

Densities of the CO₂–H₂O and CO₂–H₂O–NaCl Systems Up to 647 K and 100 MPa

Zhenhao Duan,^{*,†} Jiawen Hu,^{†,‡} Dedong Li,[†] and Shide Mao[§]

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 CO₂–H₂O in the range 0–28 MPa and 323–645 K. The equation for gaseous CO₂–H₂O 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 CO₂–H₂O and CO₂–H₂O–NaCl mixtures is developed. The most accurate experimental density data for the CO₂–H₂O 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 CO₂–H₂O–NaCl mixtures is developed on the basis of our CO₂–H₂O model and the H₂O–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

CO₂–H₂O and CO₂–H₂O–NaCl are typical geological fluids in many geochemical processes.^{1–15} Pressure–volume–temperature–composition (PVTx) properties and phase equilibrium are fundamental in the quantitative interpretation of geochemical

data.^{2,8,16–27} For example, predicting CO₂ behavior after geological storage needs accurate knowledge of both phase relations and densities.^{28–43} 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.

[†] Chinese Academy of Sciences.

[‡] Shijiazhuang University of Economics.

[§] Chinese University of Geosciences.

- (1) Roedder, E. *Rev. Miner.* **1984**, 12, 1.
- (2) Schmidt, C.; Bodnar, R. J. *Geochim. Cosmochim. Acta* **2000**, 64 (22), 3853.
- (3) Boiron, M.-C.; Barakat, A.; Cathelineau, M.; Banks, D. A.; Durisov, J.; Moravek, P. *Chem. Geol.* **2001**, 173, 207.
- (4) Chen, J.; Zheng, H.; Xiao, W.; Zeng, Y.; Weng, K. *Geochim. Cosmochim. Acta* **2004**, 68 (6), 1355.
- (5) Frezzotti, M. L.; Andersen, T.; Neumann, E.-R.; Simonsen, S. L. *Lithos* **2002**, 64, 77.
- (6) Newton, R. C.; Manning, C. E. *Geochim. Cosmochim. Acta* **2000**, 64 (17), 2993.
- (7) Fan, H.-R.; Hu, F.-F.; Yang, K.-F.; Wang, K.-Y. *J. Geochem. Exploration* **2006**, 89 (1–3), 104.
- (8) Tamic, N.; Behrens, H.; Holtz, F. *Chem. Geol.* **2001**, 174 (1–3), 333.
- (9) Newton, R. C.; Aranovich, L. Y.; Hansen, E. C.; Vandenheuvell, B. A. *Precambrian Res.* **1998**, 91, 41.
- (10) Aranovich, L. Y.; Newton, R. C. *Contrib. Mineral. Petrol.* **1996**, 125, 200.
- (11) Aranovich, L. Y.; Newton, R. C. *Am. Mineral.* **1999**, 84, 1319.
- (12) Haefner, A.; Aranovich, L. Y.; Connolly, J. A. D.; Ulmer, P. *Am. Mineral.* **2002**, 87, 822.
- (13) Shmulovich, K. I.; Yardley, B. W. D.; Graham, C. M. *Geofluids* **2006**, 6, 154.
- (14) Zakirov, I. V.; Sretenskaja, N. G.; Aranovich, L. Y.; Volchenkova, V. A. *Geochim. Cosmochim. Acta* **2007**, 71, 4251.
- (15) Evans, K. *Geofluids* **2007**, 7, 451.
- (16) Anovitz, L. M.; Blencoe, J. G.; Joyce, D. B.; Horita, J. *Geochim. Cosmochim. Acta* **1998**, 62 (5), 815.

- (17) Anovitz, L. M.; Labotka, T. C.; Blencoe, J. G.; Horita, J. *Geochim. Cosmochim. Acta* **2004**, 68 (17), 3557.
- (18) Bakker, R. J.; Dubessy, J.; Cathelineau, M. *Geochim. Cosmochim. Acta* **1996**, 60 (10), 1657.
- (19) Bakker, R. J. *Chem. Geol.* **1999**, 154 (1–4), 225.
- (20) Bakker, R. J.; Diamond, L. W. *Geochim. Cosmochim. Acta* **2000**, 64 (10), 1753.
- (21) Akinfiev, N.; Zotov, A. *Geochim. Cosmochim. Acta* **1999**, 63 (13–14), 2025.
- (22) Barton, P. B.; Chou, I.-M. *Geochim. Cosmochim. Acta* **1993**, 57 (12), 2715.
- (23) Zhang, Y.-G.; Frantz, J. D. *Chem. Geol.* **1989**, 74 (3–4), 289.
- (24) Bowers, T. S.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1983**, 47, 1247.
- (25) Papale, P.; Moretti, R.; Barbato, D. *Chem. Geol.* **2006**, 229 (1–3), 78.
- (26) Longhi, J. *Geochim. Cosmochim. Acta* **2005**, 69 (3), 529.
- (27) Chiodini, G.; Marini, L. *Geochim. Cosmochim. Acta* **1998**, 62 (15), 2673.
- (28) Baines, S. J.; Worden, R. H. *Geological Storage of Carbon Dioxide*. The Geology Society of London: London, 2004; GSL Special Publications (Vol. 233), p 264.
- (29) Haugan, P. M.; Drange, H. *Nature* **1992**, 357, 318.
- (30) Battistelli, A.; Calore, C.; Pruess, K. *Geothermics* **1997**, 26 (4), 437.
- (31) Kaszuba, J. P.; Janecky, D. R.; Snow, M. G. *Appl. Geochem.* **2003**, 18, 1065.
- (32) Kaszuba, J. P.; Janecky, D. R.; Snow, M. G. *Chem. Geol.* **2005**, 217 (3–4), 277.
- (33) Oldenburg, C. M.; Benson, S. M. *SPE (Soc. Pet. Eng.)* **2002**, 74367, 1.
- (34) Oldenburg, C. M. *Energy Convers. Manage.* **2007**, 48 (6), 1808.
- (35) Pruess, K.; García, J.; Kovscek, T.; Oldenburg, C.; Rutqvist, J.; Steefel, C.; Xu, T. *Energy* **2004**, 29 (9–10), 1431.
- (36) Talman, S. J.; Adams, J. J.; Chalaturnyk, R. J. *Comput. Geosci.* **2004**, 30 (5), 543.
- (37) Xu, T.; Apps, J. A.; Pruess, K. *Appl. Geochem.* **2004**, 19 (6), 917.

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.^{33,34,38,44–52}

The phase equilibrium and PVT_x 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 fate 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, T_C(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 PVT_x 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.²⁹

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.^{42,73,80–82} 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

(38) Ota, M.; Abe, Y.; Watanabe, M.; Smith, R. L. J.; Inomata, H. *Fluid Phase Equilib.* **2005**, 228–229, 553.

(39) Portier, S.; Rochelle, C. *Chem. Geol.* **2005**, 217 (3–4), 187.

(40) Koschel, D.; Coxam, J.-Y.; Rodier, L.; Majer, V. *Fluid Phase Equilib.* **2006**, 247 (1–2), 107.

(41) Zwingmann, N.; Mito, S.; Sorai, M.; Ohsumi, T. *Oil Gas Sci. Technol.—Rev. IFP* **2005**, 60 (2), 249.

(42) Pruess, K.; Spycher, N. *Energy Convers. Manage.* **2007**, 48 (6), 1761.

(43) Hassanzadeh, H.; Pooladi-Darvish, M.; Elsharkawy, A. M.; Keith, D. W.; Leonenko, Y. *Int. J. Greenhouse Gas Control* **2008**, 2 (1), 65.

(44) Wang, L.-S.; Lang, Z.-X.; Guo, T.-M. *Fluid Phase Equilib.* **1996**, 117 (1–2), 364.

(45) Ota, M.; Morohashi, K.; Abe, Y.; Watanabe, M.; Smith, R. L. J.; Inomata, H. *Energy Convers. Manage.* **2005**, 46 (11–12), 1680.

(46) White, C. M.; Smith, D. H.; Jones, K. L.; Goodman, A. L.; Jikich, S. A.; LaCount, R. B.; DuBose, S. B.; Ozdemir, E.; Morsi, B. I.; Schroeder, K. T. *Energy Fuels* **2005**, 19 (3), 659.

(47) Song, C. *Catal. Today* **2006**, 115, 2.

(48) Zhang, N.; Lior, N. *Energy* **2006**, 31, 1666.

(49) Al-Anezi, K.; Hilal, N. *Desalination* **2007**, 204 (1–3), 385.

(50) Pazuki, G. R.; Pahlevanzadeh, H.; Mohseni Ahooei, A. *Fluid Phase Equilib.* **2006**, 242, 57.

(51) Sloan, E. D. J. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker, Inc.: New York, 1998; p 1.

(52) Sloan, E. D. J. *Nature* **2003**, 426, 353.

(53) Hu, J.; Duan, Z.; Zhu, C.; Chou, I.-M. *Chem. Geol.* **2007**, 238 (3–4), 249.

(54) Dubessy, J.; Thiery, R. *Eur. J. Mineral.* **1998**, 10, 1151.

(55) Driesner, T.; Heinrich, C. A. *Geochim. Cosmochim. Acta* **2007**, 71 (20), 4880.

(56) Driesner, T. *Geochim. Cosmochim. Acta* **2007**, 71 (20), 4902.

(57) Carroll, J. J.; Slupsky, J. D.; Mather, A. E. *J. Phys. Chem. Ref. Data* **1991**, 20, 1201.

(58) Crovetto, R. J. *J. Phys. Chem. Ref. Data* **1991**, 20 (3), 575.

(59) Diamond, L. W.; Akinfiev, N. N. *Fluid Phase Equilib.* **2003**, 208 (1–2), 265.

(60) Duan, Z.; Sun, R. *Chem. Geol.* **2003**, 193, 253.

(61) Duan, Z.; Sun, R.; Zhu, C.; Chou, I.-M. *Mar. Chem.* **2006**, 98, 131.

(62) Spycher, N.; Pruess, K.; Ennis-King, J. *Geochim. Cosmochim. Acta* **2003**, 67 (16), 3015.

(63) Spycher, N.; Pruess, K. *Geochim. Cosmochim. Acta* **2005**, 69 (13), 3309.

(64) Ji, Y.; Ji, X.; Feng, X.; Liu, C.; Lü, L.; X., L. *Chin. J. Chem. Eng.* **2007**, 15 (3), 439.

(65) Teng, H.; Masutani, S. M.; Kinoshita, C. M.; Nihous, G. C. *Energy Convers. Manage.* **1996**, 37 (6–8), 1029.

(66) Dubessy, J.; Tarantola, A.; Sterpenich, J. *Oil Gas Sci. Technol.* **2005**, 60 (2), 339.

(67) Perakis, C.; Voutsas, E.; Magoulas, K.; Tassios, D. *Fluid Phase Equilib.* **2006**, 243, 142.

(68) Ferrando, N.; Lugo, R.; Mougin, P. *Chem. Eng. Processing* **2006**, 45, 773.

(69) dos Ramos, M. C.; Blas, F. J.; Galindo, A. *Fluid Phase Equilib.* **2007**, 261 (1–2), 359.

(70) dos Ramos, M. C.; Blas, F. J.; Galindo, A. *J. Phys. Chem. C* **2007**, 111 (43), 15924.

(71) Song, Y.; Nishio, M.; Chen, B.; Someya, S.; Ohsumi, T. *J. Visualization* **2003**, 6 (1), 41.

(72) Teng, H.; Yamasaki, A.; Chun, M.-K.; Lee, H. *J. Chem. Thermodyn.* **1997**, 29 (11), 1301.

(73) Bachu, S.; Adams, J. J. *Energy Convers. Manage.* **2003**, 44 (20), 3151.

(74) Garcia, J. E. Density of aqueous solutions of CO₂; Lawrence Berkeley National Laboratory Paper LBNL-49023; University of California at Berkeley, **2001**; p 1 (<http://repositories.cdlib.org/cgi/viewcontent.cgi?article=1839&context=lbln>).

(75) Andersen, G.; Probst, A.; Murray, L.; Butler, S. In An accurate PVT model for geothermal fluids as represented by CO₂-H₂O-NaCl mixtures. *The Seventeenth Workshop on Geothermal Reservoir Engineering*; Stanford University: Stanford, CA, 1992; pp 239.

(76) Enick, R. M.; Klara, S. M. *Chem. Eng. Commun.* **1990**, 90, 23.

(77) Iglesias, E. R.; Moya, S. L. In An accurate formulation of the solubility of CO₂ in water for geothermal applications. *The Seventeenth Workshop on Geothermal Reservoir Engineering*; Stanford University: Stanford, CA, 1992; pp 231.

(78) Sedlbauer, J.; O'Connell, J. P.; Wood, R. H. *Chem. Geol.* **2000**, 163 (1–4), 43.

(79) Plyasunov, A. V.; O'Connell, J. P.; Wood, R. H. *Geochim. Cosmochim. Acta* **2000**, 64 (3), 495.

(80) Song, Y.; Chen, B.; Nishio, M.; Akai, M. *Energy* **2005**, 30, 2298.

(81) Teng, H.; Yamasaki, A. *J. Chem. Eng. Data* **1998**, 43 (1), 2.

(82) Bando, S.; Takemura, F.; Nishio, M.; Hihara, E.; Akai, M. *J. Chem. Eng. Data* **2004**, 49–1328.

(83) Duan, Z.; Møller, N.; Weare, J. H. *Geochim. Cosmochim. Acta* **1992**, 56, 2605.

(84) Duan, Z.; Møller, N.; Weare, J. H. *Geochim. Cosmochim. Acta* **1992**, 56, 2619.

(85) Ji, X.; Tan, S. P.; Adidharma, H.; Radosz, M. *Ind. Eng. Chem. Res.* **2005**, 44, 8419.

(86) Spycher, N. F.; Reed, M. H. *Geochim. Cosmochim. Acta* **1988**, 52 (3), 739.

(87) Nitsche, J. M.; Teletzke, G. F.; E., S. L.; Davis, H. T. *Fluid Phase Equilib.* **1984**, 17 (2), 243.

(88) Churakov, S. V.; Gottschalk, M. *Geochim. Cosmochim. Acta* **2003a**, 67 (13), 2397.

(89) Churakov, S. V.; Gottschalk, M. *Geochim. Cosmochim. Acta* **2003**, 67 (13), 2415.

(90) Li, H.; Ji, X.; Yan, J. *Int. J. Energy Res.* **2006**, 30, 135.

Table 1. Constants in Equation 3

<i>i</i>	<i>A_i</i>
1	−0.624 0078 × 10 ^{−3}
2	0.924 8008 × 10 ⁰
3	0.528 2536 × 10 ^{−2}
4	−0.250 9670 × 10 ¹
5	−0.310 1373 × 10 ^{−2}
6	0.279 4819 × 10 ¹

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.⁸⁴ developed a virial-type equation of state for the CH₄–CO₂–H₂O system:

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

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*_{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 PVT_x 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:

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

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.,⁹¹ Patel et al.,⁹² Patel and Eubank,⁹³ Fenghour et al.,⁹⁴ and Warowny and Eubank⁹⁵ and

(91) Wormald, C. J.; Lancaster, N. M.; Sellars, A. J. *J. Chem. Thermodyn.* **1986**, *18*, 135.

(92) Patel, M. R.; Holste, J. C.; Hall, K. R.; Eubank, P. T. *Fluid Phase Equilib.* **1987**, *36*, 279.

(93) Patel, M. R.; Eubank, P. T. *J. Chem. Eng. Data* **1988**, *33* (2), 185.

(94) Fenghour, A.; Wakeham, W. A.; Watson, J. T. R. *J. Chem. Thermodyn.* **1996**, *28* (4), 433.

(95) Warowny, W.; Eubank, P. T. *Fluid Phase Equilib.* **1995**, *103*, 77.

those of Blencoe et al.⁹⁶ 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,⁹⁵ have been assessed and were considered to be of good accuracy.⁵³ The density data for water steam of Warowny and Eubank,⁹⁵ 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,⁹⁷ and the density data for gaseous CO₂–H₂O mixtures⁹⁵ agree well with those of Patel et al.⁹² and Patel and Eubank.⁹³ 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.⁹⁶ 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 CO₂–H₂O System

3.1. Selection and Correction of Experimental Data.

According to the assessment of Hu et al.,⁵³ 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^{71,98–100} to regress the model parameters. However, some important issues regarding these data must be clarified:

1. Ohsumi et al.⁹⁸ and Song et al.⁷¹ presented graphical reports of the density changes due to the dissolution of CO₂, leaving the corresponding densities of pure water (*ρ*_w) unknown. In order to obtain the solution densities, we supplement the pure water densities with the IAPWS97 EOS,¹⁰¹ where the EOS is considered to be highly accurate. The density differences of Ohsumi et al.⁹⁸ are read from their figure, and the ratios of the solution and pure water densities reported by Song et al.⁷¹ 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.⁹⁹ 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*_{φ,*i*}, *ρ_i*, *M_i*, 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 is found that the errors of pure water densities in the calibration of Hnedkovsky et al.⁹⁹ are generally within 0.3%, but the largest error can be up to about 2% (Figure 3). Here we use the IAPWS97 EOS¹⁰¹ to replace the calibration of Hnedkovsky et al.⁹⁹

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

(96) Blencoe, J. G.; Cole, D. R.; Horita, J.; Moline, G. R. In Experimental geochemical studies relevant to carbon sequestration; The First National Conference on Carbon Sequestration; U.S. National Energy Technology Laboratory: Washington, DC, 2001; p 14.

(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^a (%) of Predicted Molar Volumes of CO₂-H₂O Mixtures

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

^a AD = average deviation, MD = maximum deviation, *N_d* = no. of data points. ^b Under the conditions of these data, many mixtures are present in liquid.

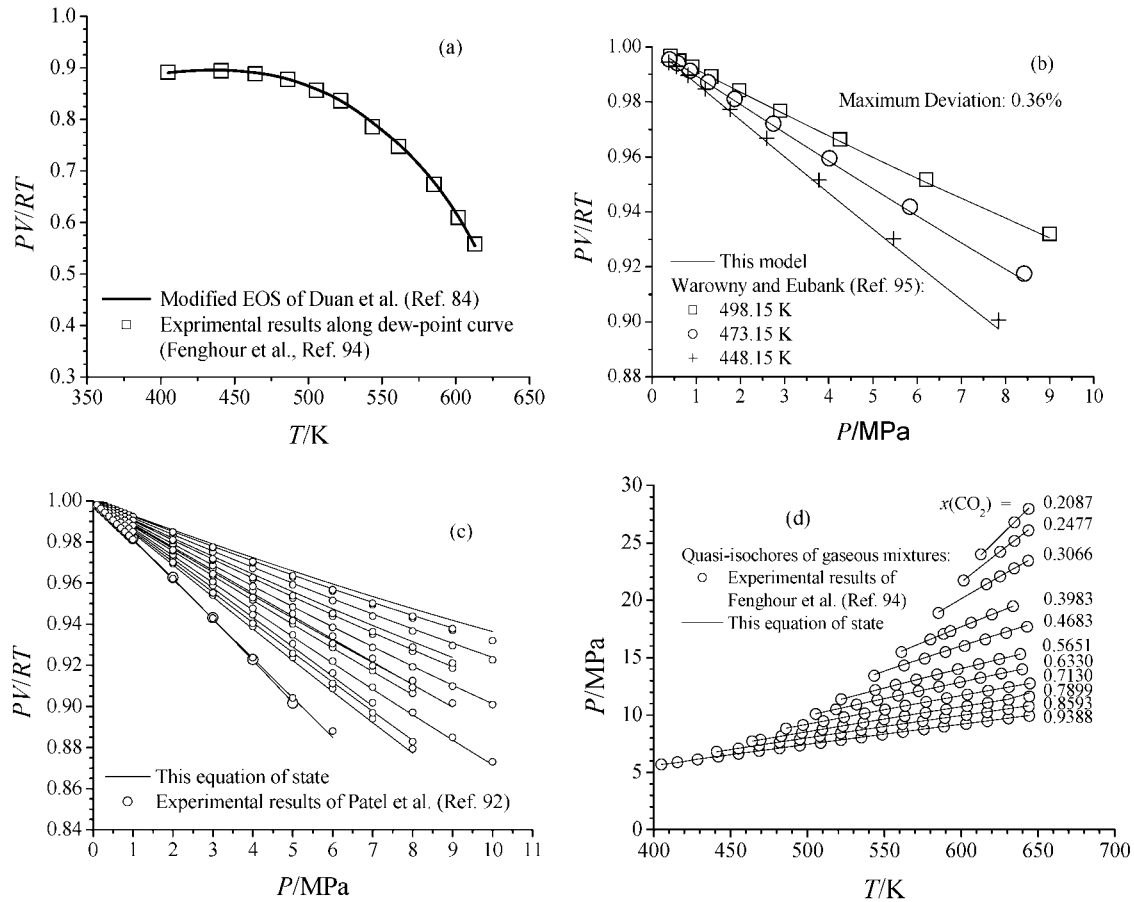


Figure 1. Compressibility factors and quasi-isochores of gaseous CO₂-H₂O mixtures. The quasi-isochores in (d) mean that the volumes of the points on a given curve are not the same, but slightly different from each other.

the National Institute of Standards and Technology (NIST, <http://webbook.nist.gov/chemistry/fluid>) based on the accepted EOS of Wagner and Pruss.⁹⁷ 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 $c_0 = 6.1653 \times 10^{-4}$, $c_1 = 1.1358 \times 10^{-4}$, $c_2 = -4.4198 \times 10^{-7}$, ρ_{cor} and ρ_{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 CO₂ 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 CO₂, ρ_{exp} is the experimental density of solution ($\text{g} \cdot \text{cm}^{-3}$), C is the concentration of CO₂ ($\text{mol} \cdot \text{cm}^{-3}$) calculated with eq (11) and eq (12) of Li et al.,¹⁰⁰ 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 CO₂-H₂O solutions are usually measured for dilute solution of CO₂ 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 CO₂ sequestration. (3) The change of molar volume due to the dissolution of CO₂ 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,

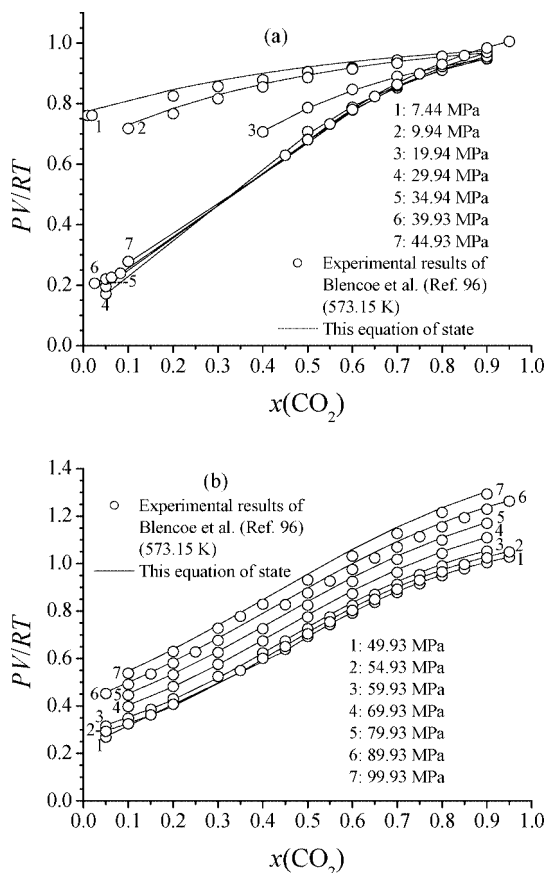


Figure 2. Isobars of the CO₂-H₂O mixtures at 573.15 K.

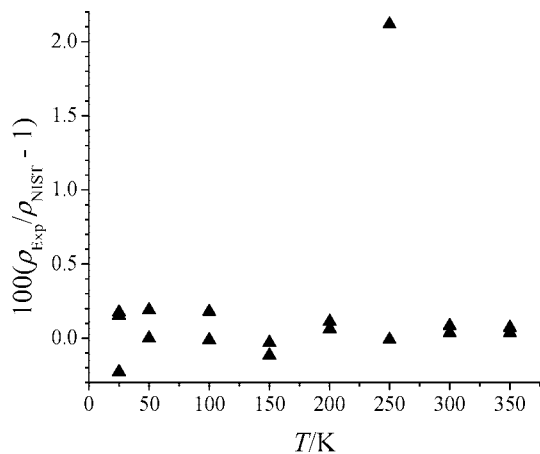


Figure 3. Calibration errors of the pure water densities of Hnedkovsky et al.⁹⁹

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 CO₂, 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_{ij} 's (Table 3) are regressed from

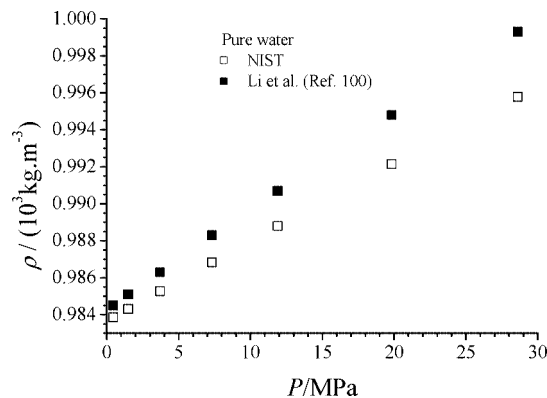


Figure 4. Systematic deviations of the densities of pure water measured by Li et al.¹⁰⁰ from the accepted values recommended by NIST.

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.^{71,98–100} 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.,⁵³ which can reproduce the water volumes of Wagner and Pruss⁹⁷ within 0.027%, where the average deviation is only 0.005%.

From eq 7, it is easy to obtain the apparent molar volume of CO₂:

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

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 Adams⁷³ 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 Quinn¹⁰³ 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 McFadden¹⁰⁴ 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.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 CO₂ 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 CO₂–H₂O Solutions and the Apparent or Partial Molar Volumes of CO₂ in Water at Infinite Dilution

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

^a t = temperature in °C. ^b κ_0 , ρ_0 , V_0 (or κ , ρ , V_1^0) = isothermal compressibility, specific density, and molar volume of water, respectively.

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

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

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

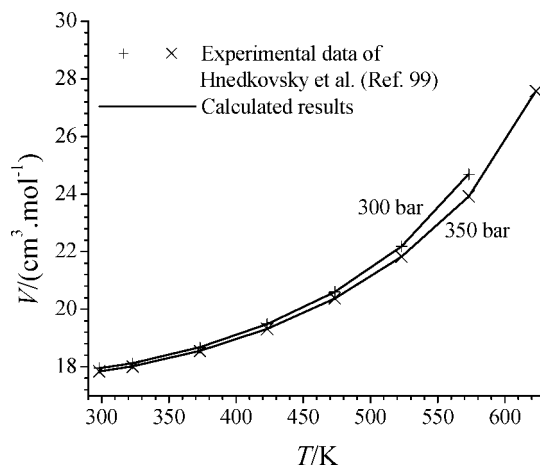
graphical report. According to our calculation, the average value is about $31.2 \pm 1.1 \text{ cm}^3 \cdot \text{mol}^{-1}$, which is in excellent agreement with this model ($31.4 \text{ cm}^3 \cdot \text{mol}^{-1}$).

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.⁹⁶ are considered to be of reasonable accuracy.⁵³ 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.⁹⁶ 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

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

^a Ellis = Ellis and McFadden,¹⁰⁴ Ohsumi = Ohsumi et al.,⁹⁸ Hnedkovsky = Hnedkovsky et al.,⁹⁹ Li = Li et al.,¹⁰⁰ Song = Song et al.⁷¹ ^b The densities are calculated from their empirical correlation of experimental results. ^c No comparison is made, because the correlation of Song et al.⁷¹ 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 CO₂ solutions.

that all the predicted isochores of the liquid CO₂–H₂O 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 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 Pitzer¹⁰⁶ 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

(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 CO₂ Fixation and Efficient Utilization of Energy*, Tokyo, 2002.

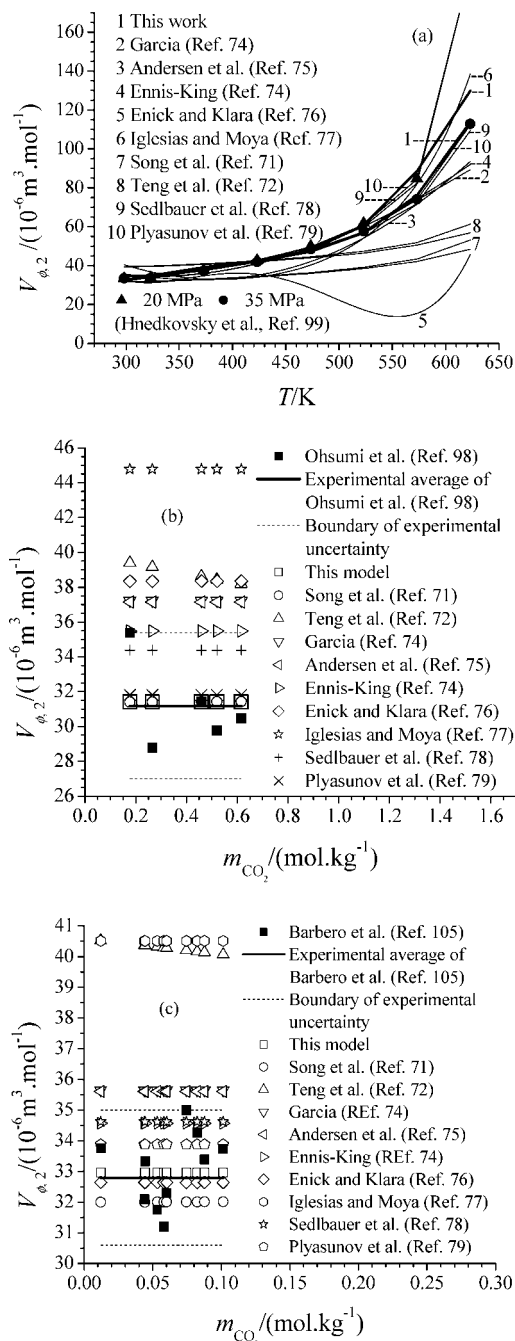


Figure 6. Predicted and experimental apparent molar volumes of CO₂ in water. In order to make the marks clearer, component figure (a) also plots the points at 623.15 K and 28 MPa onto the 20 MPa isobaric curve.

Song et al.¹⁰⁸). The other density or volume data sets for the CO₂-H₂O-NaCl liquids or CO₂-bearing brines^{81,100,109,110} were found to have systematic deviations or large uncertainties.⁵³ Recently, some new density data^{111,112} 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.

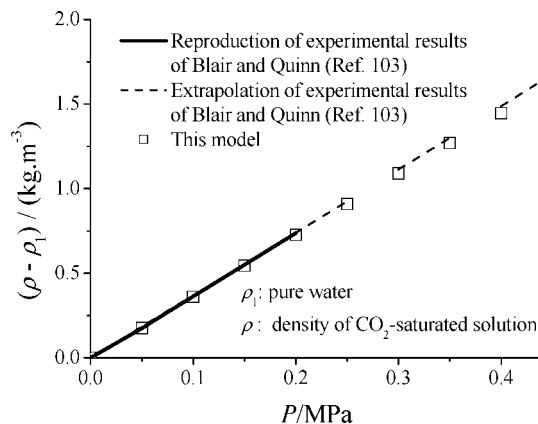


Figure 7. Predicted and experimental density differences between saturated CO₂ solution and pure water under the same condition. The experimental results of Blair and Quinn¹⁰³ were reproduced from the net increase of 0.38 kg m⁻³ in density under a CO₂ partial pressure of 1 atm (101.325 kPa) at 298.15 K. The CO₂ solubilities are calculated with the model of Duan et al.⁶¹

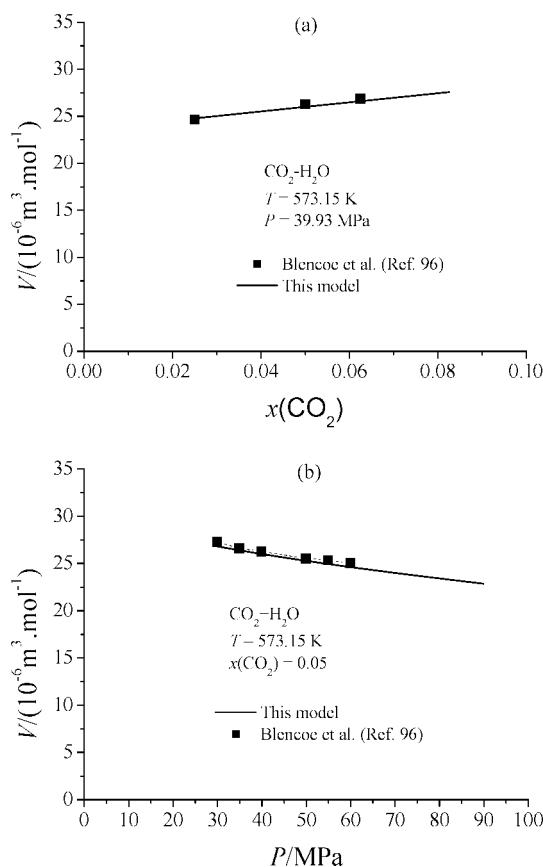
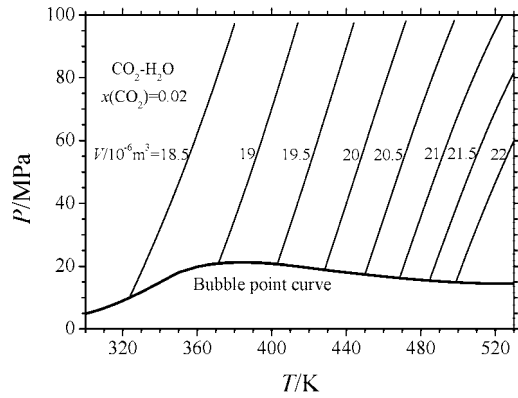
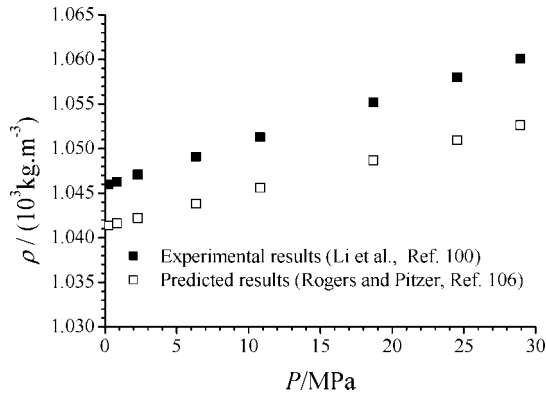


Figure 8. Extrapolation of the density model to high pressures.

of Li et al.¹⁰⁰ for the CO₂-free and CO₂-bearing Weyburn Formation brines can be corrected in a simple way. Figure 10 shows that the densities of the CO₂-free brine of Li et al.¹⁰⁰ are systematically larger than the predicted values of the accurate model of Rogers and Pitzer¹⁰⁶ 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.¹⁰⁶ The units of pressure and density are MPa and g·cm⁻³, respectively.

Figure 9. Isochores of the CO₂-H₂O solutions up to 100 MPa.Figure 10. Difference between the experimental densities of CO₂-free Weyburn brine and predicted results of the Rogers and Pitzer model.¹⁰⁶Table 7. Empirical Models for the Densities of CO₂-Bearing Brine^a

authors	model
Song et al. ⁸⁰	$\rho = \rho_b + 0.273\chi$ ($\chi = W_{CO_2}$)
Teng and Yamasaki ⁸¹	$\rho = \rho_b / (\text{kg} \cdot \text{m}^{-3}) - 42.2x_{CO_2} + 3.32 \times 10^4 x_{CO_2}^2$
Bachu and Adams ⁷³	$\rho = \rho_b / [1 - X_{sol}(1 - \rho_b V_{\varphi}^b / M_2)]$, $\rho_b V_{\varphi}^b = \rho_w V_{\varphi}^w$ ($X_{sol} = W_{CO_2}$)
Bando et al. ⁸²	$\rho = \rho_b / (\text{kg} \cdot \text{m}^{-3}) + 1.96 \times 10^2 x_{CO_2} + 1.54 \times 10^4 x_{CO_2}^2$

^a w = water, b = brine.

Because the densities of CO₂-free and CO₂-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 CO₂-free and CO₂-bearing brines at the same pressure and temperature. With this assumption, the experimental densities of the CO₂-bearing brine can be corrected as follows:

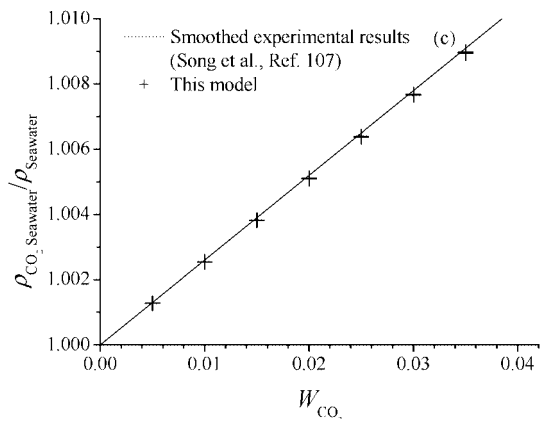
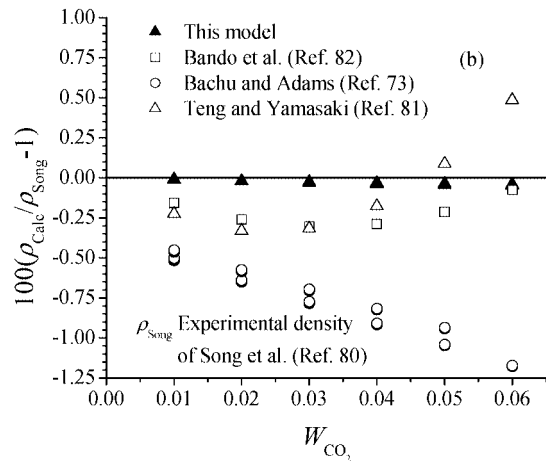
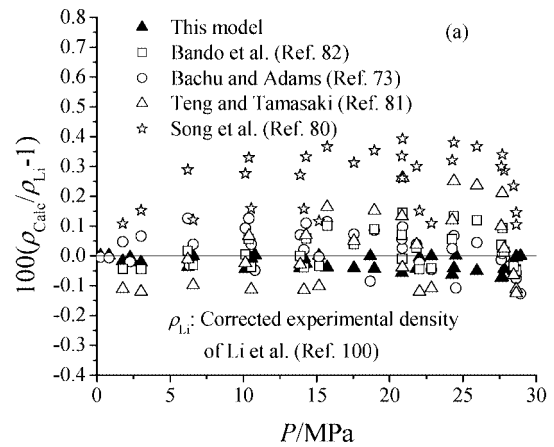
$$\rho_{cor} = \rho_{exp} - (\rho_{0,exp} - \rho_{0,Rogers}) \quad (10)$$

where ρ_{cor} and ρ_{exp} are the corrected and experimental densities of CO₂-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 CO₂-H₂O-NaCl system can be obtained by adding CO₂ to the H₂O-NaCl system, so the H₂O-NaCl system can be regarded as a hypothetical “pure” component (solvent). Accordingly, the density (ρ) and molar volume (*V*) of the CO₂-H₂O-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 CO₂-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 H₂O, CO₂, 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 CO₂ 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-H₂O 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^{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^{Ex} function of binary mixtures can be expressed as a Margules equation V^{Ex}

$= Ax_1x_2$, 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_2^{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 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 $\text{CO}_2\text{-Na}^+$ 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 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.¹⁰⁶ eq 14 is tested with the density data of Song et al.^{80,107} and the corrected density data of Li et al.¹⁰⁰ Also tested are some other density models,^{73,80–82} whose expressions are given in Table 7. Note that in the model of Bachu and Adams,⁷³ the volume of CO_2 -free brine is calculated with the model of Batzle and Wang;¹⁰² in the other models, it is calculated with the model of Rogers and Pitzer,¹⁰⁶ where water volume is calculated with the IAPWS97 EOS.¹⁰¹ 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.,¹⁰⁷ Song et al.,⁸⁰ and Li et al.¹⁰⁰ 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.⁸⁰ correlated from their own density data gives the worst prediction of the density data of Li et al.¹⁰⁰ 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 Spycher⁴² 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,⁷³ they used the apparent molar volumes of CO_2 in pure water at infinite dilution calculated from the model of Garcia,⁷⁴ which are not accurate enough at the conditions of CO_2 storage, especially at low temperatures.⁵³ 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.,⁸⁴ 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 water¹⁰¹ 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 Pitzer¹⁰⁶ 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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