} (18)

$$b = 0.07780 \frac{R T_c}{P_c}$$ \hspace{1cm} (19)

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Table 4
Experimental data used in calibration of the model.

<table>
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<tr>
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<th>Solution (m = mol kg⁻¹)</th>
<th>T(K)</th>
<th>P(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Water</td>
<td>323–373</td>
<td>25–710</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>285–313</td>
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<td>200–3500</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>323–473</td>
<td>1–54</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>373–473</td>
<td>3–80</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>288–298</td>
<td>60–250</td>
</tr>
<tr>
<td></td>
<td>0–6.5 m NaCl</td>
<td>290–673</td>
<td>35–400</td>
</tr>
<tr>
<td></td>
<td>0–0.17 m NaCl</td>
<td>353–473</td>
<td>20–100</td>
</tr>
<tr>
<td></td>
<td>4–6 m NaCl</td>
<td>313–433</td>
<td>1–100</td>
</tr>
<tr>
<td></td>
<td>0–3.9 m CaCl₂</td>
<td>348–394</td>
<td>10–700</td>
</tr>
<tr>
<td>H₂S</td>
<td>Selleck et al. (1952)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lee and Mather (1977)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Drummend (1981)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Suleimenov and Krupp (1994)</td>
<td>373.15–653.15</td>
<td>6–200</td>
</tr>
<tr>
<td></td>
<td>Xia et al. (2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>Goodman and Krase (1931)</td>
<td>273.15–442.15</td>
<td>101.3–303.9</td>
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<td></td>
<td>Wiebe et al. (1932)</td>
<td>298.15</td>
<td>25.33–1013.25</td>
</tr>
<tr>
<td></td>
<td>Wiebe et al. (1933)</td>
<td>298.15–373.15</td>
<td>25.33–1013.25</td>
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<td></td>
<td>Saddlington and Krase (1934)</td>
<td>338.15–513.15</td>
<td>101.3–304</td>
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<td></td>
<td>O’ Sullivan and Smith (1970)</td>
<td>303.15</td>
<td>11–72.6</td>
</tr>
<tr>
<td></td>
<td>Alvarez and Prini (1991)</td>
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<tr>
<td></td>
<td>Chapy et al. (2004)</td>
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<tr>
<td>CH₄</td>
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<td>40.6–469.1</td>
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<td>56.2–209.9</td>
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<td>0.0–0.6 m brine</td>
<td>311.15–394.15</td>
<td>35–345</td>
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<td>Colburn et al. (1950)</td>
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<td>36.2–667.4</td>
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<td>Colburn and Mcketta (1951)</td>
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<td>22.3–688.1</td>
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<td>Duffy et al. (1961)</td>
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<td>31.7–51.71</td>
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<td>303.15</td>
<td>21.48–957.5</td>
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<td>0–4.6 m NaCl</td>
<td>324.65–398.15</td>
<td>101.3–616.1</td>
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<td>324.65–398.15</td>
<td>101.3–616.1</td>
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<td>0–5.9 m NaCl</td>
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<td>75–1570</td>
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<td>75–1570</td>
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<td>Crovetto et al. (1982)</td>
<td>297.5–518.3</td>
<td>13.27–64.51</td>
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<td>298.15</td>
<td>24.1–51.7</td>
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<tr>
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<td>0–0.4 m KCl</td>
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<td>24.1–51.7</td>
</tr>
<tr>
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<td>0–2.16 m MgCl₂</td>
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<td>24.1–51.7</td>
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<td>0–2.0 m CaCl₂</td>
<td>298.15</td>
<td>24.1–51.7</td>
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<td>Dhima et al. (1998)</td>
<td>344</td>
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<td>Chapy et al. (2005)</td>
<td>283.2–303.2</td>
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<td>2.942–5.928 m NaCl</td>
<td>293.15–413.15</td>
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<td>2.942–5.928 m NaCl</td>
<td>313–393</td>
<td>0.1–37</td>
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<td>SO₂</td>
<td>Rumpf and Maurer (1992)</td>
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<td>313.51–393.19</td>
<td>42–97.9</td>
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<tr>
<td></td>
<td>Huang et al. (1985)</td>
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and

$$\alpha(T) = \left[ 1 + (0.37646 + 1.4522\omega - 0.26992\omega^2) \left( 1 - \frac{T}{T_c} \right) \right]^{2} \tag{20}$$

where $\omega$ is the acentric factor. To calculate the fugacity coefficient for each species, $\phi_i$, in gas mixtures, we use standard simple mixing rules and binary interaction coefficients (Prausnitz et al., 1986).

$$a = \sum_{i} \sum_{j} y_i y_j a_{ij}, \quad a_{ij} = \sqrt{a_i a_j (1 - k_{ij})}, \quad b = \sum_{i} y_i b_i \tag{21}$$

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Table 2
Calibrated parameter values for $k_i$ for various species (Eq. (24)).

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\eta$</th>
<th>$\tau$</th>
<th>$\beta$</th>
<th>$I^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$-0.114535$</td>
<td>$-5.279063$</td>
<td>$6.187967$</td>
<td>$0$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$0.77357854$</td>
<td>$0.27049433$</td>
<td>$0.27543436$</td>
<td>$0$</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>$0.198907$</td>
<td>$-1.552047$</td>
<td>$2.246564$</td>
<td>$0.009847$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$-0.008194$</td>
<td>$-5.175337$</td>
<td>$6.906469$</td>
<td>$0$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$-0.092248$</td>
<td>$-5.779280$</td>
<td>$7.262730$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

\[
\ln \phi_i = \frac{B}{B}(Z - 1) - \ln(Z - B) + \frac{A}{2.828B} \left[ \frac{B}{B} \frac{2\sum y_i a_i}{a} \right]
\]

\[
\ln \left[ \frac{Z + 2.414B}{Z - 0.414B} \right]
\]

(22)

The binary interaction coefficients for CO$_2$–SO$_2$, CO$_2$–H$_2$S, CO$_2$–CH$_4$ and CO$_2$–N$_2$ were obtained from Li and Yan (2009). As observed by Spycher et al. (2003) the current approach neglects the molar fraction of water in the mixing rule (same as assuming infinite dilution of NaP H$_2$O). This is practical since it reduces iteration demands as will be explained in the section on model calibration.

To obtain the proper value of $Z$ in Eq. (22), we follow the approach described by Danesh (1998). When Eq. (15) has three roots, the intermediate one is ignored and the root yielding the lowest Gibbs free energy between the remaining two is selected. Let $Z_0$ and $Z_i$ be the two real roots with $Z_0$ and $Z_i$ being the Gibbs free energy, and where the subscripts denote the high and low $Z$ value, respectively. The difference in Gibbs free energy is given by:

\[
\frac{(G_n - G_i)}{RT} = (Z_0 - Z_i) + \ln \left( \frac{Z_i - B}{Z_0 - B} \right) - \frac{A}{2B} \left[ \frac{Z_i + \delta B_i}{Z_i + \delta B} \right]
\]

(23)

where $\delta B_i$ and $\delta B$ for Peng–Robinson EOS are $1 + \sqrt{2}$ and $1 - \sqrt{2}$, respectively. If $(G_n - G_i)/RT$ in Eq. (23) is positive $Z_i$ is selected; otherwise $Z_0$ is the correct root.

Table 3
Calibrated second-order interaction parameters ($\lambda$) for various gases (Eq. (27)).

<table>
<thead>
<tr>
<th>Constant</th>
<th>$\lambda_{CO_2-Na}$</th>
<th>$\lambda_{SO_2-Na}$</th>
<th>$\lambda_{SO_2-Na}$</th>
<th>$\lambda_{SO_2-Na}$</th>
<th>$\lambda_{SO_2-Na}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$-0.0652869$</td>
<td>$-5.0961506E-02$</td>
<td>$-2.0939363$</td>
<td>$1.03565869$</td>
<td>$-5.7066455E-01$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$1.6970636E-04$</td>
<td>$2.8865149E-04$</td>
<td>$3.1445296E-03$</td>
<td>$-1.1784797E-03$</td>
<td>$2.2997588E-04$</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$40.833951$</td>
<td>$0$</td>
<td>$-2.9973977E-07$</td>
<td>$-4.5313285E-04$</td>
<td>$-3.1927112E-05$</td>
</tr>
<tr>
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<td>$0$</td>
<td>$0$</td>
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<tr>
<td>$c_5$</td>
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<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c_6$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c_7$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c_8$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c_9$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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<td>$c_{10}$</td>
<td>$0$</td>
<td>$0$</td>
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</tr>
</tbody>
</table>

Table 4
Calibrated third-order interaction parameters ($\zeta$) for various gases (Eq. (27)).

<table>
<thead>
<tr>
<th>Constant</th>
<th>$\xi_{CO_2-Na}$</th>
<th>$\xi_{SO_2-Na}$</th>
<th>$\xi_{SO_2-Na}$</th>
<th>$\xi_{SO_2-Na}$</th>
<th>$\xi_{SO_2-Na}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$-1.144624E-02$</td>
<td>$-1.1462699E-03$</td>
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<td>$2.9990084E-03$</td>
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<td>$c_2$</td>
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<td>$c_4$</td>
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<td>$c_5$</td>
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<td>$0$</td>
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<td>$c_6$</td>
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<td>$0$</td>
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<td>$0$</td>
</tr>
<tr>
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<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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<tr>
<td>$c_8$</td>
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<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>$c_9$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0$</td>
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<td>$c_{10}$</td>
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<td>$0$</td>
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</table>

Table 5
Calibrated binary interaction coefficients.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>H$_2$S</th>
<th>SO$_2$</th>
<th>N$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$0.19014$</td>
<td>$0.105$</td>
<td>$-1.10329$</td>
<td>$0.32547$</td>
<td>$0.47893$</td>
</tr>
</tbody>
</table>

2.3. Aqueous phase

In the next step of model development, Henry's constant, $k_{Hi}$, and the activity coefficient, $y_i$, on the right-hand side of Eq. (8), need to be quantified. For the temperature and pressure dependency of Henry's constant, we use a correlation established by Akinfiev and Diamond (2003). The correlation is a virial-like equation for the thermodynamic properties of the aqueous phase species at infinite dilution and requires but a few empirical parameters (constrained by experimental data), and these parameters are independent of temperature and pressure.

\[
\ln(k_{HI}) = (1 - \eta) \ln \left( \frac{\rho_{H_2O}^0}{M_{HI}} \right) + \eta \ln \left( \frac{RT}{M_{HI}} \right) + 2 \rho_{H_2O}^0 \Delta B
\]

(24)

where $\eta$ is a constant for each dissolved gas in water, $T$ is temperature in K; and $\rho_{H_2O}^0$ and $\rho_{HI}^0$ are fugacity and density of pure water, respectively. For calculation of properties of pure water we use the correlation of Fine and Millero (1973); see Appendix A. It should be noted that we quantify $H_{2O}$ using Eq. (A6) because Eq. (22) is not sufficiently accurate for pure water. In Eq. (24) $\Delta B$ (cm$^3$ g$^{-1}$) stands for the difference in interaction between dissimilar solvent molecules (Akinfiev and Diamond, 2003) and is calculated as follows:

\[
\Delta B = \tau + IP + \beta \sqrt{\frac{10^3}{T}}
\]

(25)

where $\tau$ (cm$^3$ g$^{-1}$), $\beta$ (cm$^3$ K$^{0.5}$ g$^{-1}$) and $IP$ (bar$^{-1}$) denote adjustable parameters. In the original version of Eq. (25) (Akinfiev and Diamond, 2003, their Eq. (15)) the term $IP$ does not occur. It is added here specifically for SO$_2$ to allow for the fact that the solubility of this species is two to three orders of magnitude higher than other considered gas species. For the latter we, therefore, set $\Gamma = 0$. It should further be noted that we only used the parameter values

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Fig. 1. Comparison between results for the new EOS (solid lines) and experimental data (symbols) for CO₂ solubility (left panels) and H₂O content of the CO₂-rich phase (right panels) for various temperatures. The data shown are identical to those used by Spycher et al. (2003; their Appendix A).

Table 6
Absolute deviation (%) from experimental data for the new model and for the models of Spycher et al. (2003) and Duan and Sun (2003).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P bar</th>
<th>xCO₂ × 100</th>
<th>New model</th>
<th>Spycher et al. (2003)</th>
<th>Duan and Sun (2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323.15</td>
<td>25.3</td>
<td>0.774</td>
<td>2.550519</td>
<td>1.720475</td>
<td>2.456373</td>
</tr>
<tr>
<td>323.15</td>
<td>40.5</td>
<td>1.09</td>
<td>6.823528</td>
<td>6.886282</td>
<td>7.069009</td>
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<tr>
<td>323.15</td>
<td>50.6</td>
<td>1.37</td>
<td>0.250958</td>
<td>0.607855</td>
<td>0.465618</td>
</tr>
<tr>
<td>323.15</td>
<td>68.2</td>
<td>1.651</td>
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<td>1.83888</td>
<td>1.273293</td>
</tr>
<tr>
<td>323.15</td>
<td>75.3</td>
<td>1.75</td>
<td>0.410151</td>
<td>1.682105</td>
<td>1.01269</td>
</tr>
<tr>
<td>323.15</td>
<td>101.33</td>
<td>1.98</td>
<td>0.425629</td>
<td>1.674057</td>
<td>1.368011</td>
</tr>
<tr>
<td>323.15</td>
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<td>2.10</td>
<td>2.974057</td>
<td>2.164378</td>
<td>2.227906</td>
</tr>
<tr>
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<td>2.906066</td>
<td>2.367484</td>
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</tr>
<tr>
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<td>2.17</td>
<td>1.334566</td>
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<tr>
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<td>2.174</td>
<td>0.070702</td>
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<td>0.004453</td>
</tr>
<tr>
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<td>0.528422</td>
<td>0.530476</td>
<td>0.780196</td>
</tr>
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<td>323.15</td>
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<td>0.862124</td>
</tr>
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<td>1.505869</td>
</tr>
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<td>500</td>
<td>2.80</td>
<td>1.321428</td>
<td>1.187714</td>
<td>0.402989</td>
</tr>
<tr>
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<td>0.747158</td>
<td>2.91481</td>
</tr>
<tr>
<td>AAD</td>
<td></td>
<td></td>
<td></td>
<td>1.219551</td>
<td>1.289952</td>
</tr>
</tbody>
</table>

AD% = 100(|x_{exp} - x_{cal}|/x_{exp}), AD&D% = \left(\sum_{i=1}^{N} 100(|x_{exp} - x_{cal}|/x_{exp})\right)/N.
for Eqs. (24) and (25) tabulated by Akinfiev and Diamond (2003) as initial guesses, and obtained new estimates of these parameters for the pressure and temperature ranges of interest during calibration (new parameter values are listed in Table 2).

For calculation of the activity coefficient of the various gas species, we developed an approach similar to Duan and Sun (2003). Reduction of the activity coefficient due to interaction with solute present in the brine (Pitzer, 1973), is based on a virial expansion of Gibbs excess energy

$$\ln \gamma_i = \sum m_C \lambda_{i-C} + \sum m_A \lambda_{i-A} + \sum m_A m_C \zeta_{i-A-C}$$  \hspace{1cm} (26)

where subscript of $m_C$ and $m_A$ denote anions and cations molality, respectively, $\lambda_{i-C}$ and $\zeta_{i-A-C}$ are second and third-order interaction parameters, respectively. Following Duan and Sun (2003) we also assume $\lambda_{i-A} = 0$. Temperature and pressure dependency of the interaction parameters is modelled using

$$\text{Par}(T, P) = c_1 + c_2 T + \frac{c_3}{T} + c_4 P + \frac{c_5}{P} + c_6 \frac{P}{T} + c_7 \frac{T}{P^2} + \frac{c_8 P}{630 - T}$$ \hspace{1cm} (27)

where $\text{Par}(T, P)$ is either $\zeta$ or $\lambda$, $P$ is pressure in bar and $T$ is temperature in K and the $c_i$, $i = 1, \ldots, 10$ are constants which are calculated by using a fitting procedure and are given in Table 3. Following Duan and Sun (2003) we reduce the number of interaction parameters by using $\lambda_{i-C} = \lambda_{i-Na}$, and by interpreting $m_C$ for the second-order interaction term in terms of equivalents per mass of brine (that is, molality multiplied by valency). For the third-order interaction parameters we assume $\zeta_{i-A-C} = \zeta_{i-Na-C}$ while maintaining molalities in Eq. (26). For instance, for a brine containing sodium, calcium, potassium and magnesium salts, Eq. (26) effectively gives

$$\ln \gamma_i = 2 \lambda_{i-Na}(m_{Na} + 2m_{Ca} + m_K + 2m_{Mg} + \zeta_{i-Na-C}m_{Cl})$$  \hspace{1cm} (28)

It may be worthy to note that, in contrast to Duan and Sun (2003) who use different equations for the pressure and temperature dependency for the various gas species, we use the single form shown in Eq. (27). Furthermore, it may be pointed out that in the absence of dissolved salts (gas dissolution in pure water), Eq. (26) yields activity coefficients equal to 1.

3. Model calibration

The Weighted Nonlinear Least Square (WNLS) method was used in model calibration. Calibration for each gas component (CO$_2$, CH$_4$, N$_2$, H$_2$S, SO$_2$) was conducted in two steps. First, the parameters in the Henry constant (Eqs. (24) and (25); $\eta$, $\lambda$, $\alpha$, and $\beta$) and the binary interaction coefficient between H$_2$O and the gas species (Eq. (21)) were obtained using experimental data for equilibrium with pure water. Second, the parameters in the relationship quantifying the activity coefficient (Eq. (27); $c_i$, $i = 1, \ldots, 10$) were determined from data for brine–gas systems. The calibration targets (experimental data sets) that were used were obtained from the literature listed in Table 1. These include both solubility data for the gas species in the aqueous phase and data on H$_2$O vapour content in the non aqueous phase. The optimized parameter values are listed in Tables 2–5.
4. Solving the model equations for systems consisting of single or mixed gases

For single gas–brine systems, partitioning of the gas species and H₂O among the aqueous and non-aqueous phase can be directly obtained from the following equations. The determination of the phase composition for single gas–brine systems is non-iterative because of the assumptions made that the fugacity of the gas in NaqP does not depend on composition, but can be computed accounting only for known P and T (illustrated here for CO₂).

\[ y_{H_2O} = \frac{1 - \frac{P_{CO_2}}{R \cdot T}}{1 - \left(1 - \frac{P_{CO_2}}{R \cdot T} \cdot \frac{P_{CO_2}}{R \cdot T} \right)} \]  \hspace{1cm} (29a)\]

\[ x_{CO_2} = \frac{P_{CO_2}}{R \cdot T} \cdot \left(1 - \frac{1 - \frac{P_{CO_2}}{R \cdot T}}{1 - \left(1 - \frac{P_{CO_2}}{R \cdot T} \cdot \frac{P_{CO_2}}{R \cdot T} \right)} \right) \] \hspace{1cm} (29b)

Eq. (29) is obtained by combination of Eqs. (8) and (14) and using the fact that

\[ \sum_{i=CO_2} x_i = 1, \sum_{i=CO_2} y_i = 1 \] \hspace{1cm} (30)

For gas mixtures the method is a little different. Because the number of equations and the number of unknowns (mole fraction of each species in gas and liquid phase) are not equal, vapour–liquid flash calculations are used (Danesh, 1998). First the mole fraction of each component in the total system, \( z_i \), (feed) is defined. The problem is to solve for \( x_i \) and \( y_i \) for given \( P, T \), and salt molality. To do this, the Rachford–Rice equation

\[ \sum_{i=1}^{N} \frac{z_i (K_i - 1)}{1 + (K_i - 1)n^i} = 0 \]  \hspace{1cm} (31)\]

is solved for \( n^i \), the mole fraction of NaqP in the system (value between 0 and 1). In Eq. (31) \( K_i \)-values are defined as follows:

\[ K_i = \frac{y_i}{x_i} \hspace{1cm} i = H_2O, N_2, CO_2, CH_4, H_2S, SO_2 \] \hspace{1cm} (32)\]

According to Eq. (14) the K-value for water is

\[ K_{H_2O} = \frac{k_{H_2O}^0 \exp[\left(\frac{(P - P_0)W_{H_2O}}{R \cdot T}\right)]}{P \cdot \Phi_{H_2O}} \] \hspace{1cm} (33)\]

And according to Eq. (8) for other components, the K-value is

\[ K_i = \frac{k_{H_2O} \cdot \Phi_i}{P \cdot \Phi_{H_2O}}, \hspace{1cm} i = N_2, CO_2, CH_4, H_2S, SO_2 \] \hspace{1cm} (34)\]
An Equation of State for thermodynamic equilibrium of gas mixtures and brines to allow simulation of the effects of impurities in subsurface CO2 storage.

Fig. 5. Comparison between results for the new EOS (solid lines) and experimental data (symbols) for SO2. (a) Solubility in pure water; data from Rumpf and Maurer (1992). (b) Solubility in NaCl brines for different salinity and temperature; data from Xia et al. (2000).

Fig. 6. (a) Comparison between results for the new EOS (solid lines) and predictions of the EOS of Mao and Duan (2006) (symbols) for N2 solubility in NaCl brines with different salinities and at a temperature of 333.15 K. (b) Comparison between results for the new EOS (solid line) and experimental data (Namiot and Bondareva, 1959) (symbols) for water content in the N2-rich phase at 366.45 K.

Fig. 7. (a) Comparison between results for the new EOS (solid lines) and predictions of the EOS of Duan and Mao (2006) (symbols) for CH₄ solubility in NaCl brines with different salinities and at a temperature of 333.15 K. (b) Comparison between results for the new EOS (solid line) and experimental data (Olds et al., 1942) (symbols) for water content in the CH₄-rich phase at 377.59 K.

With the known value of \( n^V \), \( K_i \)'s and \( z_i \)'s, the mole fraction of each phase are subsequently obtained from

\[
x_i = \frac{z_i}{1 + (K_i - 1)n^V}, \quad y_i = \frac{K_i z_i}{1 + (K_i - 1)n^V}.
\]

In the case of gas mixtures the binary interaction between dissolved gases in the aqueous phase is ignored (Battistelli and Marcolini, 2009). Binary interaction coefficients for CO₂–SO₂, CO₂–H₂S, CO₂–CH₄, CH₄–H₂S and CO₂–N₂ for the non-aqueous phase are adopted from Li and Yan (2009), while the gas–H₂O interaction coefficients, listed in Table 5 are known from model calibration.

It may be worthwhile repeating that in the mixing rule (Eq. (21)) the mole fraction of water has been neglected. This is convenient since it eliminates the need for iteration procedures.

5. Result and discussion

In this section the model performance is assessed and illustrated by showing: (1) results of calibration, (2) comparison with existing models for H₂O–NaCl–CO₂ and H₂O–CaCl₂–CO₂ systems (Spycher et al., 2003; Spycher and Pruess, 2005; Duan and Sun, 2003; Duan and Mao, 2006; Mao and Duan, 2006), and (3) how model predictions for gas mixtures compare with experimental data.

5.1. CO₂–brine

In Fig. 1 a comparison is shown of the model with respect to experimental data used in the calibration for pure water. Both CO₂ solubility and water content in the CO₂-rich phase are shown for different temperatures. Fig. 2 demonstrates that our model predictions are virtually identical to those of Spycher et al. (2003), Spycher and Pruess (2005) and Duan and Sun (2003) for different brines up to pressures of 600 bars. TheSpycher model forms the basis of the ECODN-EOS module in TOUGH2 (Pruess, 2005). To allow a further quantitative comparison with these models, we calculated the absolute deviation (AD) of these models and our model with respect to experimental data shared by all studies. Table 6 shows that our model performs favourably with respect to the existing ones. Table 6 only gives results for a small selection of data. For the full data set of 405 measurements the (average absolute deviation) AAD value of our model is about 8.3%.

5.2. H₂S–brine

For H₂S our model shows good agreement with the solubility model of Duan et al. (2007) (Fig. 3a) and with experimental data for the mole fraction of water in the gas phase (Soreide and Whitson, 1992) (Fig. 3b). Fig. 4a highlights the importance of accounting for non-ideality of H₂O in the non-aqueous phase as we do in our model. The figure indicates that the assumption of ideal mixing for water in the gas-rich phase strongly underestimates the actual water content at relatively high pressures. Fig. 4b illustrates model behaviour with respect to H₂S solubility in brine for various salinities.

5.3. SO₂–brine

Experimental data on SO₂–water or SO₂–brine systems are very scarce. Fig. 5a and b shows how the model compares with respect to the data reported in the two studies listed in Table 1. It should be noted that although the model fit is good, predictions at pressures beyond about 10 bar are not well constrained and, hence, are associated with relatively large uncertainty.
that the experimental data (Huang et al., 1985) were not involved in the model calibration, which was done for single gas–brine systems only. The favourable correspondence between data and model therefore provides some confidence that the employed method for handling gas mixtures is adequate.

The system of Qin et al. (2008) is for a 2-component gas mixture consisting of CO₂ and CH₄. Their experimental data showed that CO₂ solubility (defined as the reciprocal of apparent Henry’s law constant, \( P_{CO_2}/x_{CO_2} \)) increases in the presence of CH₄. Similarly, CH₄ solubility, \( P_{CH_4}/x_{CH_4} \), was shown to increase in the presence of CO₂. Fig. 9 shows that our model reproduces this behaviour. Unfortunately, we could not test our model against their measurements in detail because the amount of water in the experimental system was not reported.

Finally, we used our model to investigate the sensitivity of CO₂ solubility to the presence of various impurities. Fig. 10 shows the impact of 5% (by weight) admixture of each of the ‘contaminant’ gases (as listed in Table 7) on the mole fraction of carbon dioxide in the aqueous phase. Results show that CO₂ mole fraction in the aqueous phase is most sensitive to CH₄ admixture and least sensitive to the presence of SO₂ in the injected gas.

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5.4. N₂–brine

Fig. 6a demonstrates model-predicted solubilities of N₂ show good correspondence with solubilities by Mao and Duan (2006) for a large range of salinities. Model performance with regard to experimental data for the mole fraction of water in rich N₂ phase (Namiot and Bondareva, 1959) is illustrated in Fig. 6b.

5.5. CH₄–brine

Fig. 7 depicts model performance for methane. Both the correspondence with the existing model of Duan and Mao (2006) (Fig. 7a) and experimental data (Olds et al., 1942) are very satisfactory.

5.6. Gas mixture–brine

We have been able to find two studies with relevant experimental data regarding equilibrium conditions for brine and gas mixtures (Huang et al., 1985; Qin et al., 2008). The system of Huang et al. (1985) is for a 3-component gas mixture consisting of CO₂, CH₄ and H₂S with mole fractions of 0.6, 0.3 and 0.1, respectively. This gas mixture is equilibrated with various amounts of water. Data and model performance is shown in Fig. 8. It should be noted...
6. Concluding remarks

In CCS or acid gas disposal, and natural gas sweetening and gas transportation, accurate estimation of water content in the non-aqueous phase as well as solubility of gases in water/brine is important. In this paper, a new EOS has been presented which quantifies the thermodynamic equilibrium between gas mixtures and brines. Presently the model includes CO2, SO2, H2S, CH4 and N2, but the suite of gases can be readily extended. Non-NaCl brines can be handled and activity of aqueous species is based on the Pitzer formalism for high ionic strength. This model predicts the water content in non-aqueous phase and composition of the various gas components in both the aqueous and non-aqueous phase at moderate temperatures (5–110 °C), a wide pressure range (1–600 bar) and various salinities (0–6 m).

The model predictions are consistent with existing EOS’s and experimental data for single gas systems and accurately reproduces available, albeit still very limited data sets for gas mixtures. Analysis shows, amongst others, that the amount of dissolved CO2 is most sensitive to CH4 admixture and least sensitive to the presence of SO2.

An important assumption of the EOS is that it neglects binary interaction between dissolved gases in the aqueous phase. This allows use of a simple, non-iterative solving method. More comprehensive experimental data for gas mixtures are needed to ascertain the validity of this assumption. It should be further noted that uncertainty of model predictions will be strongly correlated with the P and T ranges of experimental data of the various gas species used in model calibration.

The EOS may be suitable for incorporation in reactive transport simulators in order to address, for instance, the chemical impact of co-components. Presently the model includes fugacity calculations using the Peng–Robinson EOS. However, it can be easily modified to include another EOS. In that case the model calibration parameters would have to be re-calculated. We did so for the modified RK EOS (Sypcher et al., 2003), but for H2S the prediction of the water content proved to be considerably less accurate than for the PR EOS.

A key advantage of the present model is that it is fairly simple and non-iterative and fully explicated, which makes that it can be readily adopted for use in other studies.

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Appendix A.

For calculation of properties of pure water we use the correlation of Fine and Millero (1973)

\[
V = \frac{V_0}{B + A_1P + A_2P^2},
\]

\[
V_0 = \frac{1 + 18.159725 \times 10^{-3} \theta}{0.9998396 + 18.224944 \times 10^{-3} \theta - 7.922210 \times 10^{-6} \theta^2 - 55.44846 \times 10^{-9} \theta^3 + 149.7562 \times 10^{-12} \theta^4 - 393.2952 \times 10^{-15} \theta^5},
\]

\[
B = 19654.320 + 147.037\theta - 2.215546\theta^2 + 1.0478 \times 10^{-2} \theta^3 - 2.2789 \times 10^{-5} \theta^4,
\]

\[
A_1 = 3.2891 - 2.3910 \times 10^{-3} \theta + 2.8446 \times 10^{-6} \theta^2 - 2.8200 \times 10^{-6} \theta^3 + 8.477 \times 10^{-9} \theta^4,
\]

\[
A_2 = 6.245 \times 10^{-5} - 3.913 \times 10^{-6} \theta - 3.499 \times 10^{-9} \theta^2 + 7.942 \times 10^{-10} \theta^3 - 3.299 \times 10^{-12} \theta^4,
\]

where \( \theta \) is temperature in °C and \( V = 1/\rho \) is the reciprocal of the density of pure water in cubic centimetre per gram.

For the fugacity of pure water we use the relation of King et al. (1992)

\[
\rho_{H_2O}^f = \rho_T \exp \left( \frac{(P - P_T)}{RT} \right)
\]

where \( \rho \) is molar volume, calculated by multiplying molecular weight of water (18.0152) by \( V \) in Eq. (A1). For calculation of \( P_T \) we utilize Shibue’s (2003) correlation

\[
\ln \frac{P_T}{P} = T_e \left[ a_1 \tau + a_2 \tau^1.5 + a_3 \tau^3 + a_4 \tau^{3.5} + a_5 \tau^4 + a_6 \tau^{7.5} \right]
\]

where \( \tau = 1 - T/T_c \) and \( T_e \) and \( P_T \) are critical temperature and pressure of water.

\[
a_1 = -7.85951783, a_2 = 1.84408259, a_3 = -11.7866497, a_4 = 22.6807411, a_5 = -15.9618719, a_6 = 1.80122502.
\]
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