Densities of the CO$_2$–H$_2$O and CO$_2$–H$_2$O–NaCl Systems Up to 647 K and 100 MPa

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An equation of state is established for the gas phase of CO$_2$–H$_2$O in the range 0–28 MPa and 323–645 K. The equation for gaseous CO$_2$–H$_2$O mixtures can accurately reproduce the experimental volumes with an average deviation of 0.25% and a maximum deviation of 2.8%. An accurate model for the molar volumes and densities of liquid CO$_2$–H$_2$O and CO$_2$–H$_2$O–NaCl mixtures is developed. The most accurate experimental density data for the CO$_2$–H$_2$O system in the range 273–623 K and 0.7–35 MPa can be reproduced within ±0.05%, and the average deviation is 0.008%. The model for the liquid CO$_2$–H$_2$O–NaCl mixtures is developed on the basis of our CO$_2$–H$_2$O model and the H$_2$O–NaCl model of Rogers and Pitzer (J. Phys. Chem. Ref. Data 1982, 11, 15–81). No additional empirical parameter is introduced for the ternary. This model can predict the ternary density data within experimental errors and is expected to be valid up to 573 K. It is found that both the density model and the equation of state can be extrapolated up to 100 MPa or higher pressure with accuracy close to those of experiments. Computer programs for the related calculations can be downloaded from http://www.geochemmodel.org/programs.htm.

1. Introduction

CO$_2$–H$_2$O and CO$_2$–H$_2$O–NaCl are typical geological fluids in many geochemical processes. Pressure–volume–temperature–composition (PVTx) properties and phase equilibrium are fundamental in the quantitative interpretation of geochemical data. For example, predicting CO$_2$ behavior after geological storage needs accurate knowledge of both phase relations and densities. This knowledge is also very important in many industrial processes, such as the production of oil and gas.

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1Roedder, E. Rev. Miner. 1984, 12, 1.
gas, enhanced oil and gas recovery, geothermal exploitation, natural gas clathrate engineering, the treatment of exhaust gases, wastewater and waste liquids, supercritical fluid extraction and oxidation, fertilizers, hydrometallurgy, and seawater desalination, etc. 33, 34, 38–42

The phase equilibrium and PVTx properties of the NaCl–H₂O system have been studied extensively. 53–56 There are also systematic experimental studies and thermodynamic modeling of the bubble-point compositions (or CO₂ solubilities) of the systems CO₂–H₂O and CO₂–H₂O–NaCl. 30, 43, 57–70 Some models are available for the dew-point curves (namely vapor-phase boundaries) of the two systems. 62–64 Although the existing models are accurate for the delineation of phase boundaries, they are not sufficiently accurate for the calculation of densities or other volumetric properties, which are crucial for evaluating the rate of injected CO₂ fluids and the capacity and safety of CO₂ storage in the sea or in a geological formation. 53 Therefore, this study focuses on the modeling of densities and other volumetric properties including molar volumes and apparent molar volumes of the CO₂–H₂O and CO₂–H₂O–NaCl systems below the critical temperature of H₂O, Tc(H₂O).

Because accurate data are essential for the development of an accurate model, it is necessary to make a systematic review and assessment of available experimental PVTx data of the CO₂–H₂O and CO₂–H₂O–NaCl systems. 53 It is known that the net increase in solution density due to CO₂ dissolution is usually very small (less than 2% of pure water density) under the P–T–x conditions of CO₂ storage, and a density difference of about 0.1 kg m⁻³ is enough to drive a natural CO₂-bearing solution to either sink or buoy. 20

Currently, some models have been developed to correlate or predict the apparent or partial molar volumes, or densities of the CO₂–H₂O solutions. 30, 42, 43, 69–79 There are a few models for the volumetric properties of the CO₂–H₂O–NaCl/brine solutions. 62, 73, 80–82 Many equations of state (EOS) are available for the CO₂–H₂O and CO₂–H₂O–NaCl systems, such as those of Duan et al. 83, 84 Ji et al., 85 Spycher and Reed, 86 Nitsche et al., 87 Churakov and Gottschalk, 88, 89 and Li et al. 90 as well as the numerous cubic EOS and virial EOS truncated at the second or third virial coefficient. According to our calculation, the EOS or density models mentioned above are inadequate for the thermodynamic modeling of CO₂ storage. 53

At present, using a single equation to achieve accurate prediction of volumetric properties of both liquid and vapor phases of the two systems is still a challenge. The difficulty arises from the great differences in the compositions and physicochemical properties of coexistent phases. In the CO₂–H₂O–NaCl solution, for example, there are many complex microscopic interactions (such as hydrogen bond, hydration, chemical reaction, ionization, and association), which are very

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(60) Duan, Z.; Sun, R. Chem. Geol. 2003, 193, 253.
(69) dos Ramos, M. C.; Blas, F. J.; Galindo, A. Fluid Phase Equilib. 2007, 261 (1–2), 359.
Table 1. Constants in Equation 3

<table>
<thead>
<tr>
<th>i</th>
<th>A_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.624 0078 × 10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>0.924 8008 × 10⁰</td>
</tr>
<tr>
<td>3</td>
<td>0.528 2536 × 10⁻²</td>
</tr>
<tr>
<td>4</td>
<td>-0.250 9670 × 10⁰</td>
</tr>
<tr>
<td>5</td>
<td>-0.310 1373 × 10⁻²</td>
</tr>
<tr>
<td>6</td>
<td>0.279 4819 × 10⁰</td>
</tr>
</tbody>
</table>

difficult to describe with a single theory. In this situation, using different models for the liquid and gas phase is more practical for engineering applications. In this work, we present a density model for liquids, and a modified equation of state for gases.

2. Equation of State for the Vapor Phase of CO₂–H₂O Mixtures

Duan et al. developed a virial-type equation of state for the CH₄–CO₂–H₂O system:

\[
Z = \frac{PV}{RT} = 1 + \frac{BV_c}{V} + \frac{CV_c^2}{2V^2} + \frac{DV_c^3}{4V^3} + \frac{EV_c^4}{5V^4} + \frac{FV_c^5}{6V^5} + \frac{GV_c^6}{7V^7} + \frac{HV_c^7}{8V^8} + \text{...}
\]

(1)

where only three cross virial coefficients contain the adjustable interaction parameters of components i and j:

\[
B_{ij} = \left[(B_i^{1/3} + B_j^{1/3})/2\right]^{3} \frac{C_{ijk}}{\gamma_{ijk}} = \left[(C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3\right]^{3} \frac{k_{ijk}}{\gamma_{ijk}}
\]

(2)

where \(k_{1,12}, k_{2,112}, k_{2,122}\) and \(k_{3,112}, k_{3,122}\) are empirical temperature functions fitted from experimental data. In the original equation, it was assumed that \(k_{2,112} = k_{2,122}\) and \(k_{3,112} = k_{3,122}\). This equation has good overall accuracy in both gas and liquid PVTTx properties, but its volume deviations are often larger than (or close to) the density increments due to the CO₂ dissolution, so it is still inadequate for the modeling of CO₂ sequestration. Furthermore, the equation uses segmental temperature functions for binary interaction parameters, which gives discontinuous results for some derivative properties. In this work, we use a continuous temperature function for every binary interaction parameter:

\[
k_{1,12} = A_1 T + A_2
\]

(3)

\[
k_{2,112} = A_3 T + A_4
\]

(3)

\[
k_{2,122} = A_5 T + A_6
\]

(3)

\[
k_{3,112} = K_{3,122} = 1
\]

(3)

It was found that high-order terms of temperature are disadvantageous for the extrapolability of the EOS, so only linear functions are used in the parameter expressions, where the empirical constants (Table 1) are regressed from the experimental data of Wormald et al., Patel et al., Patel and Eubank, Fenghour et al., and Warowny and Eubank.

3. Liquid Density Model for the CO₂–H₂O System

3.1. Selection and Correction of Experimental Data.

According to the assessment of Hu et al., many groups of experimental data for the aqueous CO₂ solutions prove to contain large uncertainty or systematic deviation, or to be obviously inconsistent with other data sets. Only a few data sets are reliable. In this work, we used the most reliable experimental data to regress the model parameters. However, some important issues regarding these data must be clarified:

1. Ohsumi et al. and Song et al. presented graphical reports of the density changes due to the dissolution of CO₂, leaving the corresponding densities of pure water \((\rho_w)\) unknown. In order to obtain the solution densities, we supplement the pure water densities with the IAPWS97 EOS, where the EOS is considered to be highly accurate. The density differences of Ohsumi et al. are read from their figure, and the ratios of the solution and pure water densities reported by Song et al. are calculated with their empirical model regressed from the data presented in their figures.

2. The densities of aqueous solutions and pure water reported by Hnedkovsky et al. can be reproduced with the following equation:

\[
\rho = \rho_1 + \Delta \rho = (x_1 M_1 + x_2 M_2)/(x_1 M_1 \rho_1 + x_2 V_2)
\]

(4)

where \(\rho\) is the density of solution, \(V_2/\rho_2\), \(\rho_1\), \(M_1\), and \(x_i\) are the apparent molar volume, density, molar mass, and mole fraction of pure component \(i\), respectively. The subscripts 1 and 2 denote H₂O and CO₂, respectively. It can be seen that the errors of pure water densities in the calibration of Hnedkovsky et al. are generally within 0.3%, but the largest error can be up to about 2% (Figure 3). Here we use the IAPWS97 EOS to replace the calibration of Hnedkovsky et al.

3. Figure 4 shows that the pure water densities of Li et al. have systematic deviations from the values recommended by Blencoe et al. below 35 MPa. The correlation coefficient \(R^2\) of the regression is 0.999 89. Most of these data, except for those of Warowny and Eubank, have been assessed and were considered to be of good accuracy. The density data for water steam system of Warowny and Eubank, with careful correction for the adsorption of water in the Burnett-isochoric apparatus, are in good agreement with the results predicted from the highly accurate EOS of Wagner and Pruss, and the density data for gaseous CO₂–H₂O mixtures agree well with those of Patel et al. and Patel and Eubank. With careful choice of data and the eq 3, the resulting model reproduces the experimental data very well (Table 2 and Figures 1 and 2). The volume data of Blencoe et al. above 35 MPa, which are not used for parametrization, also agree well with the predicted results of the EOS (Figure 2). The good agreement suggests that the EOS can be safely extrapolated up to 100 MPa, which is much higher than the maximum pressure of the data used for parametrization.
Based on the accepted EOS of Wagner and Pruss.97 These deviations can be corrected with the following empirical expression:

\[
F_{\text{cor}} = F_{\text{exp}} - \left( F_{\text{0,exp}} - F_{\text{0,NIST}} \right) c_0 + c_1 P + c_2 P^2 \tag{5}
\]

where \(c_0 = 6.1653 \times 10^{-4}, c_1 = 1.1358 \times 10^{-4}, c_2 = -4.4198 \times 10^{-7}\), \(F_{\text{0,exp}}\) and \(F_{\text{0,NIST}}\) are the corrected and experimental densities for mixtures, respectively, \(F_{\text{0,exp}}\) is the experimental density of pure water, and \(F_{\text{0,NIST}}\) is the pure water density recommended by NIST. The compositions of aqueous CO\(_2\) solutions are calculated as follows:

\[
W_2 = CM_2/\rho_{\text{exp}}
\]

\[
x_2 = \frac{W_2/M_2}{W_2/M_2 + (1.0 - W_2)/M_1}
\]

\[\text{where } W_2 \text{ is the mass fraction of CO}_2, \rho_{\text{exp}} \text{ is the experimental density of solution (g} \cdot \text{cm}^{-3}), C \text{ is the concentration of CO}_2 (\text{mol} \cdot \text{cm}^{-3}) \text{ calculated with eq (11) and eq (12) of Li et al.,}^{100} \text{ and } M_1 \text{ and } M_2 \text{ are the same as in eq 4.}

### 3.2. Parametrization and Test of Model

Before determining the final expression of density or molar volume, it is useful to consider the following points: (1) In the calculation of many thermodynamic properties, a molar volume model expressed in terms of \(P, T, \) and \(x\) is more convenient than a density model with the same independent variables. (2) The existing experimental \(PVTT_x\) properties of CO\(_2\)-H\(_2\)O solutions are usually measured for dilute solution of CO\(_2\) at low to medium pressures (<35 MPa), so the high-order terms of composition and pressure are unnecessary for a practical density model developed mainly for CO\(_2\) sequestration. (3) The change of molar volume due to the dissolution of CO\(_2\) is usually far smaller than the molar volume of pure water, so it can be treated as a perturbation of pure water volume. (4) According to our experiences from extensive trials, positive powers are better at lower temperatures,

### Table 2. Deviations\(^a\) (%) of Predicted Molar Volumes of CO\(_2\)-H\(_2\)O Mixtures

<table>
<thead>
<tr>
<th>ref</th>
<th>AD</th>
<th>MD</th>
<th>(T) range (K)</th>
<th>(P) range (MPa)</th>
<th>(N_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patel et al.(^{92})</td>
<td>0.0589</td>
<td>0.476</td>
<td>323.15–498.15</td>
<td>1–10</td>
<td>423</td>
</tr>
<tr>
<td>Patel and Eubank(^{93})</td>
<td>0.0468</td>
<td>0.447</td>
<td>323.15–498.15</td>
<td>0.086–10.237</td>
<td>297</td>
</tr>
<tr>
<td>Warowny and Eubank(^{95})</td>
<td>0.0971</td>
<td>0.357</td>
<td>448.15–498.15</td>
<td>0.371–8.9985</td>
<td>27</td>
</tr>
<tr>
<td>Fenghour et al.(^{94})</td>
<td>0.2900</td>
<td>2.765</td>
<td>405–644.78</td>
<td>5.7–27.964</td>
<td>110</td>
</tr>
<tr>
<td>Wormald et al.(^{91})</td>
<td>0.8283</td>
<td>2.373</td>
<td>473.2–623.2</td>
<td>1–12</td>
<td>43</td>
</tr>
<tr>
<td>Blencoe et al.(^{96})</td>
<td>1.0111</td>
<td>2.752</td>
<td>573.15–573.15</td>
<td>7.44–99.93</td>
<td>147</td>
</tr>
<tr>
<td>All the six data sets above</td>
<td>0.2459</td>
<td>2.765</td>
<td>323.15–644.78</td>
<td>0.086–99.93</td>
<td>1047</td>
</tr>
</tbody>
</table>

\[\text{a } AD = \text{average deviation, } MD = \text{maximum deviation, } N_d = \text{no. of data points.} \text{ Under the conditions of these data, many mixtures are present in liquid.} \]

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**Figure 1.** Compressibility factors and quasi-isochores of gaseous CO\(_2\)-H\(_2\)O mixtures. The quasi-isochores in (d) mean that the volumes of the points on a given curve are not the same, but slightly different from each other.
and negative powers are better at higher temperatures. This is because positive power terms are too sensitive at higher temperatures, and negative power terms are too sensitive at lower temperatures. In order to obtain good performance over a wide temperature range, both positive and negative powers are used in the parameter expressions. The considerations above lead to the following expression:

\[
V = V_1 [1 + (A_1 + A_2 P) x_2] \\
A_i = A_{i1} T^2 + A_{i2} T + A_{i3} + A_{i4} T^{-1} + A_{i5} T^{-2} \quad (i = 1, 2) \tag{7}
\]

where \(V\), \(V_1\), and \(x_2\) are solution volume, water volume, and the mole fraction of CO\(_2\), respectively. The units of \(T\) and \(P\) are K and MPa, respectively. \(V_1\) is calculated with the IAPWS97 EOS.\(^{101}\) The values of \(A_j\)'s (Table 3) are regressed from experimental data.\(^{71,98–100}\) The correlation coefficient \(R^2\) of the regression is 0.999956. In fact, if the pressure and temperature are in the range 273.15–473.15 K and 0–200 MPa, \(V_1\) can be replaced with the model of Hu et al.,\(^{53}\) which can reproduce the water volumes of Wagner and Pruss\(^{97}\) within 0.027%, where the average deviation is only 0.005%.

From eq 7, it is easy to obtain the apparent molar volume of CO\(_2\):

\[
V_{\text{app}} = (V - x_1 V_1) / x_2 = V_1 (1 + A_1 + A_2 P) \tag{8}
\]

Equation 7 or 8 can be used to obtain the liquid densities of the binary mixtures. As can be seen from eqs 7 and 8, the pressure and temperature dependences of molar volume or apparent molar volume are all taken into account in one equation, and this is distinct from many of the existing density models. The present model is compared with extensive experimental data and other models listed in Table 4. The results are given in Tables 5 and 6 and Figures 5–7. Note that in the model of Bachu and Adams\(^{73}\) the molar volume of water is calculated with the model of Batzle and Wang;\(^{102}\) in other models, it is calculated with the IAPWS97 EOS.\(^{101}\) It is interesting that the old density difference data measured by Blair and Quinn\(^{103}\) are in excellent agreement with the predicted results of this model (Figure 7). It is well-known that the apparent molar volume of a solute in water is a very sensitive indication of a density model. The relative error of this quantity is usually about 2 orders of magnitude larger than the relative error of density. It should be noted that the molar volumes of Ellis and McFadden\(^{104}\) are predicted well by this model (Table 5 and 6), although they are not used in the parametrization. The apparent molar volumes of Barbero et al.\(^{105}\) and Ohsumi et al.\(^{98}\) are also predicted very well, and the deviations are within the experimental uncertainties. Ohsumi et al.\(^{98}\) reported that the apparent molar volumes of dilute CO\(_2\) solutions at 276.15 K and 34.75 MPa are about 31 ± 0.9 cm\(^3\)·mol\(^{-1}\), which is slightly different from their

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**Figure 2.** Isobars of the CO\(_2\)–H\(_2\)O mixtures at 573.15 K.

**Figure 3.** Calibration errors of the pure water densities of Hnedkovsky et al.\(^{89}\)

**Table 3.** Constants in Equation 7

<table>
<thead>
<tr>
<th>(j)</th>
<th>(A_{j1})</th>
<th>(A_{j2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-0.383840 \times 10^{-3})</td>
<td>(-0.577093 \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>(-0.559538 \times 10^{0})</td>
<td>(0.827646 \times 10^{-2})</td>
</tr>
<tr>
<td>3</td>
<td>(0.304292 \times 10^{3})</td>
<td>(-0.438135 \times 10^{1})</td>
</tr>
<tr>
<td>4</td>
<td>(-0.720443 \times 10^{5})</td>
<td>(0.101449 \times 10^{4})</td>
</tr>
<tr>
<td>5</td>
<td>(0.630033 \times 10^{7})</td>
<td>(-0.867770 \times 10^{5})</td>
</tr>
</tbody>
</table>

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Table 4. Models for the Densities of CO₂–H₂O Solutions and the Apparent or Partial Molar Volumes of CO₂ in Water at Infinite Dilution

<table>
<thead>
<tr>
<th>authors</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Song et al.</td>
<td>ρ = ρᵣ(1 + 0.275η) (γ = wCO₂)</td>
</tr>
<tr>
<td>Teng et al.</td>
<td>ρ = ρᵣ(kg·m⁻³) + 1.96 × 10² xCO₂ + 1.54 × 10⁴ x²CO₂</td>
</tr>
<tr>
<td>Bachu and Adams</td>
<td>ρ = ρᵣ[1 − χ₀w(1 − ρSV/M₂)] (χ₀w = WCO₂)</td>
</tr>
<tr>
<td>Garcia²⁴</td>
<td>Vₑ = 37.51 − 9.585 × 10⁻²t + 8.740 × 10⁻⁴t² − 5.044 × 10⁻⁷t³</td>
</tr>
<tr>
<td>Andersen et al.</td>
<td>Vₑ = 37.36 − 7.109 × 10⁻²t − 3.812 × 10⁻⁴t² + 3.296 × 10⁻⁶t³</td>
</tr>
<tr>
<td>Ennis–King²⁴</td>
<td>Vₑ = 35.663 − 5.960 × 10⁻²t + 6.308 × 10⁻³t²</td>
</tr>
<tr>
<td>Enick and Klara</td>
<td>Vₑ = 1799.36 − 17.821t£ + 6.59297 × 10⁻²t² − 1.0579 × 10⁻⁴t³ + 6.200275 × 10⁻³t²</td>
</tr>
<tr>
<td>Iglesias and Moya</td>
<td>Vₑ = exp[154.7881 − 3582.452/t − 26.7757773 log(t) + 0.045234908t]</td>
</tr>
<tr>
<td>Sedlbauer et al.</td>
<td>Vₑ = 0.045234908t</td>
</tr>
<tr>
<td>Plyasunov et al.</td>
<td>Vₑ = 0.0235 0.2323 0.4350 0.1438 0.6835 0.6835</td>
</tr>
</tbody>
</table>

Table 5. Average Deviations (%) of Predicted Molar Volumes of Aqueous CO₂ Solutions

<table>
<thead>
<tr>
<th>modela</th>
<th>Ellis</th>
<th>Ohsumi</th>
<th>Hnedkovsky</th>
<th>Li</th>
<th>Songb</th>
<th>all data</th>
</tr>
</thead>
<tbody>
<tr>
<td>this model</td>
<td>0.0173</td>
<td>0.0304</td>
<td>0.0195</td>
<td>0.0146</td>
<td>0.003</td>
<td>0.0078</td>
</tr>
<tr>
<td>Song et al.</td>
<td>0.0039</td>
<td>0.0316</td>
<td>0.2211</td>
<td>0.2719</td>
<td></td>
<td>0.0847</td>
</tr>
<tr>
<td>Teng et al.</td>
<td>0.0114</td>
<td>0.1788</td>
<td>0.1751</td>
<td>0.1043</td>
<td>0.2907</td>
<td>0.2367</td>
</tr>
<tr>
<td>Bachu and Adams</td>
<td>0.1973</td>
<td>0.1931</td>
<td>0.7800</td>
<td>0.0792</td>
<td>0.4232</td>
<td>0.3910</td>
</tr>
<tr>
<td>Garcia²⁴</td>
<td>0.0061</td>
<td>0.1479</td>
<td>0.0626</td>
<td>0.0653</td>
<td>0.3807</td>
<td>0.2760</td>
</tr>
<tr>
<td>Andersen et al.</td>
<td>0.0038</td>
<td>0.1459</td>
<td>0.0907</td>
<td>0.1340</td>
<td>0.3766</td>
<td>0.2958</td>
</tr>
<tr>
<td>Ennis–King²⁴</td>
<td>0.0060</td>
<td>0.1080</td>
<td>0.0558</td>
<td>0.0857</td>
<td>0.2569</td>
<td>0.2017</td>
</tr>
<tr>
<td>Enick and Klara</td>
<td>0.0038</td>
<td>0.1734</td>
<td>0.3030</td>
<td>0.3516</td>
<td>0.4162</td>
<td>0.3809</td>
</tr>
<tr>
<td>Iglesias and Moya</td>
<td>0.0046</td>
<td>0.3208</td>
<td>0.0932</td>
<td>0.0956</td>
<td>0.9209</td>
<td>0.6190</td>
</tr>
<tr>
<td>Sedlbauer et al.</td>
<td>0.0093</td>
<td>0.0869</td>
<td>0.0171</td>
<td>0.0977</td>
<td>0.1843</td>
<td>0.1263</td>
</tr>
<tr>
<td>Plyasunov et al.</td>
<td>0.0094</td>
<td>0.0383</td>
<td>0.0056</td>
<td>0.0468</td>
<td>0.0817</td>
<td>0.0686</td>
</tr>
</tbody>
</table>

Graphical report. According to our calculation, the average value is about 31.2 ± 1.1 cm³·mol⁻¹, which is in excellent agreement with this model (31.4 cm³·mol⁻¹).

In the test above, the highest pressure of experimental volumetric data is 35 MPa. At higher pressures (35–100 MPa), the data of Blencoe et al.⁶⁹ are considered to be of reasonable accuracy. This data set is not used in the model parametrization, but used as a test of the predictability of the model. Figure 8 shows that the data of Blencoe et al.⁶⁹ can be predicted well. At higher pressures (>100 MPa), no volumetric data are available for the dilute CO₂ solutions. Nevertheless, it is found

Table 6. Maximum Deviations (%) of Predicted Molar Volumes of Aqueous CO₂ Solutions

<table>
<thead>
<tr>
<th>modela</th>
<th>Ellis</th>
<th>Ohsumi</th>
<th>Hnedkovsky</th>
<th>Li</th>
<th>Songb</th>
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Graphical report. According to our calculation, the average value is about 31.2 ± 1.1 cm³·mol⁻¹, which is in excellent agreement with this model (31.4 cm³·mol⁻¹).

In the test above, the highest pressure of experimental volumetric data is 35 MPa. At higher pressures (35–100 MPa), the data of Blencoe et al.⁶⁹ are considered to be of reasonable accuracy. This data set is not used in the model parametrization, but used as a test of the predictability of the model. Figure 8 shows that the data of Blencoe et al.⁶⁹ can be predicted well. At higher pressures (>100 MPa), no volumetric data are available for the dilute CO₂ solutions. Nevertheless, it is found

4. Liquid Density Model for the CO₂–H₂O–NaCl System

4.1. Selection and Correction of Experimental Data. The density data of Song et al.⁸⁰ for CO₂ seawater seem to be of high quality,⁵³ but they did not report the densities of the CO₂-free seawater (3.5 wt % NaCl), which are supplemented with the model of Rogers and Pitzer⁶⁶ in this work. Song et al.¹⁰⁷ reported some accurate ratios of CO₂-bearing seawater densities with respect to CO₂-free seawater densities (see also

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Song et al.\textsuperscript{108}. The other density or volume data sets for the CO$_2$–H$_2$O–NaCl liquids or CO$_2$-bearing brines\textsuperscript{81,100,109,110} were found to have systematic deviations or large uncertainties.\textsuperscript{53} Recently, some new density data\textsuperscript{111,112} are reported, but they also have similar quality problem. Nevertheless, the density data of Li et al.\textsuperscript{100} for the CO$_2$-free and CO$_2$-bearing Weyburn Formation brines can be corrected in a simple way. Figure 10 shows that the densities of the CO$_2$-free brine of Li et al.\textsuperscript{100} are systematically larger than the predicted values of the accurate model of Rogers and Pitzer\textsuperscript{106} for NaCl solutions. The deviations can be accurately formulated with the following function:

$$F_{\text{0,exp}} - F_{\text{0,Rogers}} = c_0 + c_1 P + c_2 P^2 \tag{9}$$

where $c_0 = 4.61111 \times 10^{-3}$, $c_1 = +1.06999 \times 10^{-4}$, $c_2 = -2.84112 \times 10^{-7}$, $F_{\text{0,exp}}$ is experimental density, $F_{\text{0,Rogers}}$ is the density calculated from the model of Rogers and Pitzer\textsuperscript{106} for NaCl solutions. The CO$_2$ solubilities are calculated with the model of Duan et al.\textsuperscript{61}
Because the densities of CO$_2$-free and CO$_2$-bearing Weyburn Formation brines were measured with the same technique under similar P–T conditions, it should be a good approximation to assume the same density deviation for the CO$_2$-free and CO$_2$-bearing brines at the same pressure and temperature. With this assumption, the experimental densities of the CO$_2$-bearing brine can be corrected as follows:

$$ F_{\text{cor}} = F_{\exp} - (F_{0,\exp} - F_{0,\text{Rogers}}) \quad (10) $$

where $F_{\text{cor}}$ and $F_{\exp}$ are the corrected and experimental densities of CO$_2$-bearing brine, respectively.

According to the analysis above, we use the density data of Song et al.$^{80,107}$ and the corrected density data of Li et al.$^{100}$ to test the density model in this work.

### 4.2. The Density Model

The CO$_2$–H$_2$O–NaCl system can be obtained by adding CO$_2$ to the H$_2$O–NaCl system, so the H$_2$O–NaCl system can be regarded as a hypothetical “pure” component (solvent). Accordingly, the density ($\rho$) and molar volume ($V$) of the CO$_2$–H$_2$O–NaCl system can be rigorously formulated as

$$ \rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V} \quad (11) $$

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Ax_1x_2, where A is an interaction parameter depending on P, T, and x. This suggests that the contribution of ion–CO_2 interactions to the *excess partial molar volume* of CO_2 (V_{2Ex}) at given P and T tends to *vanish* if the salinity is low enough. Similarly, the effect of salts on V_{φ,2} at low salinity is also very small. In fact, the brines in the CO_2 sequestration environments and many industrial processes are usually dilute, typically of the order of seawater salinity or lower. On the other hand, because of the low solubility of CO_2 in water, the CO_2 concentrations are usually less than 3 mol %. In brines, the solubility of CO_2 decreases rapidly with increasing salinity. Therefore, the possibilities of the CO_2–Na^+ and CO_2–Cl^- pairs appearing in solutions are usually very small. In these cases, we can neglect the effect of salts on V_{φ,2}. That is, V_{φ,2} can be approximated with the apparent molar volume of CO_2 in pure water (V_{φ,2}^B):

\[ V = x_1 V_1 + x_2 V_{φ,2}^B + x_3 V_{φ,3}^B \]  

(14)

where V_{φ,2}^B is predicted with eq 8, and V_{φ,3}^B is predicted from the model of Rogers and Pitzer. Eq 14 is tested with the density data of Song et al. and the corrected density data of Li et al. Also tested are some other density models, whose expressions are given in Table 7. Note that in the model of Bachu and Adams, the volume of CO_2-free brine is calculated with the model of Batzle and Wang; in the other models, it is calculated with the model of Rogers and Pitzer, where water volume is calculated with the IAPWS97 EOS. The results of these calculations are summarized in Figure 11.

As can be seen, eq 14 can accurately reproduce the experimental data within the error ranges without using any ternary interaction parameter, where the average deviations of eq 14 from the three experimental results of Song et al. and Li et al. are 0.010%, 0.029%, and 0.026%, respectively, and the maximum deviations are 0.016%, 0.050%, and 0.075%, respectively. The model of Song et al. and Li et al. correlated from their own density data gives the worst prediction of the density data of Li et al. Similarly, the other models cannot give satisfactory prediction of the two sets of data. The large deviations of these models should be attributed to their simple approximations, where the effects of pressure, temperature and composition on density are not completely or properly taken into account.

Recently, Pruess and Spycher proposed a density model for the CO_2–H_2O–NaCl system by using an approximation equivalent to eq 12. Like the work of Bachu and Adams, they used the apparent molar volumes of CO_2 in pure water at infinite dilution calculated from the model of Garcia, which are not accurate enough at the conditions of CO_2 storage, especially at low temperatures. The results in Figure 6 and Tables 5 and 6 also suggest that the model is inadequate.

### 5. Conclusions

A hybrid model is proposed for the PVTx properties of the CO_2–H_2O and CO_2–H_2O–NaCl systems up to 100 MPa, where the gaseous CO_2–H_2O mixtures are represented with a revised equation of state of Duan et al. and the liquid CO_2–H_2O mixtures with a density model with P, T, and x as independent variables. The IAPWS97 EOS for the volumes of pure water is used as a reference of the density model. Based on the above liquid density model and the H_2O–NaCl model of Rogers and Pitzer a predictive model is developed for the ternary liquid volumes and densities. The models above can accurately predict the experimental PVTx properties within the range of experimental errors, where the binary models can be used up to 623 K, and the ternary model is valid up to 573 K.

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