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# Densities of the CO<sub>2</sub>–H<sub>2</sub>O and CO<sub>2</sub>–H<sub>2</sub>O–NaCl Systems Up to 647 K and 100 MPa

Zhenhao Duan,<sup>\*,†</sup> Jiawen Hu,<sup>†,‡</sup> Dedong Li,<sup>†</sup> and Shide Mao<sup>§</sup>

*The Key Laboratory of the Study of Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China; College of Resources, Shijiazhuang University of Economics, Shijiazhuang 050031, Hebei, China; and School of Earth Sciences and Resources, Chinese University of Geosciences, 100083 Beijing, China*

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An equation of state is established for the gas phase of CO<sub>2</sub>–H<sub>2</sub>O in the range 0–28 MPa and 323–645 K. The equation for gaseous CO<sub>2</sub>–H<sub>2</sub>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<sub>2</sub>–H<sub>2</sub>O and CO<sub>2</sub>–H<sub>2</sub>O–NaCl mixtures is developed. The most accurate experimental density data for the CO<sub>2</sub>–H<sub>2</sub>O system in the range 273–623 K and 0.7–35 MPa can be reproduced within  $\pm 0.05\%$ , and the average deviation is 0.008%. The model for the liquid CO<sub>2</sub>–H<sub>2</sub>O–NaCl mixtures is developed on the basis of our CO<sub>2</sub>–H<sub>2</sub>O model and the H<sub>2</sub>O–NaCl model of Rogers and Pitzer (*J. Phys. Chem. Ref. Data* 1982, 11 (1), 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<sub>2</sub>–H<sub>2</sub>O and CO<sub>2</sub>–H<sub>2</sub>O–NaCl are typical geological fluids in many geochemical processes.<sup>1–15</sup> Pressure–volume–temperature–composition (PVTx) properties and phase equilibrium are fundamental in the quantitative interpretation of geochemical

data.<sup>2,8,16–27</sup> For example, predicting CO<sub>2</sub> behavior after geological storage needs accurate knowledge of both phase relations and densities.<sup>28–43</sup> This knowledge is also very important in many industrial processes, such as the production of oil and

\* Author to whom correspondence should be addressed. E-mail: duanzhenhao@yahoo.com.

<sup>†</sup> Chinese Academy of Sciences.

<sup>‡</sup> Shijiazhuang University of Economics.

<sup>§</sup> Chinese University of Geosciences.

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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.<sup>33,34,38,44–52</sup>

The phase equilibrium and PVT<sub>x</sub> properties of the NaCl-H<sub>2</sub>O system have been studied extensively.<sup>53–56</sup> There are also systematic experimental studies and thermodynamic modeling of the bubble-point compositions (or CO<sub>2</sub> solubilities) of the systems CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl.<sup>30,43,57–70</sup> Some models are available for the dew-point curves (namely vapor-phase boundaries) of the two systems.<sup>62–64</sup> 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 fate of injected CO<sub>2</sub> fluids and the capacity and safety of CO<sub>2</sub> storage in the sea or in a geological formation.<sup>53</sup> Therefore, this study focuses on the modeling of densities and other volumetric properties including molar volumes and apparent

molar volumes of the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl systems below the critical temperature of H<sub>2</sub>O, *T*<sub>C</sub>(H<sub>2</sub>O).

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 PVT<sub>x</sub> data of the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl systems.<sup>53</sup> It is known that the net increase in solution density due to CO<sub>2</sub> dissolution is usually very small (less than 2% of pure water density) under the *P*-*T*-*x* conditions of CO<sub>2</sub> storage, and a density difference of about 0.1 kg·m<sup>-3</sup> is enough to drive a natural CO<sub>2</sub>-bearing solution to either sink or buoy.<sup>29</sup>

Currently, some models have been developed to correlate or predict the apparent or partial molar volumes, or densities of the CO<sub>2</sub>-H<sub>2</sub>O solutions.<sup>30,42,43,69–79</sup> There are a few models for the volumetric properties of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl/brine solutions.<sup>42,73,80–82</sup> Many equations of state (EOS) are available for the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl systems, such as those of Duan et al.,<sup>83,84</sup> Ji et al.,<sup>85</sup> Spycher and Reed,<sup>86</sup> Nitsche et al.,<sup>87</sup> Churakov and Gottschalk,<sup>88,89</sup> and Li et al.<sup>90</sup> 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 CO<sub>2</sub> storage.<sup>53</sup>

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 CO<sub>2</sub>-H<sub>2</sub>O-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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**Table 1. Constants in Equation 3**

<i>i</i>	<i>A<sub>i</sub></i>
1	−0.624 0078 × 10 <sup>−3</sup>
2	0.924 8008 × 10 <sup>0</sup>
3	0.528 2536 × 10 <sup>−2</sup>
4	−0.250 9670 × 10 <sup>1</sup>
5	−0.310 1373 × 10 <sup>−2</sup>
6	0.279 4819 × 10 <sup>1</sup>

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 CO<sub>2</sub>–H<sub>2</sub>O Mixtures

Duan et al.<sup>84</sup> developed a virial-type equation of state for the CH<sub>4</sub>–CO<sub>2</sub>–H<sub>2</sub>O system:

$$Z = \frac{PV}{RT} = 1 + \frac{BV_C}{V} + \frac{CV_C^2}{V^2} + \frac{DV_C^4}{V^4} + \frac{EV_C^5}{V^5} + \frac{FV_C^2}{V^2} \left( \beta + \frac{\gamma V_C^2}{V^2} \right) \exp \left( -\frac{\gamma V_C^2}{V^2} \right) \quad (1)$$

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

$$B_{ij} = [(B_i^{1/3} + B_j^{1/3})/2]^3 k_{1,ij}, \quad C_{ijk} = [(C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3]^3 k_{2,ijk} \\ \gamma_{ijk} = [(\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3})/3]^3 k_{3,ijk} \quad (2)$$

where *k*<sub>1,12</sub>, *k*<sub>2,112</sub>, *k*<sub>2,122</sub> and *k*<sub>3,112</sub>, *k*<sub>3,122</sub> are empirical temperature functions fitted from experimental data. In the original equation, it was assumed that *k*<sub>2,112</sub> = *k*<sub>2,122</sub> and *k*<sub>3,112</sub> = *k*<sub>3,122</sub>. This equation has good overall accuracy in both gas and liquid PVT<sub>x</sub> properties, but its volume deviations are often larger than (or close to) the density increments due to the CO<sub>2</sub> dissolution, so it is still inadequate for the modeling of CO<sub>2</sub> 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:

$$k_{1,12} = A_1 T + A_2 \\ k_{2,112} = A_3 T + A_4 \\ k_{2,122} = A_5 T + A_6 \\ k_{3,112} = K_{3,122} = 1 \quad (3)$$

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.,<sup>91</sup> Patel et al.,<sup>92</sup> Patel and Eubank,<sup>93</sup> Fenghour et al.,<sup>94</sup> and Warowny and Eubank<sup>95</sup> and

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those of Blencoe et al.<sup>96</sup> below 35 MPa. The correlation coefficient *R*<sup>2</sup> of the regression is 0.999 89. Most of these data, except for those of Warowny and Eubank,<sup>95</sup> have been assessed and were considered to be of good accuracy.<sup>53</sup> The density data for water steam of Warowny and Eubank,<sup>95</sup> 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,<sup>97</sup> and the density data for gaseous CO<sub>2</sub>–H<sub>2</sub>O mixtures<sup>95</sup> agree well with those of Patel et al.<sup>92</sup> and Patel and Eubank.<sup>93</sup> 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.<sup>96</sup> 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.

## 3. Liquid Density Model for the CO<sub>2</sub>–H<sub>2</sub>O System

### 3.1. Selection and Correction of Experimental Data.

According to the assessment of Hu et al.,<sup>53</sup> many groups of experimental data for the aqueous CO<sub>2</sub> 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<sup>71,98–100</sup> to regress the model parameters. However, some important issues regarding these data must be clarified:

1. Ohsumi et al.<sup>98</sup> and Song et al.<sup>71</sup> presented graphical reports of the density changes due to the dissolution of CO<sub>2</sub>, leaving the corresponding densities of pure water (*ρ*<sub>w</sub>) unknown. In order to obtain the solution densities, we supplement the pure water densities with the IAPWS97 EOS,<sup>101</sup> where the EOS is considered to be highly accurate. The density differences of Ohsumi et al.<sup>98</sup> are read from their figure, and the ratios of the solution and pure water densities reported by Song et al.<sup>71</sup> 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.<sup>99</sup> can be reproduced with the following equation:

$$\rho = \rho_1 + \Delta\rho = (x_1 M_1 + x_2 M_2) / (x_1 M_1 / \rho_1 + x_2 V_{\varphi,2}) \quad (4)$$

where *ρ* is the density of solution, *V*<sub>φ,*i*</sub>, *ρ<sub>i</sub>*, *M<sub>i</sub>*, and *x<sub>i</sub>* are the apparent molar volume, density, molar mass, and mole fraction of pure component *i*, respectively. The subscripts 1 and 2 denote H<sub>2</sub>O and CO<sub>2</sub>, respectively. It is found that the errors of pure water densities in the calibration of Hnedkovsky et al.<sup>99</sup> are generally within 0.3%, but the largest error can be up to about 2% (Figure 3). Here we use the IAPWS97 EOS<sup>101</sup> to replace the calibration of Hnedkovsky et al.<sup>99</sup>

3. Figure 4 shows that the pure water densities of Li et al.<sup>100</sup> have systematic deviations from the values recommended by

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(97) Wagner, W.; Pruss, A. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387.

(98) Ohsumi, T.; Nakashiki, N.; Shitashima, K.; Hiram, K. *Energy Convers. Manage.* **1992**, *33* (5–8), 685.

(99) Hnedkovsky, L.; Wood, R. H.; Majer, V. *J. Chem. Thermodyn.* **1996**, *28* (2), 125.

(100) Li, Z.; Dong, M.; Li, S.; Dai, L. *J. Chem. Eng. Data* **2004**, *49* (4), 1026.

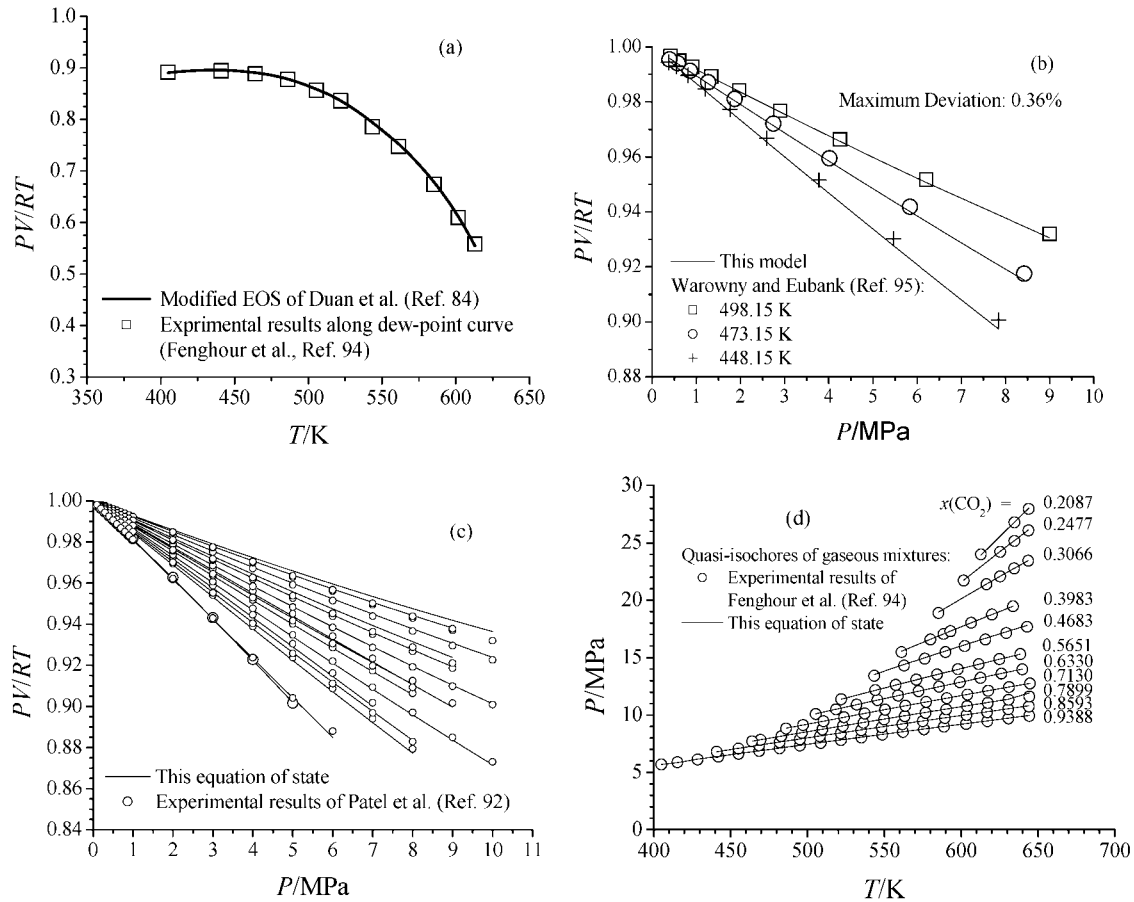
(101) Wagner, W.; Cooper, J. R.; Dittmann, A.; Kijima, J.; Kretschmar, H.-J.; Kruse, A.; Mares, R.; Oguchi, K.; Sato, H.; Stocker, I.; Sifner, O.; Takaishi, Y.; Tanishita, I.; Trubenbach, J.; Willkommen, T. *J. Eng. Gas Turbines Power* **2000**, *122* (1), 150.



Table 2. Deviations<sup>a</sup> (%) of Predicted Molar Volumes of CO<sub>2</sub>-H<sub>2</sub>O Mixtures

ref	AD	MD	<i>T</i> range (K)	<i>P</i> range (MPa)	<i>N<sub>d</sub></i>
Patel et al. <sup>92</sup>	0.0589	0.476	323.15–498.15	1–10	423
Patel and Eubank <sup>93</sup>	0.0468	0.447	323.15–498.15	0.086–10.237	297
Warowny and Eubank <sup>95</sup>	0.0971	0.357	448.15–498.15	0.371–8.9985	27
Fenghour et al. <sup>94</sup>	0.2900	2.765	405–644.78	5.7–27.964	110
Wormald et al. <sup>91</sup>	0.8283	2.373	473.2–623.2	1–12	43
Blencoe et al. <sup>96</sup>	1.011	2.752	573.15–573.15	7.44–99.93	147 <sup>b</sup>
All the six data sets above	0.2459	2.765	323.15–644.78	0.086–99.93	1047

<sup>a</sup> AD = average deviation, MD = maximum deviation, *N<sub>d</sub>* = no. of data points. <sup>b</sup> Under the conditions of these data, many mixtures are present in liquid.



**Figure 1.** Compressibility factors and quasi-isochores of gaseous CO<sub>2</sub>-H<sub>2</sub>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.

the National Institute of Standards and Technology (NIST, <http://webbook.nist.gov/chemistry/fluid>) based on the accepted EOS of Wagner and Pruss.<sup>97</sup> These deviations can be corrected with the following empirical expression:

$$\begin{aligned} \rho_{\text{cor}} &= \rho_{\text{exp}} - (\rho_{0,\text{exp}} - \rho_{0,\text{NIST}}) \\ \rho_{0,\text{exp}} - \rho_{0,\text{NIST}} &= c_0 + c_1 P + c_2 P^2 \end{aligned} \quad (5)$$

where  $c_0 = 6.1653 \times 10^{-4}$ ,  $c_1 = 1.1358 \times 10^{-4}$ ,  $c_2 = -4.4198 \times 10^{-7}$ ,  $\rho_{\text{cor}}$  and  $\rho_{\text{exp}}$  are the corrected and experimental densities for mixtures, respectively,  $\rho_{0,\text{exp}}$  is the experimental density of pure water, and  $\rho_{0,\text{NIST}}$  is the pure water density recommended by NIST. The units of pressure and density are MPa and  $\text{g} \cdot \text{cm}^{-3}$ , respectively. The compositions of aqueous CO<sub>2</sub> solutions are calculated as follows:

$$\begin{aligned} W_2 &= CM_2 / \rho_{\text{exp}} \\ x_2 &= \frac{W_2 / M_2}{W_2 / M_2 + (1.0 - W_2) / M_1} \end{aligned} \quad (6)$$

where  $W_2$  is the mass fraction of CO<sub>2</sub>,  $\rho_{\text{exp}}$  is the experimental density of solution ( $\text{g} \cdot \text{cm}^{-3}$ ),  $C$  is the concentration of CO<sub>2</sub> ( $\text{mol} \cdot \text{cm}^{-3}$ ) calculated with eq (11) and eq (12) of Li et al.,<sup>100</sup> and  $M_i$  and  $x_i$  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  $PVTx$  properties of CO<sub>2</sub>-H<sub>2</sub>O solutions are usually measured for dilute solution of CO<sub>2</sub> 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<sub>2</sub> sequestration. (3) The change of molar volume due to the dissolution of CO<sub>2</sub> 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,

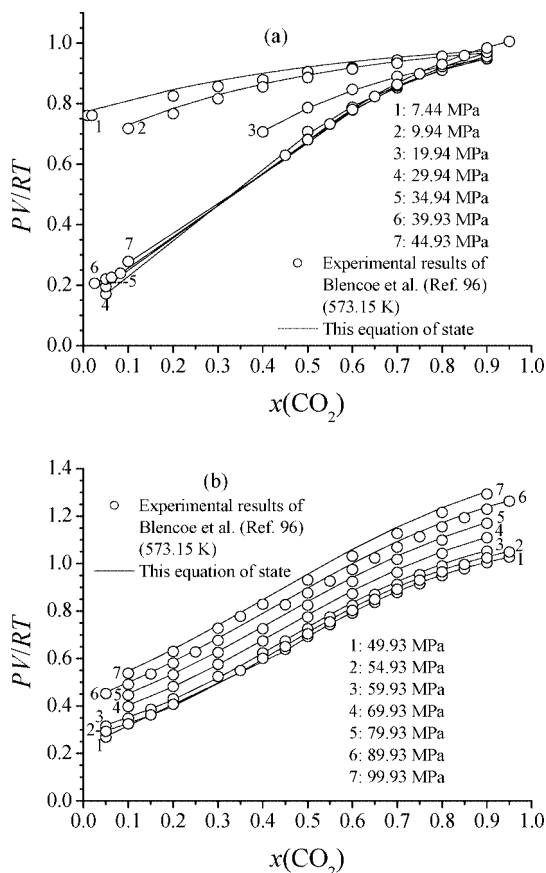


Figure 2. Isobars of the CO<sub>2</sub>-H<sub>2</sub>O mixtures at 573.15 K.

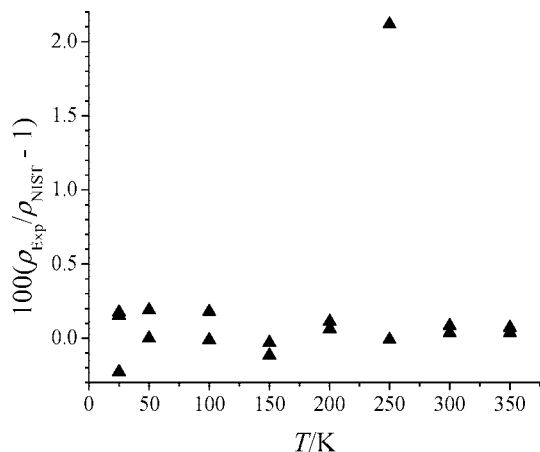


Figure 3. Calibration errors of the pure water densities of Hnedkovsky et al.<sup>99</sup>

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:

$$V = V_1[1 + (A_1 + A_2P)x_2] \\ A_i = A_{i1}T^2 + A_{i2}T + A_{i3} + A_{i4}T^{-1} + A_{i5}T^{-2} \quad (i = 1, 2) \quad (7)$$

where  $V$ ,  $V_1$ , and  $x_2$  are solution volume, water volume, and the mole fraction of CO<sub>2</sub>, respectively. The units of  $T$  and  $P$  are K and MPa, respectively.  $V_1$  is calculated with the IAPWS97 EOS.<sup>101</sup> The values of  $A_{ij}$ 's (Table 3) are regressed from

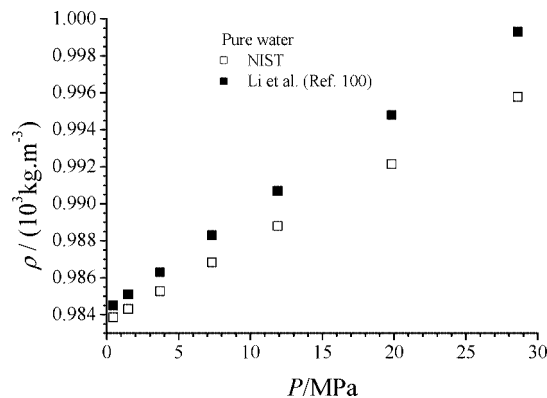


Figure 4. Systematic deviations of the densities of pure water measured by Li et al.<sup>100</sup> from the accepted values recommended by NIST.

Table 3. Constants in Equation 7

$j$	$A_{1j}$	$A_{2j}$
1	$0.383\,840\,20 \times 10^{-3}$	$-0.577\,093\,32 \times 10^{-5}$
2	$-0.559\,538\,50 \times 10^0$	$0.827\,646\,53 \times 10^{-2}$
3	$0.304\,292\,68 \times 10^3$	$-0.438\,135\,56 \times 10^1$
4	$-0.720\,443\,05 \times 10^5$	$0.101\,449\,07 \times 10^4$
5	$0.630\,033\,88 \times 10^7$	$-0.867\,770\,45 \times 10^5$

experimental data.<sup>71,98–100</sup> The correlation coefficient  $R^2$  of the regression is 0.999 956. 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.,<sup>53</sup> which can reproduce the water volumes of Wagner and Pruss<sup>97</sup> 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<sub>2</sub>:

$$V_{\phi,2} = (V - x_1V_1)/x_2 = V_1(1 + A_1 + A_2P) \quad (8)$$

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<sup>73</sup> the molar volume of water is calculated with the model of Batzle and Wang;<sup>102</sup> in other models, it is calculated with the IAPWS97 EOS.<sup>101</sup> It is interesting that the old density difference data measured by Blair and Quinn<sup>103</sup> 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<sup>104</sup> are predicted well by this model (Tables 5 and 6), although they are not used in the parametrization. The apparent molar volumes of Barbero et al.<sup>105</sup> and Ohsumi et al.<sup>98</sup> are also predicted very well, and the deviations are within the experimental uncertainties. Ohsumi et al.<sup>98</sup> reported that the apparent molar volumes of dilute CO<sub>2</sub> solutions at 276.15 K and 34.75 MPa are about  $31 \pm 0.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ , which is slightly different from their

(102) Batzle, M.; Wang, Z. *Geophysics* **1992**, 57 (11), 1396.

(103) Blair, L. M.; Quinn, J. A. *Rev. Sci. Instrum.* **1968**, 39 (1), 75.

(104) Ellis, A. J.; McFadden, I. M. *Geochim. Cosmochim. Acta* **1972**, 36, 413.

(105) Barbero, J.; Hepler, L. G.; McCurdy, K. G.; Tremaine, P. R. *Can. J. Chem.* **1983**, 61, 2509.

**Table 4. Models for the Densities of CO<sub>2</sub>–H<sub>2</sub>O Solutions and the Apparent or Partial Molar Volumes of CO<sub>2</sub> in Water at Infinite Dilution**

authors	model
Song et al. <sup>71</sup>	$\rho = \rho_w(1 + 0.275\chi)$ ( $\chi = w_{\text{CO}_2}$ )
Teng et al. <sup>72</sup>	$\rho = \rho_w/(\text{kg}\cdot\text{m}^{-3}) + 1.96 \times 10^2 x_{\text{CO}_2} + 1.54 \times 10^4 x^2 \text{CO}_2$
Bachu and Adams <sup>73</sup>	$\rho = \rho_w/[1 - X_{\text{sol}}(1 - \rho_w V_\varphi/M_2)]$ ( $X_{\text{sol}} = W_{\text{CO}_2}$ )
Garcia <sup>74a</sup>	$V_\varphi = 37.51 - 9.585 \times 10^{-2}t + 8.740 \times 10^{-4}t^2 - 5.044 \times 10^{-7}t^3$
Andersen et al. <sup>75a</sup>	$V_\varphi = 37.36 - 7.109 \times 10^{-2}t - 3.812 \times 10^{-5}t^2 + 3.296 \times 10^{-6}t^3 - 3.702 \times 10^{-9}t^4$
Ennis–King <sup>74a</sup>	$V_\varphi = 35.663 - 5.960 \times 10^{-2}t + 6.308 \times 10^{-4}t^2$
Enick and Klara <sup>76</sup>	$V_\varphi = 1799.36 - 17.8218T + 6.59297 \times 10^{-2}T^2 - 1.0579 \times 10^{-4}T^3 + 6.200275 \times 10^{-8}T^4$
Iglesias and Moya <sup>77</sup>	$V_\varphi = \exp[154.7881 - 3582.452/T - 26.7757773 \log(T) + 0.045234908T]$
Sedlbauer et al. <sup>78b</sup>	$V_2^0 = \kappa_0 RT + d(V_0 - \kappa_0 RT) + \kappa_0 RT \rho_0 \{a + c \exp(\theta/T) + b[\exp(\theta \rho_0) - 1] + \delta[\exp(\lambda \rho_0) - 1]\}$
Plyasunov et al. <sup>79b</sup>	$V_2^0 = NV_1^0 + \kappa RT(1 - N) + \kappa RT \rho \{2\Omega(B_{12} - NB_{11}) \exp(-c_1 \rho) + (a/T^5 + b)[\exp(c_2 \rho) - 1]\}$

<sup>a</sup>  $t$  = temperature in °C. <sup>b</sup>  $\kappa_0$ ,  $\rho_0$ ,  $V_0$  (or  $\kappa$ ,  $\rho$ ,  $V_1^0$ ) = isothermal compressibility, specific density, and molar volume of water, respectively.

**Table 5. Average Deviations (%) of Predicted Molar Volumes of Aqueous CO<sub>2</sub> Solutions**

model <sup>a</sup>	Ellis	Ohsumi	Hnedkovsky	Li	Song <sup>b</sup>	all data
this model	0.0173	0.0304	0.0195	0.0146	0.003	0.0078
Song et al. <sup>71</sup>	0.0039	0.0316	0.2211	0.2719	<sup>c</sup>	0.0847
Teng et al. <sup>72</sup>	0.0114	0.1788	0.1751	0.1043	0.2907	0.2367
Bachu and Adams <sup>73</sup>	0.1973	0.1931	0.7800	0.0792	0.4232	0.3910
Garcia <sup>74</sup>	0.0061	0.1479	0.0626	0.0653	0.3807	0.2760
Andersen et al. <sup>75</sup>	0.0038	0.1459	0.0907	0.1430	0.3766	0.2958
Ennis–King <sup>74</sup>	0.0060	0.1080	0.0558	0.0857	0.2569	0.2017
Enick and Klara <sup>76</sup>	0.0038	0.1734	0.3030	0.3516	0.4162	0.3809
Iglesias and Moya <sup>77</sup>	0.0046	0.3208	0.0932	0.0956	0.9209	0.6190
Sedlbauer et al. <sup>78</sup>	0.0093	0.0869	0.0171	0.0997	0.1843	0.1263
Plyasunov et al. <sup>79</sup>	0.0094	0.0383	0.0056	0.0468	0.0817	0.0686
no. of data	8	5	17	29	109	173

<sup>a</sup> Ellis = Ellis and McFadden,<sup>104</sup> Ohsumi = Ohsumi et al.,<sup>98</sup> Hnedkovsky = Hnedkovsky et al.,<sup>99</sup> Li = Li et al.,<sup>100</sup> Song = Song et al.<sup>71</sup> <sup>b</sup> The densities are calculated from their empirical correlation of experimental results. <sup>c</sup> No comparison is made, because the correlation of Song et al.<sup>71</sup> was regressed from their own experimental data (presented in figures), whose maximum deviation is within 0.1%.

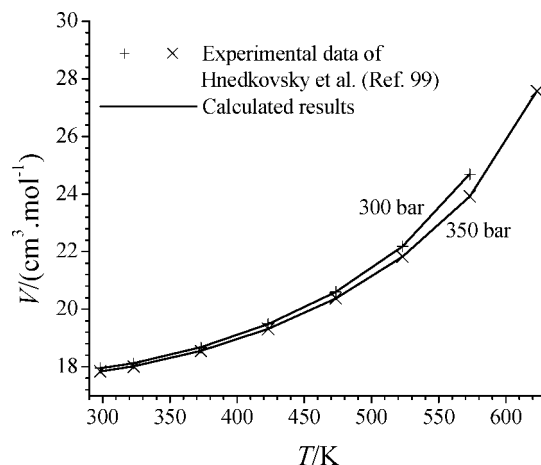
graphical report. According to our calculation, the average value is about  $31.2 \pm 1.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ , which is in excellent agreement with this model ( $31.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ ).

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.<sup>96</sup> are considered to be of reasonable accuracy.<sup>53</sup> 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.<sup>96</sup> can be predicted well. At higher pressures (>100 MPa), no volumetric data are available for the dilute CO<sub>2</sub> solutions. Nevertheless, it is found

**Table 6. Maximum Deviations (%) of Predicted Molar Volumes of Aqueous CO<sub>2</sub> Solutions**

model <sup>a</sup>	Ellis	Ohsumi	Hnedkovsky	Li	Song <sup>b</sup>	all data
this model	0.0257	0.0453	0.0447	0.0431	0.009	0.0455
Song et al. <sup>71</sup>	0.0064	0.0460	0.8179	0.3873	<sup>c</sup>	0.8179
Teng et al. <sup>72</sup>	0.0190	0.2653	0.7367	0.2924	0.3479	0.7367
Bachu and Adams <sup>73</sup>	0.3026	0.2773	6.025	0.1832	0.7665	6.0254
Garcia <sup>74</sup>	0.0235	0.2323	0.4350	0.1438	0.6835	0.6835
Andersen et al. <sup>75</sup>	0.0135	0.2293	0.3944	0.2541	0.6861	0.6861
Ennis–King <sup>74</sup>	0.0231	0.1720	0.4089	0.1811	0.4608	0.4608
Enick and Klara <sup>76</sup>	0.0057	0.2708	0.8615	0.4894	0.7988	0.8615
Iglesias and Moya <sup>77</sup>	0.0111	0.4936	0.2603	0.2097	1.6736	1.6736
Sedlbauer et al. <sup>78</sup>	0.0270	0.1337	0.0346	0.2120	0.3578	0.3578
Plyasunov et al. <sup>79</sup>	0.0275	0.0575	0.0155	0.1287	0.1917	0.1917
no. of data	8	5	17	29	109	173

<sup>a</sup> Ellis = Ellis and McFadden,<sup>104</sup> Ohsumi = Ohsumi et al.,<sup>98</sup> Hnedkovsky = Hnedkovsky et al.,<sup>99</sup> Li = Li et al.,<sup>100</sup> Song = Song et al.<sup>71</sup> <sup>b</sup> The densities are calculated from their empirical correlation of experimental results. <sup>c</sup> No comparison is made, because the correlation of Song et al.<sup>71</sup> was regressed from their own experimental data (presented in figures), whose maximum deviation is within 0.1%.

**Figure 5.** Predicted and experimental molar volumes of aqueous CO<sub>2</sub> solutions.

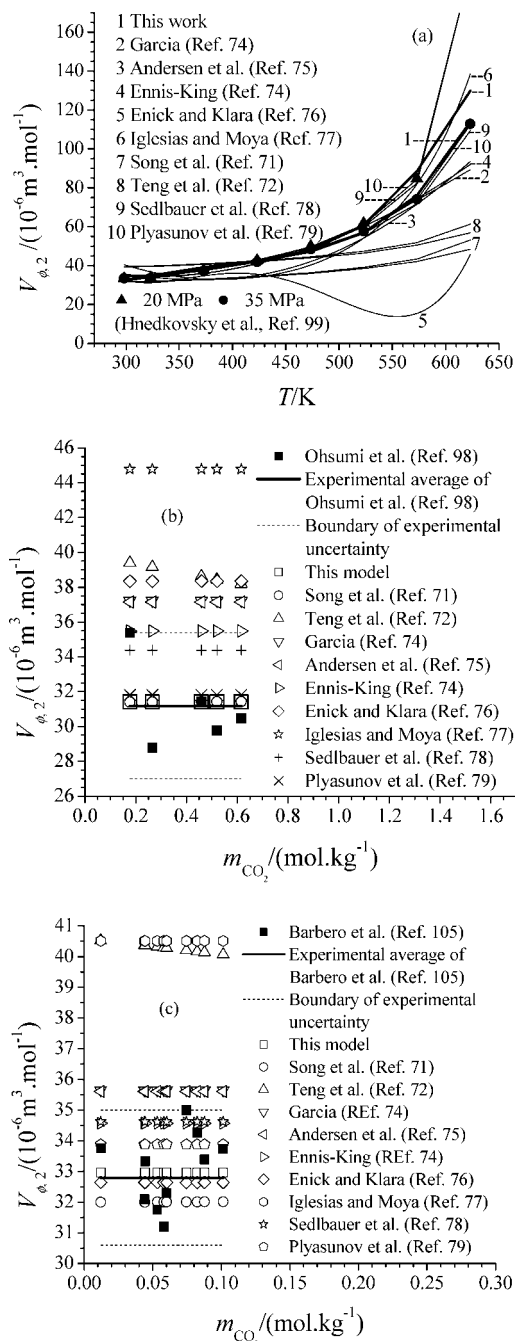
that all the predicted isochores of the liquid CO<sub>2</sub>–H<sub>2</sub>O mixtures up to 100 MPa (or higher pressure) are almost straight lines (Figure 9), which suggests that this model can be extrapolated to 100 MPa with reasonable accuracy.

#### 4. Liquid Density Model for the CO<sub>2</sub>–H<sub>2</sub>O–NaCl System

**4.1. Selection and Correction of Experimental Data.** The density data of Song et al.<sup>80</sup> for CO<sub>2</sub> seawater seem to be of high quality,<sup>53</sup> but they did not report the densities of the CO<sub>2</sub>–free seawater (3.5 wt % NaCl), which are supplemented with the model of Rogers and Pitzer<sup>106</sup> in this work. Song et al.<sup>107</sup> reported some accurate ratios of CO<sub>2</sub>-bearing seawater densities with respect to CO<sub>2</sub>-free seawater densities (see also

(106) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem. Ref. Data* **1982**, *11* (1), 15.

(107) Song, Y.; Chen, B.; Nishio, M.; Akai, M. In The study on carbon dioxide sea water solution density at high pressure and low temperature. *Proceedings of the 5th International Symposium on CO<sub>2</sub> Fixation and Efficient Utilization of Energy*, Tokyo, 2002.



**Figure 6.** Predicted and experimental apparent molar volumes of CO<sub>2</sub> in water. In order to make the marks clearer, component figure (a) also plots the points at 623.15 K and 28 MPa onto the 20 MPa isobaric curve.

Song et al.<sup>108</sup>). The other density or volume data sets for the CO<sub>2</sub>-H<sub>2</sub>O-NaCl liquids or CO<sub>2</sub>-bearing brines<sup>81,100,109,110</sup> were found to have systematic deviations or large uncertainties.<sup>53</sup> Recently, some new density data<sup>111,112</sup> are reported, but they also have similar quality problem. Nevertheless, the density data

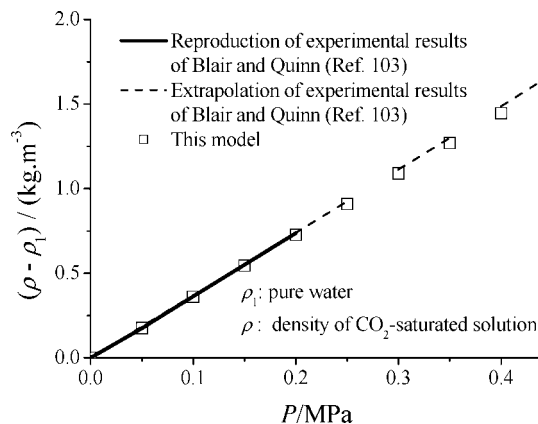
(108) Song, Y.-C.; Chen, B.-X.; Shen, S.-Q. *J. Thermal Sci. Technol. (China)* **2003**, 2 (4), 358.

(109) Gehrig, M. Phasengleichgewichte und pVT-daten ternärer mischungen aus wasser, kohlendioxid und natriumchlorid bis 3 kbar und 550 °C; Thesis, Univ. Karlsruhe; Hochschul Verlag: Freiburg, Germany, 1980.

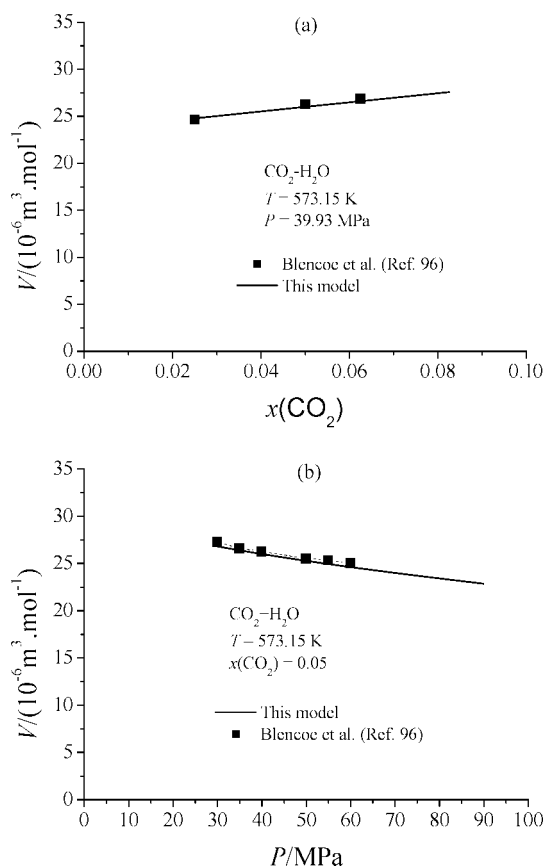
(110) Nighswander, J. A.; Kalogerakis, N.; Mehrotra, A. K. *J. Chem. Eng. Data* **1989**, 34, 355.

(111) Yang, C.; Gu, Y. *Ind. Eng. Chem. Res.* **2006**, 45 (8), 2430.

(112) Chiquet, P.; Daridon, J.-L.; Broseta, D.; Thibeau, S. *Energy Convers. Manage.* **2007**, 48, 736.



**Figure 7.** Predicted and experimental density differences between saturated CO<sub>2</sub> solution and pure water under the same condition. The experimental results of Blair and Quinn<sup>103</sup> were reproduced from the net increase of 0.38 kg m<sup>-3</sup> in density under a CO<sub>2</sub> partial pressure of 1 atm (101.325 kPa) at 298.15 K. The CO<sub>2</sub> solubilities are calculated with the model of Duan et al.<sup>61</sup>



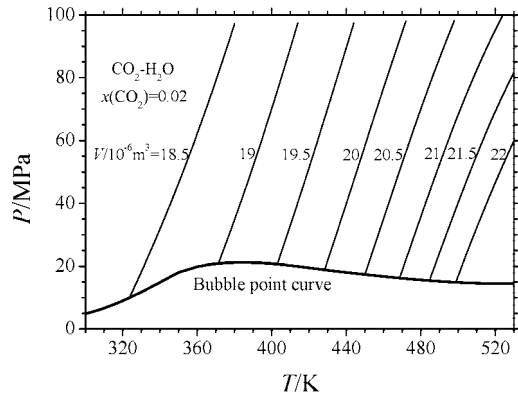
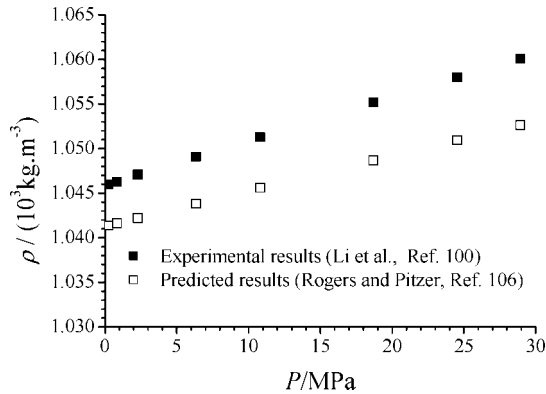
**Figure 8.** Extrapolation of the density model to high pressures.

of Li et al.<sup>100</sup> for the CO<sub>2</sub>-free and CO<sub>2</sub>-bearing Weyburn Formation brines can be corrected in a simple way. Figure 10 shows that the densities of the CO<sub>2</sub>-free brine of Li et al.<sup>100</sup> are systematically larger than the predicted values of the accurate model of Rogers and Pitzer<sup>106</sup> for NaCl solutions. The deviations can be accurately formulated with the following function:

$$\rho_{0,\text{exp}} - \rho_{0,\text{Rogers}} = c_0 + c_1 P + c_2 P^2 \quad (9)$$

where  $c_0 = 4.61111 \times 10^{-3}$ ,  $c_1 = +1.06999 \times 10^{-4}$ ,  $c_2 = -2.84112 \times 10^{-7}$ ,  $\rho_{0,\text{exp}}$  is experimental density,  $\rho_{0,\text{Rogers}}$  is the density calculated from the model of Rogers and Pitzer.<sup>106</sup> The units of pressure and density are MPa and g·cm<sup>-3</sup>, respectively.



Figure 9. Isochores of the CO<sub>2</sub>-H<sub>2</sub>O solutions up to 100 MPa.Figure 10. Difference between the experimental densities of CO<sub>2</sub>-free Weyburn brine and predicted results of the Rogers and Pitzer model.<sup>106</sup>Table 7. Empirical Models for the Densities of CO<sub>2</sub>-Bearing Brine<sup>a</sup>

authors	model
Song et al. <sup>80</sup>	$\rho = \rho_b + 0.273\chi$ ( $\chi = W_{\text{CO}_2}$ )
Teng and Yamasaki <sup>81</sup>	$\rho = \rho_b/(\text{kg}\cdot\text{m}^{-3}) - 42.2x_{\text{CO}_2} + 3.32 \times 10^4 x_{\text{CO}_2}^2$
Bachu and Adams <sup>73</sup>	$\rho = \rho_b/[1 - X_{\text{sol}}(1 - \rho_b V_{\varphi}^b/M_2)]$ , $\rho_b V_{\varphi}^b = \rho_w V_{\varphi}^w$ ( $X_{\text{sol}} = W_{\text{CO}_2}$ )
Bando et al. <sup>82</sup>	$\rho = \rho_b/(\text{kg}\cdot\text{m}^{-3}) + 1.96 \times 10^2 x_{\text{CO}_2} + 1.54 \times 10^4 x_{\text{CO}_2}^2$

<sup>a</sup> w = water, b = brine.

Because the densities of CO<sub>2</sub>-free and CO<sub>2</sub>-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<sub>2</sub>-free and CO<sub>2</sub>-bearing brines at the same pressure and temperature. With this assumption, the experimental densities of the CO<sub>2</sub>-bearing brine can be corrected as follows:

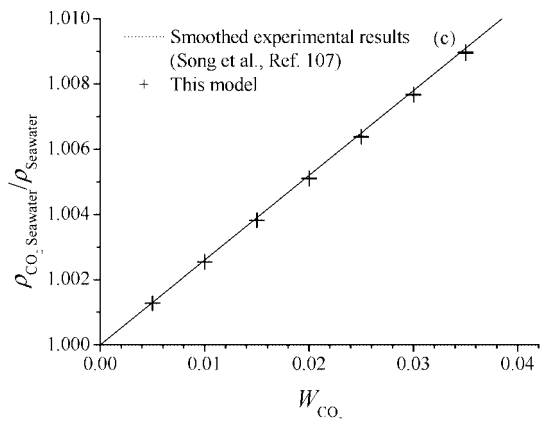
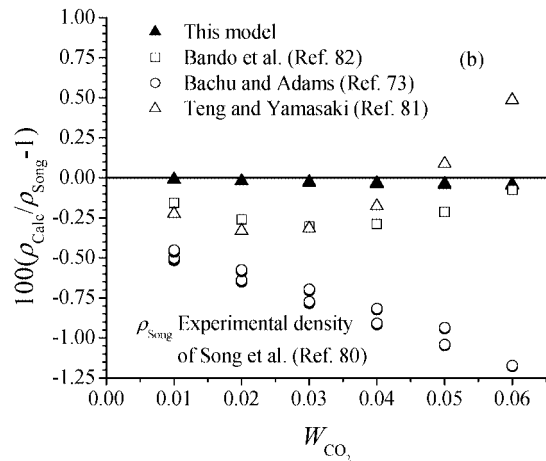
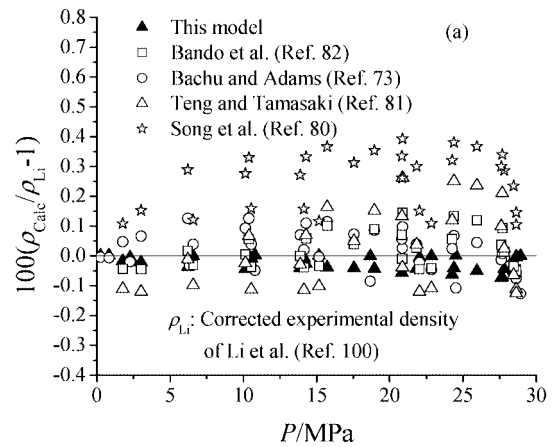
$$\rho_{\text{cor}} = \rho_{\text{exp}} - (\rho_{0,\text{exp}} - \rho_{0,\text{Rogers}}) \quad (10)$$

where  $\rho_{\text{cor}}$  and  $\rho_{\text{exp}}$  are the corrected and experimental densities of CO<sub>2</sub>-bearing brine, respectively.

According to the analysis above, we use the density data of Song et al.<sup>80,107</sup> and the corrected density data of Li et al.<sup>100</sup> to test the density model in this work.

**4.2. The Density Model.** The CO<sub>2</sub>-H<sub>2</sub>O-NaCl system can be obtained by adding CO<sub>2</sub> to the H<sub>2</sub>O-NaCl system, so the H<sub>2</sub>O-NaCl system can be regarded as a hypothetical “pure” component (solvent). Accordingly, the density ( $\rho$ ) and molar volume (*V*) of the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system can be rigorously formulated as

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

Figure 11. Predicted densities of CO<sub>2</sub>-bearing seawater.

$$V = (x_1 + x_3)(y_1 V_1 + y_3 V_{\varphi,3}^B) + x_2 V_{\varphi,2} \quad (12)$$

$$y_1 = x_1/(x_1 + x_3), \quad y_3 = x_3/(x_1 + x_3)$$

where the subscripts 1, 2, and 3 denote H<sub>2</sub>O, CO<sub>2</sub>, and NaCl, respectively,  $V_1$  is the molar volume of pure water,  $V_{\varphi,3}^B$  is the apparent molar volume of NaCl in water (where “B” means “binary”),  $V_{\varphi,2}$  is the apparent molar volume of CO<sub>2</sub> in the ternary,  $x_i$  is the mole fraction of component *i* in the ternary, and  $y_i$  is the mole fraction of component *i* in the NaCl-H<sub>2</sub>O system. After simple manipulation, eq 12 can be changed into

$$V = x_1 V_1 + x_2 V_{\varphi,2} + x_3 V_{\varphi,3}^B \quad (13)$$

It is accepted that the *excess volume* ( $V^{\text{Ex}}$ ) of a mixture is a high-order function of composition, where the order of composition is not smaller than 2. For example, the  $V^{\text{Ex}}$  function of binary mixtures can be expressed as a Margules equation  $V^{\text{Ex}}$

$= Ax_1x_2$ , where  $A$  is an interaction parameter depending on  $P$ ,  $T$ , and  $x$ . This suggests that the contribution of ion- $\text{CO}_2$  interactions to the excess partial molar volume of  $\text{CO}_2$  ( $V_2^{\text{Ex}}$ ) at given  $P$  and  $T$  tends to vanish if the salinity is low enough. Similarly, the effect of salts on  $V_{\varphi,2}$  at low salinity is also very small. In fact, the brines in the  $\text{CO}_2$  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  $\text{CO}_2$  in water, the  $\text{CO}_2$  concentrations are usually less than 3 mol %. In brines, the solubility of  $\text{CO}_2$  decreases rapidly with increasing salinity. Therefore, the possibilities of the  $\text{CO}_2\text{-Na}^+$  and  $\text{CO}_2\text{-Cl}^-$  pairs appearing in solutions are usually very small. In these cases, we can neglect the effect of salts on  $V_{\varphi,2}$ . That is,  $V_{\varphi,2}$  can be approximated with the apparent molar volume of  $\text{CO}_2$  in pure water ( $V_{\varphi,2}^{\text{B}}$ ):

$$V = x_1V_1 + x_2V_{\varphi,2}^{\text{B}} + x_3V_{\varphi,3}^{\text{B}} \quad (14)$$

where  $V_{\varphi,2}^{\text{B}}$  is predicted with eq 8, and  $V_{\varphi,3}^{\text{B}}$  is predicted from the model of Rogers and Pitzer.<sup>106</sup> eq 14 is tested with the density data of Song et al.<sup>80,107</sup> and the corrected density data of Li et al.<sup>100</sup> Also tested are some other density models,<sup>73,80–82</sup> whose expressions are given in Table 7. Note that in the model of Bachu and Adams,<sup>73</sup> the volume of  $\text{CO}_2$ -free brine is calculated with the model of Batzle and Wang;<sup>102</sup> in the other models, it is calculated with the model of Rogers and Pitzer,<sup>106</sup> where water volume is calculated with the IAPWS97 EOS.<sup>101</sup> 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.,<sup>107</sup> Song et al.,<sup>80</sup> and Li et al.<sup>100</sup> 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.<sup>80</sup> correlated from their own density data gives the worst prediction of the density data of Li et al.<sup>100</sup> 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<sup>42</sup> proposed a density model for the  $\text{CO}_2\text{-H}_2\text{O-NaCl}$  system by using an approximation equivalent to eq 12. Like the work of Bachu and Adams,<sup>73</sup> they used the apparent molar volumes of  $\text{CO}_2$  in pure water at infinite dilution calculated from the model of Garcia,<sup>74</sup> which are not accurate enough at the conditions of  $\text{CO}_2$  storage, especially at low temperatures.<sup>53</sup> 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  $\text{CO}_2\text{-H}_2\text{O}$  and  $\text{CO}_2\text{-H}_2\text{O-NaCl}$  systems up to 100 MPa, where the gaseous  $\text{CO}_2\text{-H}_2\text{O}$  mixtures are represented with a revised equation of state of Duan et al.,<sup>84</sup> and the liquid  $\text{CO}_2\text{-H}_2\text{O}$  mixtures with a density model with  $P$ ,  $T$ , and  $x$  as independent variables. The IAPWS97 EOS for the volumes of pure water<sup>101</sup> is used as a reference of the density model. Based on the above liquid density model and the  $\text{H}_2\text{O-NaCl}$  model of Rogers and Pitzer<sup>106</sup> 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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