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A thermodynamic model for predicting carbon dioxide solubility in aqueous sodium chloride solutions using an association equation of state

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Abstract: An activity coefficient-fugacity coefficient type thermodynamic model, i.e., CPA-P, based on the cubic-plus-association equation of state (CPA EoS) and Pitzer's activity model, is presented to study the phase behavior of carbon dioxide (CO₂)-water (H₂O) and CO₂-H₂O-sodium chloride (NaCl) systems at 273.15 to 573.15 K, 0.1 to 350 MPa, and 0-6 molality of NaCl. This model involves the hydrogen-bond interactions between H₂O and CO₂ molecules. The vapor-liquid equilibrium condition results in the extended Henry's law for CO₂ and Raoult's law for H₂O. Moreover, the properties of pure water are calculated by the IAPWS-95 EoS to improve the accuracy of the CPA-P model. The activity coefficients of CO₂ and the osmotic coefficient of H₂O are calculated by Pitzer's approach in aqueous electrolyte solution. The average absolute relative deviations (AARDs) of the CPA-P predictions for CO₂ solubility in pure water and aqueous NaCl solutions are 3.53% and 3.50%, respectively.

Keywords: CCS; solubility; CPA equation of state; Henry's law; CO₂-brine mixtures.

1. Introduction

Carbon dioxide (CO₂) capture and storage (CCS) has emerged as a fundamental strategy for mitigating the greenhouse effect and curbing global warming (Xiong et al., 2024; Springer et al., 2012; Xiong et al., 2025b). The CO₂-water (H₂O) and CO₂-H₂O-sodium chloride (NaCl) systems are of critical importance in various engineered geologic processes (Zhao et al., 2025; Zhao et al., 2015c). Accurate thermodynamic models are essential for quantifying CO₂ sequestration efficiency in geological aquifers (Xiong et al., 2025c). Therefore, developing a robust thermodynamic model grounded in extensive experimental data and a sound physical basis is necessary. Previous thermophysical studies have shown that the density and viscosity behaviors of non-ideal liquid mixtures reflect the combined effects of intermolecular interactions and

molecular packing or structural changes (Verma et al., 2019). Similar analyses of multicomponent liquid mixtures have further demonstrated that changes in composition and temperature can alter the relative contributions of intermolecular interactions and structural effects (Suman et al., 2020).

Duan and Sun (2003) proposed a model combining Duan's equation of state (EoS) with Pitzer's theory (Duan et al., 1992; Pitzer, 1973) to calculate CO₂ solubility in brine, which also proved reliable for predicting CO₂ solubility in seawater. Subsequently, a simplified version of Duan's model was introduced, employing a non-iterative EoS to compute CO₂ solubility in brine over ranges of 273.15–533.15 K, 0.1–200 MPa, and 0–4.5 mol·kg⁻¹ (Duan et al., 2006). Li and Duan (2007) extended this framework to describe the phase behavior of H⁺, OH⁻, HCO₃⁻, and CO₃²⁻ in the CO₂-H₂O-NaCl system at 273–523 K, 0–100 MPa, and NaCl molalities up to 5 mol·kg⁻¹.

Later improvements enabled the model to compute CO₂ solubility in brine for fluid inclusions and in aqueous solutions containing MgSO₄, MgCl₂, K₂SO₄, CaCl₂, and KCl (Mao et al., 2013; Shi and Mao, 2017). However, none of these models can be applied to calculate water solubility in the gas phase for the aforementioned systems.

Alternative thermodynamic models have been developed based on the activity coefficient (γ) of the liquid phase and the fugacity coefficient (ϕ) of the gas phase (Hassanzadeh et al., 2008; Salari et al., 2011; Zhao et al., 2015c; Zirrahi et al., 2010; Zirrahi et al., 2012). Spycher et al. (2003) presented a non-iterative γ - ϕ model using the Redlich–Kwong (RK) EoS to describe the phase behavior of the CO₂–H₂O system at 285.15–383.15 K and 0.1–60 MPa, and later extended it to compute CO₂ solubility in saline solutions with NaCl molalities up to 6 mol·kg⁻¹ (Spycher et al., 2003; 2005). Spycher and Pruess (2010) applied this model to study a geothermal system involving CO₂ injection. Zhao et al. (2015) developed the PSUCO₂ model based on Pitzer’s formalism (Pitzer, 1991), which was further extended to compute CO₂ solubility in aqueous solutions containing KCl, MgCl₂, NaCl, and CaCl₂ (Zhao et al., 2015a; 2015b). Springer et al. (2012) introduced a γ - ϕ phase-equilibrium model using the Soave–Redlich–Kwong (SRK) EoS for CO₂–H₂O–chloride salt systems. Portier and Rochelle (2005) employed the Peng–Robinson (PR) EoS to compute molar volumes and fugacity coefficients in the gas phase for CO₂ solubility in brines. Subsequently, the PR EoS was used to construct γ - ϕ models for H₂S–brine, SO₂–brine, N₂–brine, CH₄–brine, CO₂–brine, and gas-mixture–brine systems (Ziabakhsh-Ganji and Kooi, 2012; Zirrahi et al., 2012). While these models can predict water content in the gas phase, they do not incorporate more accurate EoS formulations, such as the statistical association fluid theory (SAFT) or the cubic-plus-association (CPA) EoS.

The SAFT family of EoS has been extensively applied to study CO₂ solubility in aqueous solutions (Ji and Zhu, 2012; Sun and Dubessy, 2012; Yan and Chen, 2010; Ji et al., 2005; Jiang et al., 2016; Xu et al., 2017; Sun and Dubessy, 2010). Ji et al. (2005) extended the SAFT1-RPM model to compute phase equilibria of the CO₂–brine system, treating CO₂ and H₂O molecules with 3B and 4C association schemes, respectively. Yan and Chen (2010) combined the PC-SAFT EoS with the eNRTL model to study CO₂ solubility in brine. Sun and Dubessy (2012) used the SAFT-LJ EoS to predict solubility in the CO₂–brine system. Ji and Zhu (2012) investigated vapor–liquid equilibria (VLE) of the H₂S–CO₂–H₂O–NaCl system using the SAFT2 EoS. Jiang et al. (2016) improved the mean spherical approximation to develop the SAFT2-KMSA model, which can describe liquid densities of electrolyte solutions at 298.15–473.15 K. Nevertheless, the prediction accuracy of SAFT-type EoS for CO₂ solubility in pure water and brine generally falls below that of the γ - ϕ thermodynamic models.

The CPA EoS, introduced by Kontogeorgis et al. (1996), has been widely adopted for predicting phase equilibria in CO₂–H₂O systems (Kontogeorgis et al., 2006a; Kontogeorgis et al., 2006b; Xiong et al., 2020). Ahmadi and Chapoy (2018) proposed a simplified CPA EoS (sCPA-EoS) to compute CO₂ solubility in mixed-salt

aqueous solutions, but its accuracy was below that of Duan’s model. Chabab et al. (2019) developed an electrolyte PR-CPA EoS (e-PR-CPA) for the CO₂–H₂O–NaCl system, which proved more accurate than Duan’s model under geological storage conditions. Xiong et al. presented an electrolyte CPA EoS (e-CPA) that provides a more consistent framework for all phases (Xiong et al., 2023; Xiong et al., 2025a). Bian et al. (2019) constructed the CPA-WS model by combining CPA with the Wong–Sandler mixing rules (Wong and Sandler, 1992) to study mutual solubility in the CO₂–H₂O system and CO₂ solubility in brine.

Existing thermodynamic models have distinct advantages and limitations for CO₂–H₂O–electrolyte systems. Duan/Pitzer-type models (Duan and Sun, 2003; Zirrahi et al., 2012) have been widely used for CO₂ solubility in aqueous electrolyte solutions over broad temperature, pressure, and salinity ranges, and can accommodate different electrolyte compositions. However, these models mainly focus on CO₂ solubility in the aqueous phase and are less suitable for describing mutual CO₂–H₂O solubility. Conventional γ - ϕ models, such as PSUCO₂ (Zhao et al., 2015c), separately describe the gas and aqueous phases and benefit from the established treatment of electrolyte non-ideality by Pitzer’s model. Their limitation is that commonly used cubic EoS do not explicitly account for CO₂–H₂O association, which can affect the description of water content in the gas phase. SAFT-type models (Zuo et al., 2024) provide a more detailed molecular description of association and electrolyte effects and can be extended to multicomponent systems, but this generally requires additional interaction parameters and a more involved parameterization procedure. CPA-based models (Xiong et al., 2023; Bian et al., 2019; Coelho et al., 2025) retain the relatively simple cubic-EoS structure while explicitly accounting for molecular association, thereby improving the description of CO₂–H₂O interactions. Nevertheless, extension of CPA to electrolyte systems introduces additional ion–molecule and association parameters, increasing model complexity. Accordingly, an effective thermodynamic framework should capture both CO₂–H₂O association and electrolyte non-ideality without excessive parameterization. To the best of our knowledge, however, no study has yet reported an unsymmetrical framework based on CPA EoS for modeling CO₂ solubility in brine.

In this study, we developed a thermodynamic model, designated CPA-P, by coupling the CPA EoS with Pitzer’s activity model for the CO₂–H₂O and CO₂–H₂O–NaCl systems. Compared with conventional γ - ϕ models based on RK, SRK, or PR equations of state, CPA-P employs the CPA EoS for the gas phase, allowing CO₂–H₂O cross-association to be explicitly considered in the calculation of fugacity coefficients. Compared with existing CPA-based models, CPA-P adopts an unsymmetrical treatment in which the CPA EoS describes molecular association in the gas phase, whereas Pitzer’s activity model accounts for electrolyte non-ideality in the aqueous phase. This formulation combines the respective strengths of CPA and Pitzer without requiring a unified CPA-based treatment of both phases.

CPA has been widely applied to model associating CO₂–H₂O systems (Kontogeorgis et al., 2006a;

Kontogeorgis et al., 2006b; Xiong et al., 2020), while Pitzer's formalism has been extensively used to describe electrolyte effects on CO₂ solubility in aqueous solutions (Pitzer, 1991; Zhao et al., 2015c). Compared with PSUCO₂ (Zhao et al., 2015c), CPA-P retains the Pitzer treatment of the aqueous electrolyte phase but introduces the CPA association term to account for CO₂-H₂O interactions. In contrast to e-CPA (Xiong et al., 2023; Xiong et al., 2025a) and CPA-WS (Bian et al., 2019), CPA-P assigns the CPA EoS and Pitzer's activity model separately to the gas and aqueous phases. This treatment preserves the description of molecular association by CPA and the established representation of electrolyte non-ideality by the Pitzer model within the same phase-equilibrium calculation. The performance of the CPA-P model is compared with that of the PSUCO₂ and CPA-WS models.

2. Review of experimental data

The experimental datasets were collected from

published measurements covering the temperature, pressure, and NaCl molality ranges considered in the CPA-P model. When data from different sources were available under comparable conditions, their consistency was examined, and data showing substantial disagreement with other measurements were excluded from model development. The selected data were divided into three groups: CO₂ solubility in the aqueous phase (Table 1), H₂O content in the gas phase (Table 2), and CO₂ solubility in aqueous NaCl solutions (Table 3). Tables 1 and 2 contain 554 and 303 data points, respectively, all of which were used for parameter evaluation of the CO₂-H₂O system. For the CO₂-H₂O-NaCl system, Table 3 contains 1100 data points, of which 376 were used for parameter correlation, and the remaining 724 were used only for model validation. Thus, a total of 1233 data points were used for model development and parameter correlation, while 724 independent data points were retained for validation.

Table 1. AARDs of CO₂ solubility in aqueous phase.

References	<i>T</i> (K)	<i>P</i> (MPa)	<i>N_p</i>	AARD (%)		
				CPA-P	PSUCO ₂ *	CPA-WS**
Valtz et al. (2004)	278.20-308.20	0.50-7.96	32	5.17	6.36	10.46
Bamberger et al. (2000)	323.15-353.15	4.05-14.11	29	1.27	5.64	2.68
Briones et al. (1987)	323.15	6.82-17.68	7	2.48	3.66	2.53
Tong et al. (2013)	373.15	7.21-27.26	5	2.42	5.44	4.11
Guo et al. (2014)	273.15-573.15	10.00-120.00	89	2.96	5.04	3.27
Hou et al. (2013a)	298.15-423.15	1.09-17.55	30	4.95	6.54	4.68
Liu et al. (2011)	308.20-323.15	2.10-15.99	15	1.59	2.78	5.44
King et al. (1992)	288.15-298.15	6.08-24.32	27	0.47	0.92	2.34
Malinin (1959)	473.15-573.15	9.80-49.03	76	5.80	4.08	3.47
Müller et al. (1988)	373.15-473.15	0.33-8.11	49	2.76	3.69	12.41
Nighswander et al. (1989)	393.15-473.15	2.04-10.21	25	7.44	9.55	15.49
Prutton and Savage (1945)	393.15	2.33-70.32	12	6.38	6.77	9.62
D'souza et al. (1988)	323.15-348.15	10.13-15.20	4	4.02	1.74	7.04
Sako et al. (1991)	348.15	10.34-15.31	2	7.39	11.59	9.52
Takenouchi and Kennedy (1965)	423.15-573.15	10.00-140.00	35	6.01	6.85	6.21
Toedheide and Franck (1963)	323.15-573.15	20.00-350.00	92	1.98	5.44	3.45
Wiebe and Gaddy (1939)	348.15-373.15	5.07-70.93	16	0.49	4.92	5.73
Wiebe and Gaddy (1940)	323.15	5.07-70.93	9	0.41	2.54	3.68
Overall			554	3.53	5.07	5.14

N_p: Number of experimental data points evaluated.

$$AARD = \frac{1}{n} \sum_{i=1}^n \frac{|x_i^{\text{exp}} - x_i^{\text{cal}}|}{x_i^{\text{exp}}};$$

x^{exp} stands for the experimental solubility of CO₂ in H₂O-rich phase;

x^{cal} stands for the calculated solubility of CO₂ in H₂O-rich phase.

* indicates that the calculated ranges of the PSUCO₂ model are 273.15-573.15 K and 0.1-200 MPa.

** indicates that the calculated ranges of the CPA-WS model are 288.15-523.15 K and 0.1-350 MPa.

Table 2. AARD of H₂O content in CO₂-rich phase.

References	<i>T</i> (K)	<i>P</i> (MPa)	<i>N_p</i>	AARD (%)		
				CPA-P	PSUCO ₂ *	CPA-WS**
Valtz et al. (2004)	278.20-308.20	0.50-7.96	22	11.21	10.51	14.49
Bamberger et al. (2000)	323.15-353.15	4.05-14.11	29	3.85	6.88	3.51
Briones et al. (1987)	323.15	6.82-17.68	7	3.45	10.22	1.91
Dohrn et al. (1993)	323.15	10.10-30.10	3	10.41	12.71	9.04
D'souza et al. (1988)	323.15-348.15	10.13-15.20	4	13.85	17.53	13.10
King et al. (1992)	288.15-308.20	5.17-20.27	35	6.91	19.28	7.52
Malinin (1959)	473.15-573.15	19.61-58.84	34	6.30	6.38	5.52
Miiller et al. (1988)	373.15-473.15	0.33-8.11	49	6.40	6.94	7.88
Toedheide and Franck (1963)	323.15-573.15	20.00-350.00	90	2.52	3.15	4.77
Wiebe and Gaddy (1941)	298.15-348.15	0.10-70.93	30	9.99	15.31	6.24
Overall			303	5.83	8.77	6.65

Table 3. AARD of CO₂ solubility in aqueous NaCl solutions.

References	<i>T</i> (K)	<i>P</i> (MPa)	<i>m</i> _{NaCl} (mol·kg ⁻¹ H ₂ O)	<i>N_p</i>	AARD (%)		
					CPA-P	PSUCO ₂ *	CPA-WS**
Bando et al. (2003)	303.15-333.15	10.00-20.00	0.173-0.529	36	3.72	1.11	2.48
Zhao et al. (2015)	323.15-423.15	15.00	0-6.000	21	3.78	5.79	4.56
Hou et al. (2013b)	323.15-423.15	2.61-18.21	2.500-4.000	36	5.16	5.31	5.06
Kiepe et al. (2002)	313.15-353.15	0.10-10.10	0.520-4.340	64	5.06	5.24	10.63
Koschel et al. (2006)	323.15-373.15	5.00-20.24	1.000-3.000	14	3.31	4.74	3.52
Malinin and Kurovskaya (1975)	298.15-423.15	4.80	0-5.915	16	2.81	3.74	4.80
Malinin and Kurovskaya (1972)	298.15-348.15	4.80	0-4.458	16	9.01	7.67	7.46
Nighswander et al. (1989)	353.15-473.15	2.11-10.03	0.173	34	6.00	5.38	8.43
Rumpf et al. (1994)	313.15-433.15	0.47-9.64	3.997-5.999	63	1.56	7.20	11.45
Takenouchi and Kennedy (1965)	423.15-523.15	10.00-140.00	1.091-4.274	40	7.03	20.96	-
Yan et al. (2011)	323.15-413.15	5.00-40.00	1.000-5.000	36	3.26	5.31	4.64
Messabeb et al. (2016)***	323.15-423.15	4.99-20.23	0-6.000	40	4.34	4.93	7.13
Guo et al. (2016)***	273.15-473.15	10.00-40.00	1.000-5.000	180	3.97	4.50	6.78
Wang et al. (2019)***	303.15-353.15	3.00-30.00	0-3.000	504	2.58	2.48	9.31
Overall				1100	3.50	4.41	8.38

*m*_{NaCl} is the molality of NaCl in H₂O. ** indicates the calculated ranges of the CPA-WS model are 298.15-413.15 K and 0.1-50 MPa. *** indicates these experimental data are only used to verify the CPA-P model. - indicates the *P-T* range of experimental data exceeds the range of calculation of the model.

The experimental data of CO₂ solubility in H₂O in Table 1 are shown in Fig. 1 (a). Experimental data measured below 20 MPa account for 55% of the dataset, and 33% of experimental data are below 10 MPa. Moreover, the percentages of pressure at 20-50 MPa, 50-150 MPa, and 150-350 MPa are 26%, 15%, and 4%, respectively. Hence, lots of experimental data belong to the range of low pressures (Bamberger et al., 2000; Briones et al., 1987; D'souza et al., 1988; Hou et al., 2013a; King et al., 1992; Liu et al., 2011; Miiller et al., 1988; Nighswander et al.,

1989; Sako et al., 1991; Tong et al., 2013; Valtz et al., 2004). Experimental data at very high pressures were only presented by Toedheide and Franck (1963). The temperature distribution of experimental data is uniform, and the percentages of temperature at 273-323 K, 323-373 K, 373-423 K, 423-473 K, and 473-573 K are 26%, 17%, 14%, 19%, and 24%, respectively. The number of experimental data points for water content in the CO₂-rich phase in Fig. 1 (b) is below that of the solubility data in Fig. 1 (a). The percentages of pressure at 0-10 MPa, 10-20 MPa, 20-50

MPa, 50-100 MPa, and 100-350 MPa are 37%, 25%, 17%, 9%, and 12%, respectively. The experimental data are scarce at pressures above 20 MPa (Malinin, 1959; Dohrn et al., 1993; Toedheide and Franck, 1963; Wiebe and Gaddy, 1941). Meanwhile, the temperature distribution of experimental data is not uniform, and the percentages of temperature at 273-323 K, 323-373 K, 373-423 K, 423-

473 K, and 473-573 K are 36%, 15%, 7%, 14%, and 28%, respectively. Most of the experimental data are concentrated at 273-373 K. The experimental data for the CO₂-H₂O system extend to 573.15 K and 350 MPa, although the available measurements become relatively limited at high pressures, particularly above 150 MPa.

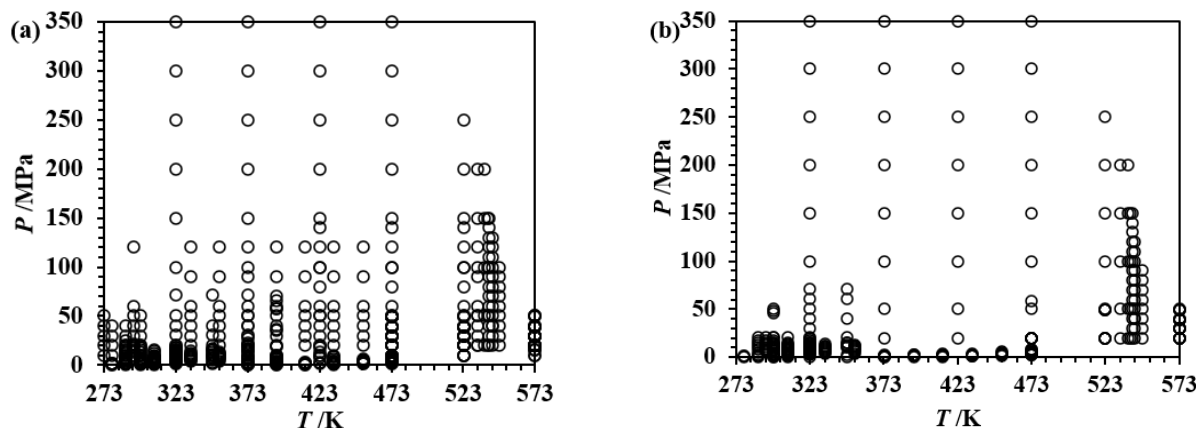


Fig. 1. P - T distributions of experimental data of CO₂ solubility in the liquid phase (a) and H₂O content in CO₂-rich phase (b) at 273.15-573.15 K and 0.1-350 MPa.

The experimental data of carbon dioxide solubility in brine (in Table 3) are shown in Fig. 2. 79% of the experimental data are below 20 MPa, and 48% of the experimental data are below 10 MPa. Most of the experimental data belong to the range of 273.15-323.15 K (43%), and 323.15-373.15 K (39%), and only 8% of experimental data are collected at 423.15-523.15 K. 80% of experimental data is below 3 mol·kg⁻¹ in Table 3, including 211 experimental data points at 0 mol·kg⁻¹ (Malinin and Kurovskaya, 1972; Malinin and Kurovskaya, 1975; Messabeb et al., 2016; Wang et al., 2019; Zhao et al., 2015c). Fig. 3 indicates that the experimental data of Zhao

et al. (2015) are consistent with Hou et al. (2013b) and Messabeb et al. (2016) at 423.15 K. However, the experimental results of Takenouchi and Kennedy (1965) are significantly below those of Zhao et al. (2015) and Messabeb et al. (2016) at 4.274 mol·kg⁻¹, and they are not used in this study. For the CO₂-H₂O-NaCl system, the available experimental data extend to 523.15 K and 140 MPa. Therefore, the range up to 573.15 K and 350 MPa represents the calculation range of the CPA-P model, whereas experimental evaluation of the brine system is limited to the range covered by the available measurements.

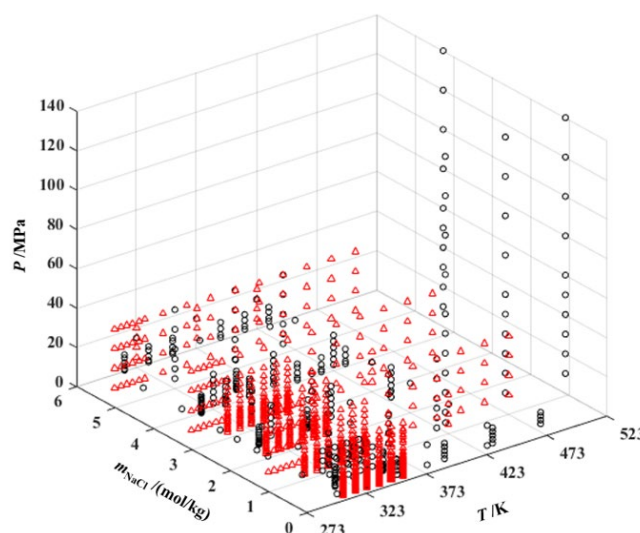


Fig. 2. P - T - m_{NaCl} distribution of experimental data of CO₂ solubility in brine at 273.15-523.15 K, 0.1-140 MPa, and 0-6 mol·kg⁻¹. Circles indicate that these experimental data are used to correlate with the CPA-P model. Triangles indicate that these experimental data are only used to verify the CPA-P model.

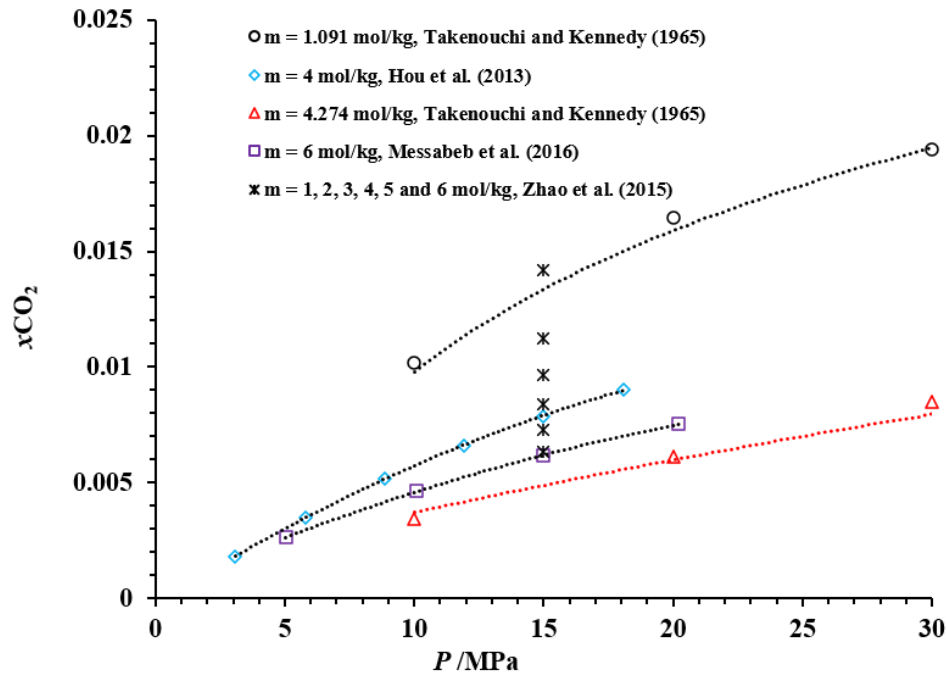


Fig. 3. Experimental data of CO₂ solubility in aqueous NaCl solutions at 423.15 K. Dashed lines refer to trend lines of experimental data. The experimental data points were taken from Takenouchi and Kennedy (1965); Hou et al. (2013b); Messabeh et al. (2016); Zhao et al. (2015).

3. CPA-P approach

3.1. Thermodynamic framework

To model carbon dioxide solubility in aqueous sodium chloride solutions, the reference state is pure liquid for the chemical potential of H₂O at the system temperature and pressure (Rumpf and Maurer, 1993), while the reference state for dissolved CO₂ (Eq. 2) is infinitely diluted gas in pure H₂O at unit molality (Kurz et al., 1996; Pérez-Salado Kamps et al., 2007; Zhao et al., 2015c).

$$\mu_{H_2O} = \mu_{H_2O}^{\text{pure}}(T, P) + R \cdot T \cdot \ln(\gamma_{H_2O} \cdot x_{H_2O}) \quad (1)$$

$$\mu_{CO_2} = \mu_{CO_2} \left(T, P, m_{CO_2} \rightarrow 1(\text{amount}), m_{CO_2} \rightarrow 0(\text{interaction}) \text{ in pure H}_2\text{O} \right) + R \cdot T \cdot \ln(\gamma_{CO_2} \cdot x_{CO_2}) \quad (2)$$

where μ_{CO_2} and μ_{H_2O} are respectively the chemical potentials of CO₂ and H₂O; T is system temperature, K; P is system pressure, MPa; x_{CO_2} and x_{H_2O} are respectively the mole fractions of carbon dioxide and water in the liquid phase; m_{CO_2} is molality of CO₂, mol·kg⁻¹; γ_{CO_2} and γ_{H_2O} are the activity coefficients of CO₂ and H₂O, respectively; R is equal to 8.314 MPa·cm³·mol⁻¹·K⁻¹.

The VLE condition results in the extended Henry's

law for carbon dioxide (Eq. 3, Rumpf and Maurer, 1993) and Raoult's law for H₂O (Eq. 4) by using the above reference states (Zhao et al., 2015c).

$$\varphi_{CO_2} y_{CO_2} P = k_{H,CO_2}^0 \exp \left(\frac{\bar{v}_{CO_2} (P - P_w^s)}{RT} \right) a_{CO_2} \quad (3)$$

$$\varphi_{H_2O} y_{H_2O} P = P_w^s \varphi_w^s \exp \left(\frac{\bar{v}_w (P - P_w^s)}{RT} \right) a_{H_2O} \quad (4)$$

where φ_{CO_2} and φ_{H_2O} are respectively the fugacity coefficients of carbon dioxide and water, which are calculated by CPA EoS; a_{CO_2} and a_{H_2O} are respectively the activity of carbon dioxide and water; k_{H,CO_2}^0 refers to Henry's constant of CO₂ in pure H₂O (Eq. 5); y_{CO_2} and y_{H_2O} are respectively the mole fractions of carbon dioxide and water in the gas phase; P_w^s and φ_w^s are respectively the vapor pressure and the fugacity coefficient for pure water vapor, which are determined by IAPWS-95 EoS (Wagner and Prüss, 2002); $\bar{v}_w$ is the partial molar volume of liquid H₂O, cm³·mol⁻¹, which can be approximate by the molar volume of saturated H₂O and calculated by IAPWS-95 EoS; $\bar{v}_{CO_2}$ is the partial molar volume of carbon dioxide, which is determined by fitting experimental data of H₂O-CO₂ system (Tables 1 and 2), and the results are presented in Table 4.

$$\ln(k_{H,CO_2}^0) = \begin{cases} 277.716 - 362.801 \left(\frac{T}{T_c} \right) + 57.7716 \left(\frac{T_c}{T} \right) + 300.135 \ln \left(\frac{T}{T_c} \right) & 273.15 \leq T \leq 363.15; P < 2 \text{ MPa} \\ 7.25021 + 11.5385 \left(\frac{T}{T_c} \right) - 15.1174 \left(\frac{T_c}{T} \right) - 30.5448 \ln \left(\frac{T}{T_c} \right) & 273.15 \leq T \leq 573.15; P \geq 2 \text{ MPa} \end{cases} \quad (5)$$

where T_c is the critical temperature of H₂O (647.096 K).

Table 4. The parameter of $\bar{v}_{\text{CO}_2}$ of CPA-P model.

T (K)	P (MPa)													
	1	5	10	20	30	40	50	70	100	150	200	250	300	350
273.15	23.0	22.0	21.5	20.9	20.4	20.0	19.6	19.0	18.5	18.3	18.1	17.9	17.7	17.4
278.22	30.0	26.0	24.5	23.8	23.5	23.0	22.5	22.0	21.5	21.3	21.1	20.9	20.7	20.5
288.15	47.0	40.0	33.5	28.8	27.5	26.5	26.0	25.0	24.5	24.3	24.1	23.9	23.7	23.4
293.15	50.0	43.5	36.6	30.1	28.1	27.5	26.3	25.8	25.6	25.4	25.2	25.0	24.8	24.5
298.15	51.0	44.0	36.9	31.9	28.5	27.8	26.7	26.5	26.4	26.2	26.0	25.8	25.6	25.3
308.20	50.0	43.0	36.8	30.0	28.7	28.0	27.1	26.7	26.6	26.4	26.2	26.0	25.8	25.5
323.15	55.0	46.1	40.2	36.9	35.7	34.5	32.6	31.5	30.7	30.3	29.9	29.5	29.1	28.7
333.15	54.0	43.1	38.0	35.5	34.0	33.0	31.0	29.5	29.0	28.8	28.6	28.4	28.2	27.9
348.15	57.0	46.7	43.0	39.7	37.8	36.4	35.5	34.0	33.8	33.5	33.2	32.9	32.6	32.2
353.15	50.0	41.0	39.0	36.5	35.0	34.0	33.0	31.5	30.0	29.6	29.3	29.0	28.7	28.3
373.15	65.0	55.9	46.7	42.0	39.0	37.2	36.0	34.0	32.2	31.7	31.3	30.8	30.4	30.0
393.15	61.0	50.0	44.0	39.9	38.4	37.5	36.2	34.0	32.0	31.5	31.0	30.5	30.0	29.5
413.15	66.0	55.0	43.0	40.0	39.0	38.0	37.1	35.0	33.5	33.0	32.5	32.0	31.5	31.0
423.15	75.0	65.0	55.0	45.0	42.2	40.7	39.5	38.0	36.5	35.0	34.0	33.2	32.4	31.6
433.15	66.0	55.0	48.0	40.3	37.9	36.7	35.4	33.5	32.7	32.2	31.7	31.2	30.8	30.2
453.15	64.0	52.5	45.5	41.0	38.5	36.6	35.6	34.0	32.5	32.0	31.5	31.0	30.5	30.0
473.15	67.0	53.5	45.0	40.3	37.3	36.7	36.0	35.6	35.2	34.9	34.6	34.3	33.8	33.3
523.15			26.4	24.0	22.4	21.4	21.0	21.5	23.5	25.8	27.4	29.4		
533.15				33.9	27.6	23.6	21.3	20.7	21.7	23.1	23.6			
538.15				39.7	28.5	21.1	19.5	21.0	22.0	20.5	16.5			
540.15				39.8	23.0	19.5	20.0	21.0	19.0	17.5				
541.15				40.0	15.2	17.0	18.6	20.5	19.8	13.0				
543.15				42.0	11.9	14.0	16.5	19.3	18.0	14.0*				
548.15				45.0	15.1	15.5	16.6	19.0	13.5					
573.15				46.0	20.8	18.2	20.2							

* indicates that the pressure at this point is 130 MPa.

3.2. Fugacity coefficient of CPA EoS

A two-parameter mixing rule presented by Panagiotopoulos and Reid (1986) is used for the CPA EoS in the Supplementary Materials as follows:

$$\alpha = \sum_i \sum_j y_i y_j \sqrt{\alpha_i \alpha_j} (1 - k_{ij} + (k_{ij} - k_{ji}) y_i) \quad (6)$$

$$b = \sum_i y_i b_i \quad (7)$$

where α is the energy parameter of the CPA EoS; b is the co-volume of the CPA EoS; k_{ij} is a binary interaction parameter.

The parameters of k_{ij} and k_{ji} of the CO_2 - H_2O system are determined by fitting experimental data in Tables 1 and 2. These parameters are temperature-dependent below 473.15 K (Eqs. 8 and 9). Moreover, the parameters of $k_{\text{CO}_2\text{-H}_2\text{O}}$ (in Table 5) are temperature-dependent and pressure-dependent above 473.15 K.

$$k_{\text{H}_2\text{O-CO}_2} = -0.40141 + 0.0012619T \quad (8)$$

$$273.15 \leq T \leq 573.15$$

$$k_{\text{CO}_2\text{-H}_2\text{O}} = -3.844375 + 0.0125T \quad (9)$$

$$273.15 \leq T \leq 473.15$$

Carbon dioxide is considered a non-self-associating compound (pseudo-associating component), and it has only one electron acceptor (Tsvintzelis et al., 2011). H_2O is modeled using the 4C association scheme. (Wolbach and Sandler, 1998). Hence, the cross-association strength between H_2O and CO_2 can be calculated using the equation proposed by Li and Firoozabadi (2009). A combining rule (Eq. 10) presented by Li and Firoozabadi (2009) is utilized for calculating the cross-association strength with an adjustable parameter (i.e., F), and the values of F (in Table 6) are determined by fitting experimental data in Tables 1-2. The X_{A_j} is calculated by Eq. (11) (Bian et al., 2019).

$$\Delta^{A_i B_j} = F_{ij} \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (10)$$

$$X_{A_j} = \frac{-1 + \sqrt{1 + 4\rho^2 X_{B_i} \Delta^{A_j B_i}}}{2\rho^2 X_{B_i} \Delta^{A_j B_i}} \quad (11)$$

where ρ is the molar density, $\text{mol} \cdot \text{cm}^{-3}$; i refers to H_2O ; j refers to CO_2 ; F is the interaction parameter ($F_{ij} = F_{ji}$); X_{A_j} is the approximate mole fraction of carbon dioxide molecules not bonded at site A; A and B stand for bonding sites; $\Delta^{A_i B_j}$ is the association strength.

Table 5. The parameter of $k_{\text{CO}_2-\text{H}_2\text{O}}$ of CPA-P model.

P (MPa)	T (K)							
	523.15	533.15	538.15	540.15	541.15	543.15	548.15	573.15
20	1.91	1.52	1.56	1.55	1.51	1.48	1.45	1.12
30	1.93	1.66	1.65	1.64	1.65	1.66	1.63	1.43
40	1.91	1.72	1.69	1.68	1.71	1.69	1.65	1.47
50	1.87	1.73	1.68	1.67	1.64	1.61	1.59	1.4
60	1.81	1.70	1.64	1.63	1.59	1.56	1.49	
70	1.75	1.63	1.58	1.56	1.5	1.46	1.41	
80	1.68	1.55	1.50	1.48	1.41	1.38	1.33	
90	1.61	1.46	1.42	1.38	1.35	1.31	1.25	
100	1.56	1.38	1.35	1.29	1.28	1.25	1.17	
110	1.52	1.32	1.29	1.23	1.23	1.18		
120	1.50	1.28	1.25	1.18	1.17	1.13		
130	1.48	1.25	1.21	1.14	1.09	1.09		
140	1.48	1.23	1.19	1.12	1.02			
150	1.47	1.22	1.17	1.10	0.94			
200	1.43	1.17	0.96					
250	1.46							

Table 6. AARD of CO_2 solubility in the pure H_2O phase and water content in the gas phase.

T (K)	F	AARD (%)					
		CPA-P		PSUCO2*		CPA-WS**	
		x_{CO_2}	$y_{\text{H}_2\text{O}}$	x_{CO_2}	$y_{\text{H}_2\text{O}}$	x_{CO_2}	$y_{\text{H}_2\text{O}}$
273.15	0.00	1.49	--	5.28	--	-	--
278.20	0.00	4.70	17.64	7.52	23.00	-	-
288.15	2.73	2.24	13.83	4.29	23.78	5.62	15.18
293.15	2.91	0.60	7.90	2.87	21.86	2.88	9.07
298.15	2.96	3.33	6.90	4.42	12.97	6.35	5.53
308.20	3.15	2.94	5.64	3.86	8.65	6.23	9.87
323.15	3.46	1.62	6.91	3.20	14.02	3.57	6.09
333.15	3.50	1.40	3.90	5.11	5.72	2.77	3.61
348.15	3.55	2.79	14.09	4.99	20.84	6.63	11.20
353.15	3.60	1.02	3.68	5.82	2.44	3.10	2.81
373.15	4.50	2.07	10.58	5.09	13.66	3.78	6.67
393.15	5.10	4.13	9.68	6.19	3.12	9.39	10.61
413.15	5.70	2.16	2.18	4.94	7.41	3.00	0.77
423.15	6.03	3.09	2.15	5.51	2.60	4.92	1.65
433.15	6.70	3.73	1.84	6.90	12.02	6.45	-
453.15	8.08	2.54	2.77	2.57	13.40	6.53	2.91
473.15	9.64	3.07	6.27	3.77	2.03	6.15	3.98
523.15	12.66	4.67	5.81	5.81	6.31	4.22	5.69
533.15	12.70	4.20	1.18	5.29	0.15	-	-
538.15	13.00	1.60	2.91	5.12	0.24	-	-
540.15	13.03	1.56	1.80	4.79	0.80	-	-
541.15	13.06	3.38	0.34	6.16	0.24	-	-
543.15	13.10	3.62	1.27	6.23	0.31	-	-
548.15	13.20	2.16	0.84	10.94	0.24	-	-
573.15	13.50	13.97	3.84	7.35	4.33	-	-
Overall AARD (%)		3.53	5.83	5.07	8.77	5.14	6.65

F is an interaction parameter of the CPA-P model in the association term. * indicates that the calculated range of the PSUCO2 model is 273.15-573.15 K and 0.1-200 MPa. ** indicates the calculated range of the CPA-WS model is 288.15-523.15 K and 0.1-350 MPa. - indicates the P - T range of experimental data exceeds the CPA-WS model. -- indicates a lack of experimental data.

φ_{CO_2} and $\varphi_{\text{H}_2\text{O}}$ are computed by CPA EoS as follows:

$$\ln \varphi_i = -\ln \left(\frac{v-b}{v} \right) + \frac{b_i}{v-b} - \frac{\alpha}{bRT} \times \left[\frac{\sum_j y_j (\alpha_{ji} + \alpha_{ij}) - \sum_j \sum_k y_j^2 y_k (k_{jk} - k_{kj}) \sqrt{\alpha_j \alpha_k} + y_i \sum_j y_j (k_{ij} - k_{ji}) \sqrt{\alpha_i \alpha_j}}{\alpha} - \frac{b_i}{b} \right] \times \ln \left(\frac{v+b}{v} \right) - \frac{\alpha}{bRT} \left(\frac{b_i}{v+b} \right) + \sum_A^{NS_i} (X_{Ai}) - \frac{1}{2} \left(\frac{1.9b_i}{4v-1.9b} \right) \sum_j^{NS_j} y_j \sum_A (1-X_{Aj}) - \ln Z \quad (12)$$

$$\ln \gamma_{\text{CO}_2} = 2m_{\text{CO}_2} \lambda_{nn} + 3m_{\text{CO}_2}^2 \mu_{nnn} + 2m_{\text{NaCl}} (\lambda_{nc} + \lambda_{na}) + 6m_{\text{CO}_2} m_{\text{NaCl}} (\mu_{nnc} + \mu_{nna}) + m_{\text{NaCl}}^2 \xi_{nca} \quad (13)$$

$$\phi - 1 = \frac{2}{2m_{\text{NaCl}} + m_{\text{CO}_2}} \left\{ -A^\phi \frac{I^{1.5}}{1 + 1.2I^{0.5}} + m_{\text{NaCl}}^2 [\beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-2I^{0.5}) + 2m_{\text{NaCl}} C_{ca}^\phi] + \frac{1}{2} m_{\text{CO}_2}^2 \lambda_{nn} + m_{\text{CO}_2}^3 \mu_{nnn} + m_{\text{CO}_2} m_{\text{NaCl}} (\lambda_{nc} + \lambda_{na}) + 3m_{\text{CO}_2}^2 m_{\text{NaCl}} (\mu_{nnc} + \mu_{nna}) + m_{\text{CO}_2} m_{\text{NaCl}}^2 \xi_{nca} \right\} \quad (14)$$

where subscripts i, j , and k stand for CO_2 or H_2O ; v is molar volume, $\text{cm}^3 \cdot \text{mol}^{-1}$; NS_i stands for the total number of bonding sites of component i ; Z is the deviation factor.

3.3. Pitzer's activity model

The a_{CO_2} and $a_{\text{H}_2\text{O}}$ are respectively calculated by Eq. (15) and Eq. (16) (Zhao et al., 2015c).

$$a_{\text{CO}_2} = \gamma_{\text{CO}_2} m_{\text{CO}_2} \quad (15)$$

$$\ln a_{\text{H}_2\text{O}} = -\frac{\phi M_{\text{H}_2\text{O}}}{1000} (2m_{\text{NaCl}} + m_{\text{CO}_2}) \quad (16)$$

where ϕ is the osmotic coefficient of H_2O ; $M_{\text{H}_2\text{O}}$ is molar mass of H_2O , $\text{g} \cdot \text{mol}^{-1}$; m_{NaCl} is molality of NaCl , $\text{mol} \cdot \text{kg}^{-1}$.

The γ_{CO_2} (Eq. 13) and ϕ (Eq. 14) can be calculated by Pitzer's approach in aqueous electrolyte solution (Pitzer, 1991; Akinfiev and Diamond, 2010). $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and C_{ca}^ϕ are Pitzer parameters for $\text{NaCl}-\text{H}_2\text{O}$ system (Pitzer et al., 1984); λ_{nn} and μ_{nnn} are Pitzer interaction parameters of neutral species in Supplementary Materials, their units are $\text{kg} \cdot \text{mol}^{-1}$ and $\text{kg}^2 \cdot \text{mol}^{-2}$, respectively; λ_{nc} and λ_{na} are Pitzer parameters of ions and neutral species, $\text{kg} \cdot \text{mol}^{-1}$; μ_{nna} , μ_{nnc} and ξ_{nca} are Pitzer parameters of ions and neutral species, $\text{kg}^2 \cdot \text{mol}^{-2}$; A^ϕ and I are respectively Debye-Hückel slope for ϕ and ionic strength, which can be calculated by Eqs. (17) and (18).

$$A^\phi = \frac{1}{3} (2\pi N_A \rho_w)^{0.5} \left(\frac{e^2}{4\pi \epsilon_0 \epsilon_r k_B T} \right)^{1.5} \quad (17)$$

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (18)$$

where π is Pi (3.14159); N_A is Avogadro constant (6.0221367×10^{23}); ρ_w is the density of H_2O ($\text{kg} \cdot \text{m}^{-3}$), which can be computed by IAPWS-95 EoS; e is elementary charge, and it is equal to 1.60218×10^{-19} ; ϵ_0 and ϵ_r are the vacuum permittivity ($8.85419 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$) and the relative permittivity of pure H_2O computed by Fernández et al. (1997) equations; k_B is Boltzmann constant, and it is equivalent to $1.38065 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$; z_i is the ionic charge of Na^+ or Cl^- .

The parameter of ξ_{nca} (in Table 7) is determined by fitting experimental data for the CO_2 -brine system listed in Table 3. It is primarily influenced by temperature and the molality of NaCl .

3.4. Calculation method

Since the total mole fraction of the gas phase is equal to 1 (Eq. 19), Eqs. (3) and (4) can be combined into Eq. (20).

$$y_{\text{H}_2\text{O}} + y_{\text{CO}_2} = 1 \quad (19)$$

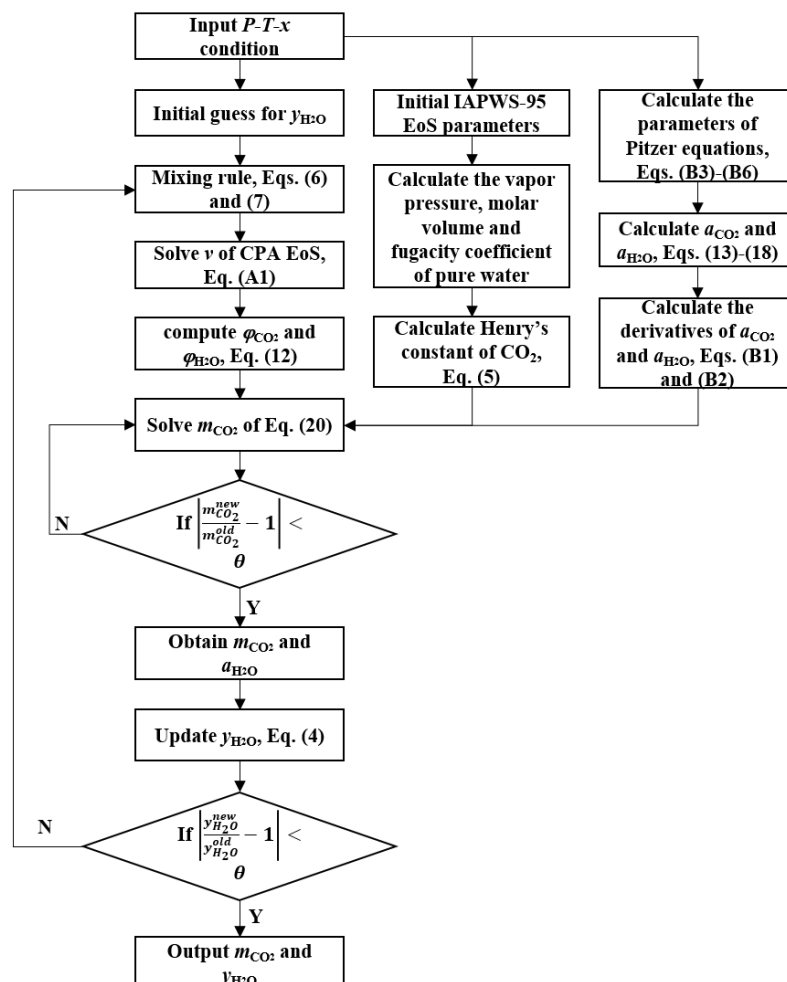
$$\frac{P_w^s \varphi_w^s \exp \left(\frac{\bar{v}_w (P - P_w^s)}{RT} \right) a_{\text{H}_2\text{O}}}{\varphi_{\text{H}_2\text{O}} P} + \frac{k_{\text{H},\text{CO}_2}^0 \exp \left(\frac{\bar{v}_{\text{CO}_2} (P - P_w^s)}{RT} \right) a_{\text{CO}_2}}{\varphi_{\text{CO}_2} P} - 1 = 0 \quad (20)$$

Eq. (20) can be solved by the Newton-Raphson method with respect to m_{CO_2} at a given temperature, pressure, and salt molality. The flow chart is shown in Fig. 4, and the main calculation steps are listed:

- Step 1: Input temperature, pressure, and molality of NaCl , and the initial guess of $y_{\text{H}_2\text{O}}$ is equal to P_w^s/P . Calculate the $\bar{v}_w$, P_w^s and φ_w^s of pure H_2O by using IAPWS-95 EoS. Calculate the interaction parameters of the Pitzer equations. Calculate Henry's constant for CO_2 in pure H_2O .
- Step 2: Calculate α and b of the CPA EoS for the gas-phase mixture using the mixing rule.
- Step 3: Solve the molar volume of the CPA EoS. Calculate φ_{CO_2} and $\varphi_{\text{H}_2\text{O}}$.
- Step 4: Calculate a_{CO_2} and $a_{\text{H}_2\text{O}}$ by Eqs. (13)-(18). Calculate the derivatives of a_{CO_2} and $a_{\text{H}_2\text{O}}$ with respect to m_{CO_2} by Eqs. (S7) and (S8). Update m_{CO_2} by the Newton-Raphson method ($m_{\text{CO}_2}^{(\text{new})} = m_{\text{CO}_2}^{(\text{old})} - f(m_{\text{CO}_2})/f'(m_{\text{CO}_2})$).
- Step 5: If $|m_{\text{CO}_2}^{(\text{new})}/m_{\text{CO}_2}^{(\text{old})} - 1| > 10^{-5}$, then go to Step 4, or else go to Step 6.
- Step 6: Obtain m_{CO_2} and $a_{\text{H}_2\text{O}}$ from Step 4, and update $y_{\text{H}_2\text{O}}$ by Eq. (4).
- Step 7: If $|y_{\text{H}_2\text{O}}^{(\text{new})}/y_{\text{H}_2\text{O}}^{(\text{old})} - 1| > 10^{-5}$, then go to Step 2, or else output m_{CO_2} and $y_{\text{H}_2\text{O}}$.

Table 7. The parameter of ξ_{nca} of CPA-P model.

T (K)	m_{NaCl} (mol·kg ⁻¹)						
	0.1	1	2	3	4	5	6
273.15	0.01700	0.00540	0.00302	-0.00180	-0.00217	-0.00270	-0.00410
298.15	0.01888	0.00690	0.00050	-0.00155	-0.00207	-0.00245	-0.00450
303.15	0.01950	0.00750	0.00050	-0.00150	-0.00205	-0.00240	-0.00452
313.15	0.02172	0.00900	0.00100	-0.00140	-0.00200	-0.00230	-0.00450
323.15	0.02527	0.01090	0.00217	-0.00130	-0.00195	-0.00220	-0.00440
333.15	0.02881	0.01490	0.00556	0.00084	-0.00112	-0.00218	-0.00422
348.15	0.03413	0.02090	0.01064	0.00405	0.00013	-0.00215	-0.00380
353.15	0.03590	0.02290	0.01233	0.00512	0.00054	-0.00214	-0.00360
373.15	0.04298	0.03090	0.01910	0.00940	0.00220	-0.00210	-0.00310
393.15	0.07000	0.04840	0.02438	0.01016	0.00240	-0.00100	-0.00210
413.15	0.10000	0.06590	0.02966	0.01093	0.00371	0.00200	-0.00020
423.15	0.14000	0.10300	0.04730	0.01322	0.00660	0.00250	0.00010
433.15	0.19000	0.13026	0.05200	0.01600	0.00700	0.00300	0.00050
473.15	0.26000	0.18900	0.07500	0.03000	0.01500	0.00800	0.00200
523.15	0.35000	0.27200	0.13000	0.07000	0.04600	0.02600	0.00600
573.15	0.40000	0.32000	0.17000	0.10000	0.07200	0.04200	0.00900


Fig. 4. The flow chart of the CPA-P model. θ is the convergence criterion (10^{-5}).

4. Results and Discussion

4.1. Parameter evaluation

There are five adjustable parameters ($\bar{v}_{\text{CO}_2}$, $k_{\text{CO}_2-\text{H}_2\text{O}}$, $k_{\text{H}_2\text{O}-\text{CO}_2}$, F , and ζ_{ncal}) in the CPA-P model. The data in Tables 1 and 2 are used to determine the parameters for the CO_2 - H_2O system. For the CO_2 - H_2O -NaCl system, the datasets reported by Messabeh et al. (2016), Guo et al. (2016), and Wang et al. (2019), comprising 724 data points, are reserved for model verification. These datasets were selected as independent literature sources covering different temperature, pressure, and NaCl molality ranges. The remaining 376 data points in Table 3 are used for parameter fitting. The 724 verification data points are not involved in the fitting procedure, and the fitted parameters are kept unchanged during model verification. For the CO_2 - H_2O system, $\bar{v}_{\text{CO}_2}$, $k_{\text{CO}_2-\text{H}_2\text{O}}$, $k_{\text{H}_2\text{O}-\text{CO}_2}$, and F were empirically evaluated using the experimental data listed in Tables 1 and 2. The results show that $k_{\text{H}_2\text{O}-\text{CO}_2}$ is a function of temperature, and its value is therefore regressed using Eq. (8). After $k_{\text{H}_2\text{O}-\text{CO}_2}$ is determined, $k_{\text{CO}_2-\text{H}_2\text{O}}$ is evaluated and regressed using Eq. (9). Finally, F , $\bar{v}_{\text{CO}_2}$, and ζ_{ncal} are successively determined. Some of these parameters depend on temperature, pressure, and NaCl molality, and cubic spline interpolation is used to determine their values over the temperature range of 273.15–573.15 K, pressure range of 0.1–350 MPa, and NaCl molality range of 0–6 mol·kg⁻¹.

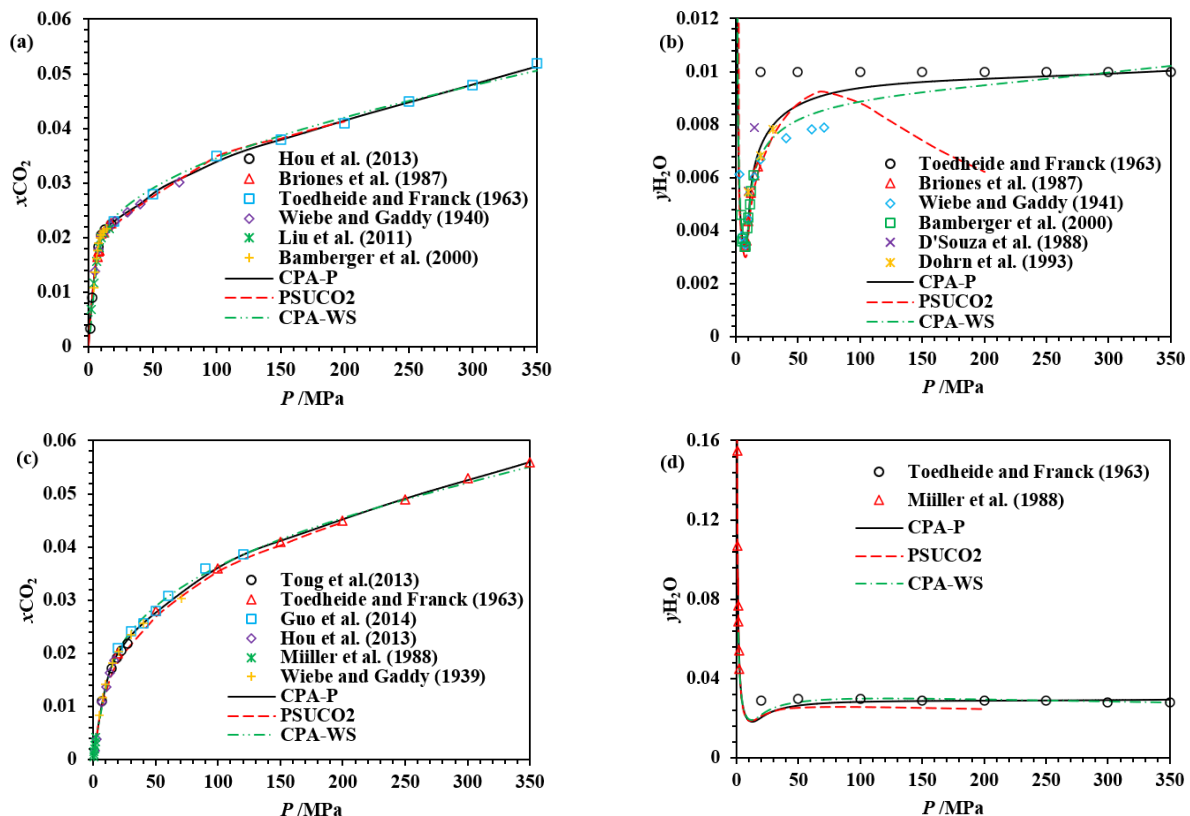
4.2. CO_2 - H_2O system

The PSUCO2 (Zhao et al., 2015c) and CPA-WS (Bian et al., 2019) models are used to compare with the CPA-P model. The temperature and pressure ranges of the

PSUCO2 model for the CO_2 - H_2O system are 273.15–573.15 K and 0.1–200 MPa, while the ranges for the CPA-WS model are from 288.15 to 523.15 K and 0.1 to 350 MPa.

Fig. 5 shows that CPA-P and CPA-WS models can accurately calculate the phase behavior of both CO_2 solubility in the liquid phase (Fig. 5a, c, e, and g) and H_2O content in the gas phase (Fig. 5b, d, f, and h) up to 350 MPa, while the CPA-P model is more accurate at 423.15 K to 473.15 K. Moreover, the CPA-P model is more accurate than the PSUCO2 model at pressures above 100 MPa (Fig. 5b, d, and g), and the predictions of the PSUCO2 model are not consistent with experimental data at 323.15 K and pressures above 70 MPa.

The sensitivity of the CPA-P predictions to the adjustable parameters is not uniform for different phase-equilibrium properties. The calculated H_2O content in the gas phase is particularly sensitive to the binary interaction parameter $k_{\text{CO}_2-\text{H}_2\text{O}}$ and the association parameter F , both of which directly affect the CO_2 - H_2O interactions represented by the CPA EoS. In contrast, CO_2 solubility in the aqueous phase is more strongly influenced by $\bar{v}_{\text{CO}_2}$ than by these CPA interaction parameters. The influence of the binary interaction parameters also varies with thermodynamic conditions. Both $k_{\text{CO}_2-\text{H}_2\text{O}}$ and $k_{\text{H}_2\text{O}-\text{CO}_2}$ are treated as temperature-dependent parameters, and $k_{\text{CO}_2-\text{H}_2\text{O}}$ is additionally pressure-dependent above 473.15 K. These results indicate that the CPA-P predictions, particularly the calculated H_2O content in the gas phase, are sensitive to the binary interaction and association parameters, and their temperature and pressure dependence must therefore be considered over the investigated range.



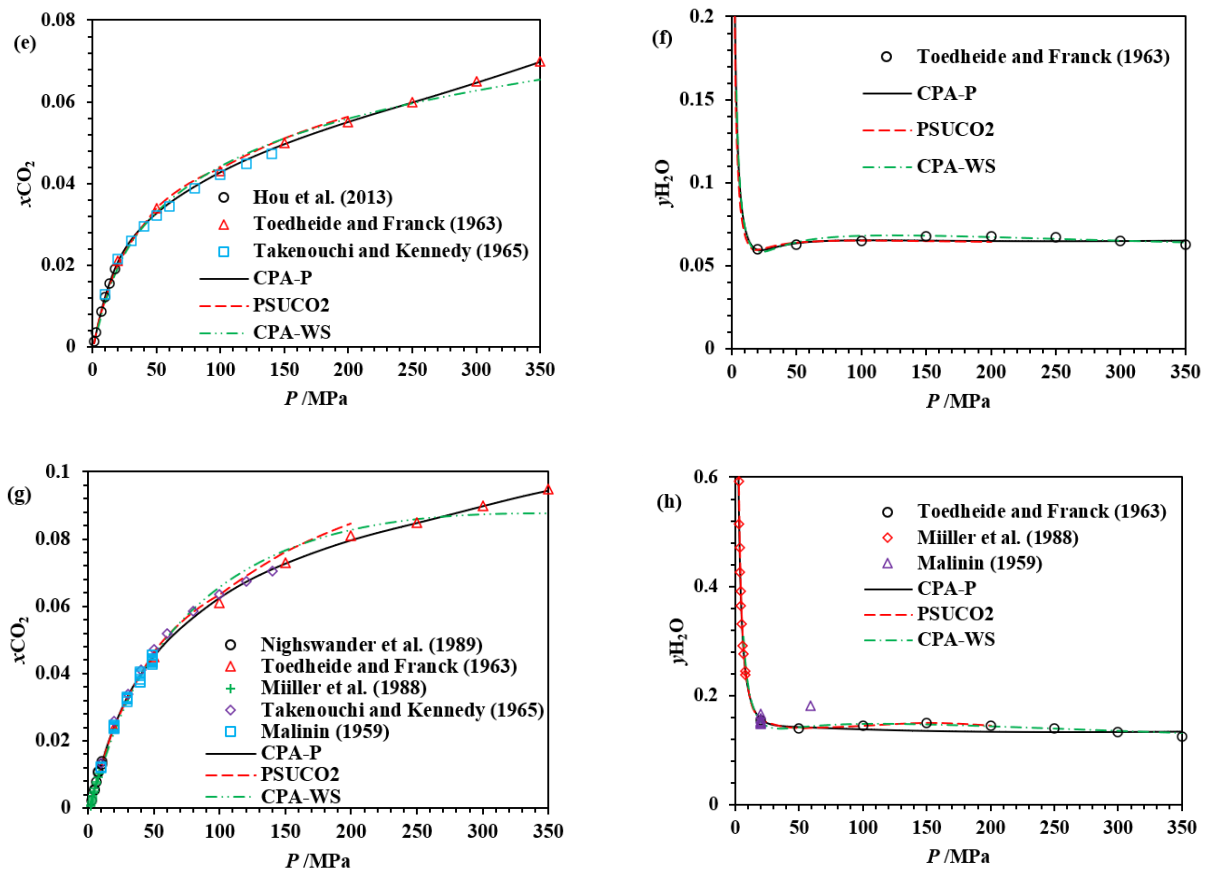
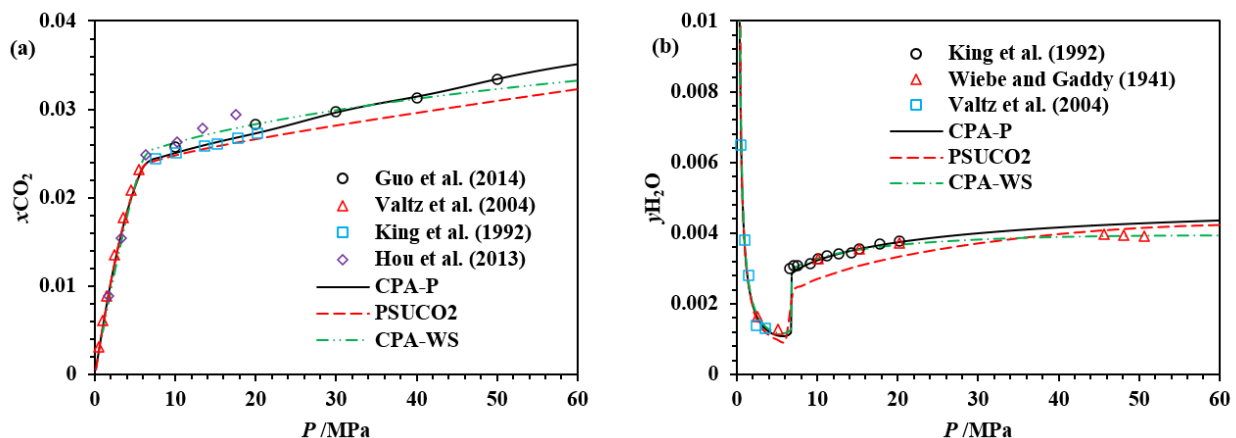


Fig. 5. CO₂-H₂O VLE at 323.15 K (a and b), 373.15 K (c and d), 423.15 K (e and f) and 473.15 K (g and h). CPA-P calculations for H₂O liquid phase (a, c, e, and g) and CO₂ gas phase (b, d, f, and h). The experimental data points were taken from Malinin (1959); Takenouchi and Kennedy (1965); Toedheide and Franck (1963); Wiebe and Gaddy (1939); Wiebe and Gaddy (1940); Wiebe and Gaddy (1941); Bamberger et al. (2000); Briones et al. (1987); Dohrn et al. (1993); D'souza et al. (1988); Guo et al. (2014); Hou et al. (2013a); Liu et al. (2011); Miiller et al. (1988); Nighswander et al. (1989); Tong et al. (2013).

Fig. 6 (b), (d), (f), and (h) show that the calculations of the CPA-P and CPA-WS models are more accurate than PSUCO2 for water content in the carbon dioxide gas phase at 298.15 K to 348.15 K, and 0.1-80 MPa, because the CPA-P and CPA-WS models take into account the interaction of hydrogen bonds between H₂O molecules and CO₂ molecules. Meanwhile, Fig. 6 (b) and (d) show that the calculations of the PSUCO2 model are below the

experimental value at 298.15 K to 308.15 K and 10 to 20 MPa, while Fig. 6 (h) indicates that the calculations of the PSUCO2 model are substantially above the experimental value at 348.15 K and 20 to 80 MPa. Fig. 6 (a), (c), (e), and (g) show that the calculations of the three models are accurate for carbon dioxide solubility in the H₂O-rich phase at 298.15 K to 348.15 K, and the CPA-P model is the most accurate.



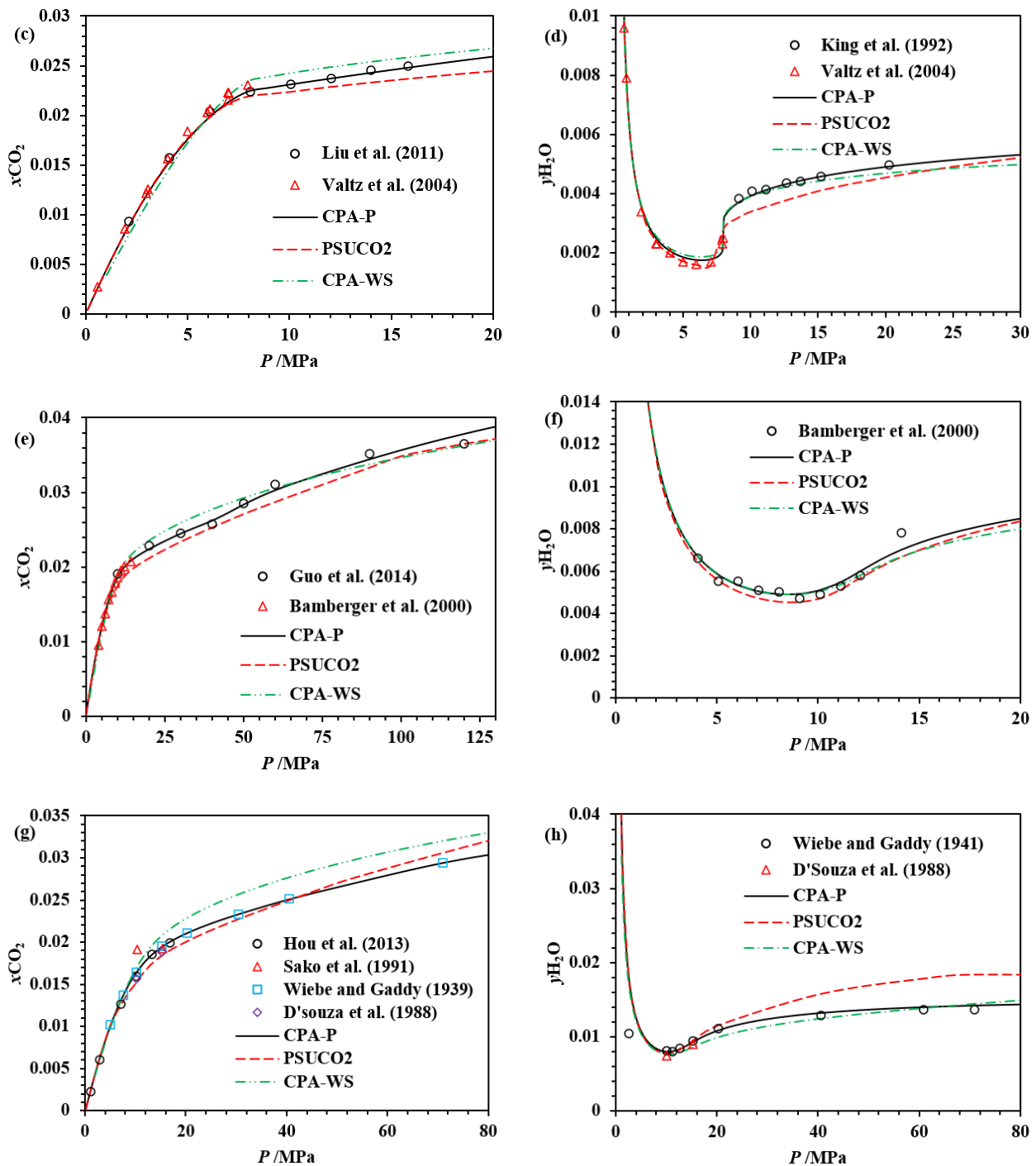


Fig. 6. H₂O-CO₂ VLE at 298.15 K (a and b), 308.20 K (c and d), 333.15 K (e and f), and 348.15 K (g and h). CPA-P calculations for H₂O liquid phase (a, c, e, and g) and CO₂ gas phase (b, d, f, and h). The experimental data points were taken from Wiebe and Gaddy (1939); Wiebe and Gaddy (1941); Bamberger et al. (2000); D'souza et al. (1988); Guo et al. (2014); Hou et al. (2013a); King et al. (1992); Liu et al. (2011); Sako et al. (1991); Valtz et al. (2004).

Fig. 7 (b), (d), (f), and (h) show that the calculations of the CPA-P model are consistent with the experimental data of water content in carbon dioxide gas phase at 393.15 K to 453.15 K and 0.6 to 6.3 MPa, while the calculations of the PSUCO2 model are slightly below experimental data at 413.15 K to 453.15 K (Fig. 7 d, f, and

h). Fig. 7 (a), (c), (e), and (g) show that the calculations of the CPA-P model are the most accurate for carbon dioxide solubility in the liquid phase at pressures up to 125 MPa. However, the PSUCO2 and CPA-WS models produce large errors at 433.15 K and above 90 MPa.

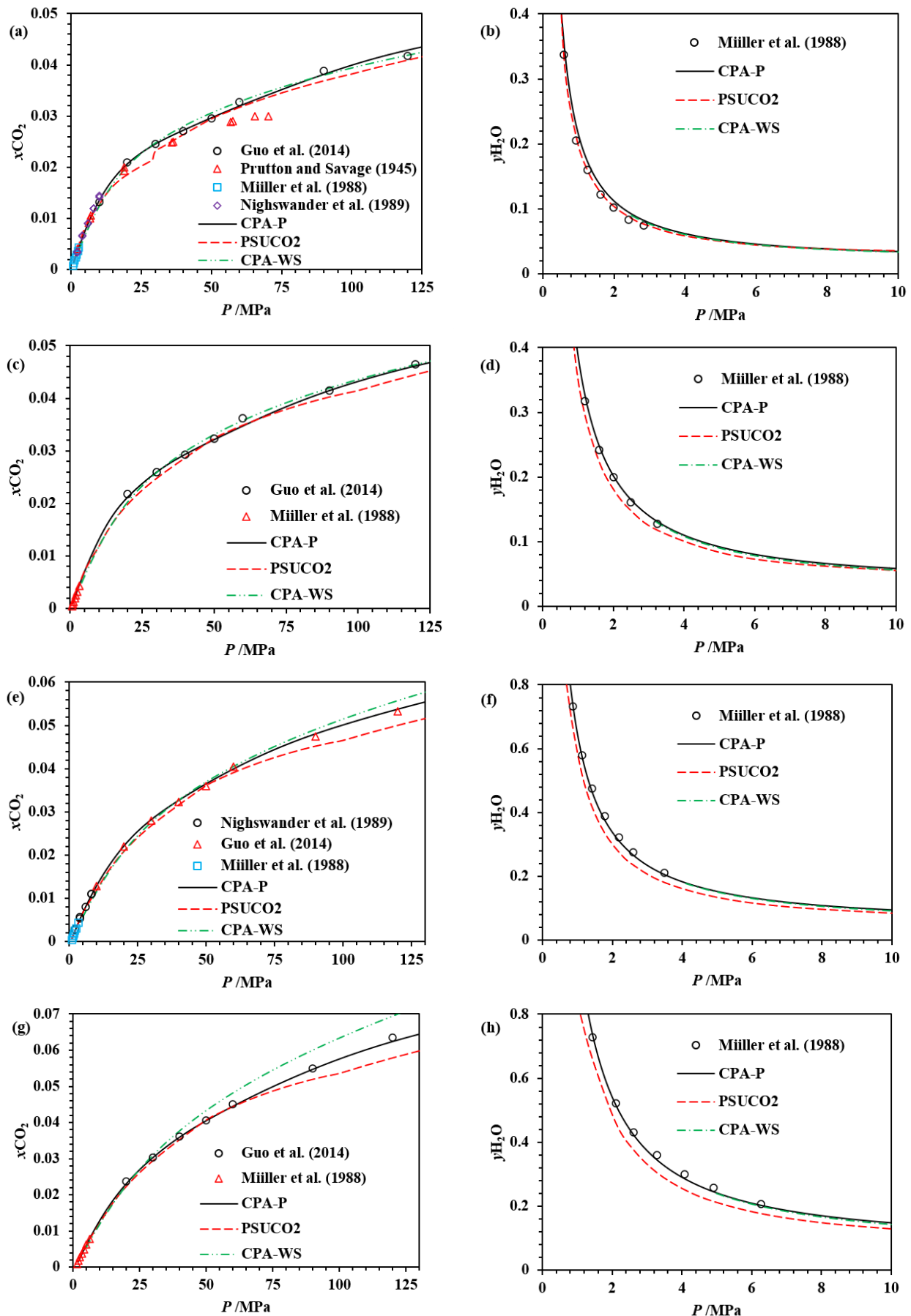


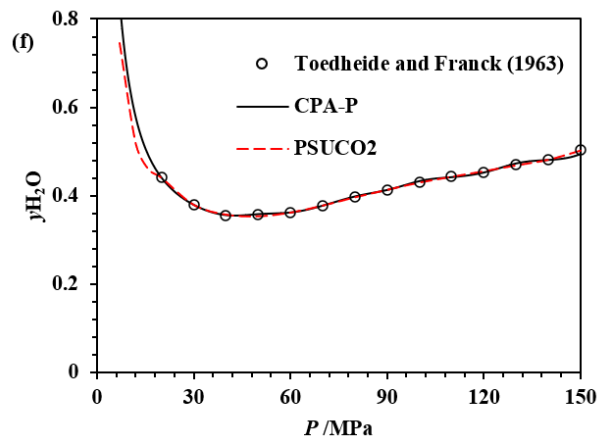
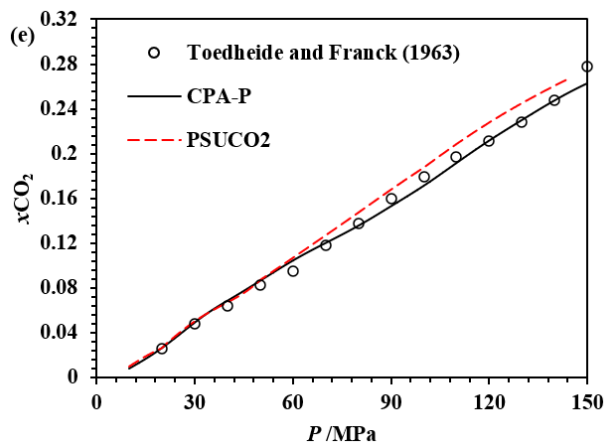
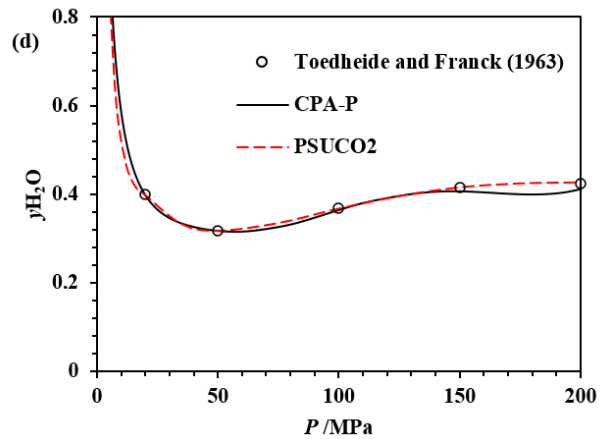
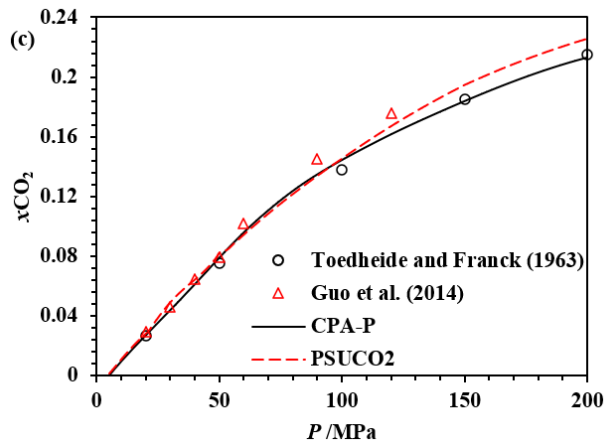
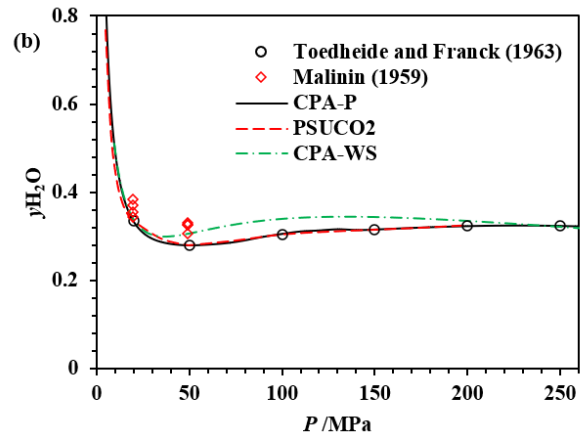
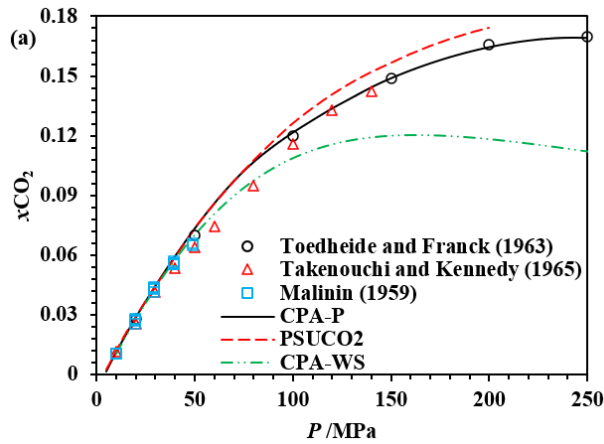
Fig. 7 CO₂-H₂O VLE at 393.15 K (a and b), 413.15 K (c and d), 433.15 K (e and f), and 453.15 K (g and h). CPA-P calculations for H₂O liquid phase (a, c, e, and g) and CO₂ gas phase (b, d, f, and h). The experimental data points were taken from Prutton and Savage (1945); Guo et al. (2014); Müller et al. (1988); Nighswander et al. (1989).

Fig. 8 shows that the calculations of the CPA-P and PSUCO2 models are in agreement with experimental data at 523.15–573.15 K, while the CPA-WS model is not accurate at 523.15 K when the pressure is above 100 MPa (Fig. 8 a). Table 6 shows that the average absolute relative deviations (AARDs) of carbon dioxide solubility in the liquid phase of CPA-P, PSUCO2, and CPA-WS models are 3.53%, 5.07%, and 5.14%, and the AARDs of these models for water content in the CO₂-rich phase are 5.83%,

8.77%, and 6.65%, respectively.

$$AARD = \frac{1}{n} \sum_{i=1}^n \frac{|x_i^{\text{exp}} - x_i^{\text{cal}}|}{x_i^{\text{exp}}} \quad (21)$$

where x^{exp} is experimental data in mole fraction; x^{cal} is calculated data in mole fraction.



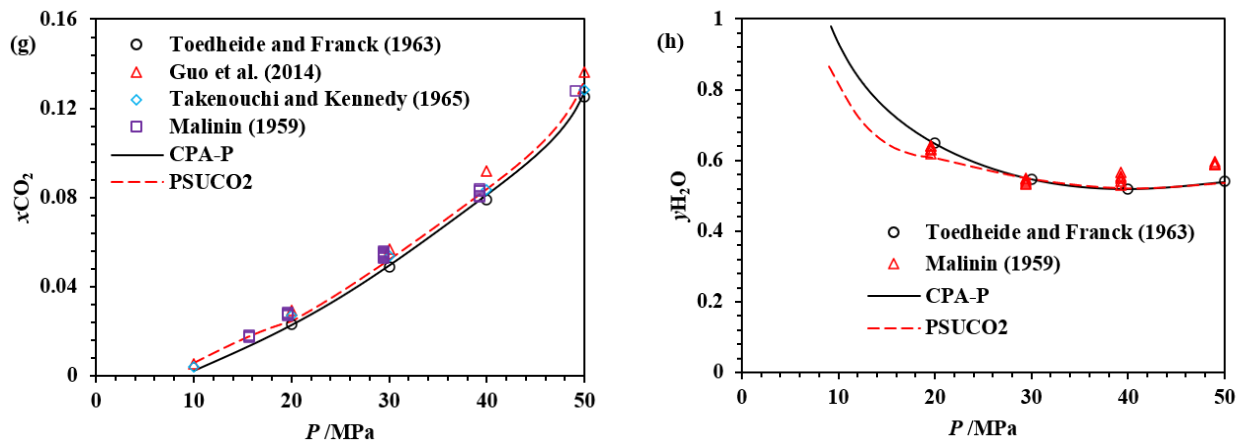


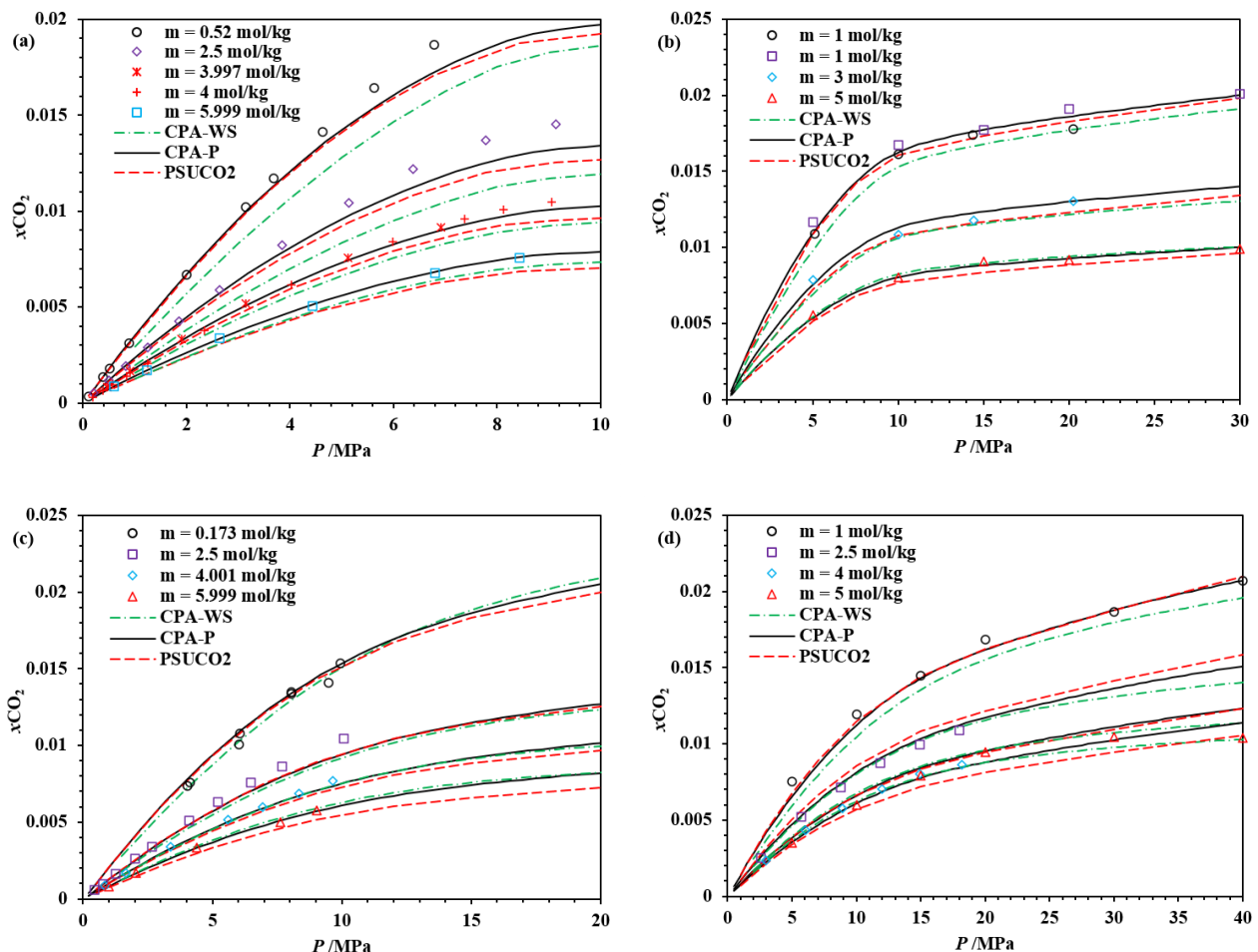
Fig. 8. CO₂-H₂O VLE at 523.15 K (a and b), 533.15 K (c and d), 541.15 K (e and f), and 573.15 K (g and h). CPA-P calculations for H₂O liquid phase (a, c, e, and g) and CO₂ gas phase (b, d, f, and h). The experimental data points were taken from Malinin (1959); Takenouchi and Kennedy (1965); Toedheide and Franck (1963); Guo et al. (2014).

4.3. CO₂-H₂O-NaCl system

The PSUCO2 and CPA-WS models are utilized to compare with the CPA-P model for carbon dioxide solubility in brine. The temperature and pressure ranges of the PSUCO2 model are 273.15 to 573.15 K and 0.1 to 200 MPa, while the ranges for the CPA-WS model are 298.15 to 413.15 K and 0.1 to 50 MPa.

Fig. 9 (a-e) show that the calculations of the CPA-P

and PSUCO2 models are more accurate than those of CPA-WS at 313.15-393.15 K, and salinities from 0 to 6 mol·kg⁻¹, and pressures up to 40 MPa. The CPA-WS produces large errors at low molality of NaCl (Fig. 9a and e). Fig. 9 (f-h) show that the calculations of the CPA-P model are more accurate than those of PSUCO2 at 423.15-523.15 K and 0.1-140 MPa. The predictions of the PSUCO2 model are above the experimental data at 423.15 K to 523.15 K in Fig. 9 (f-h).



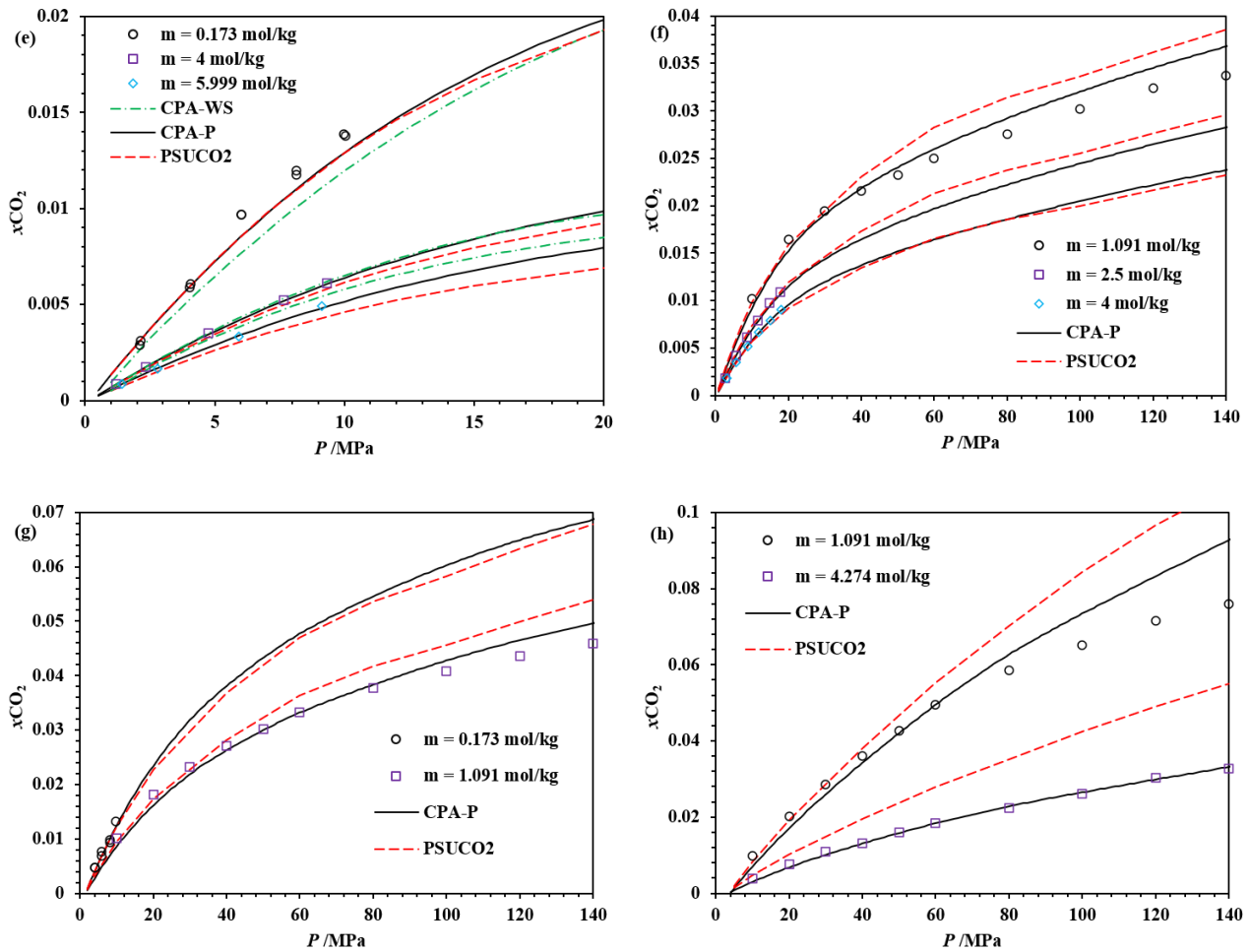
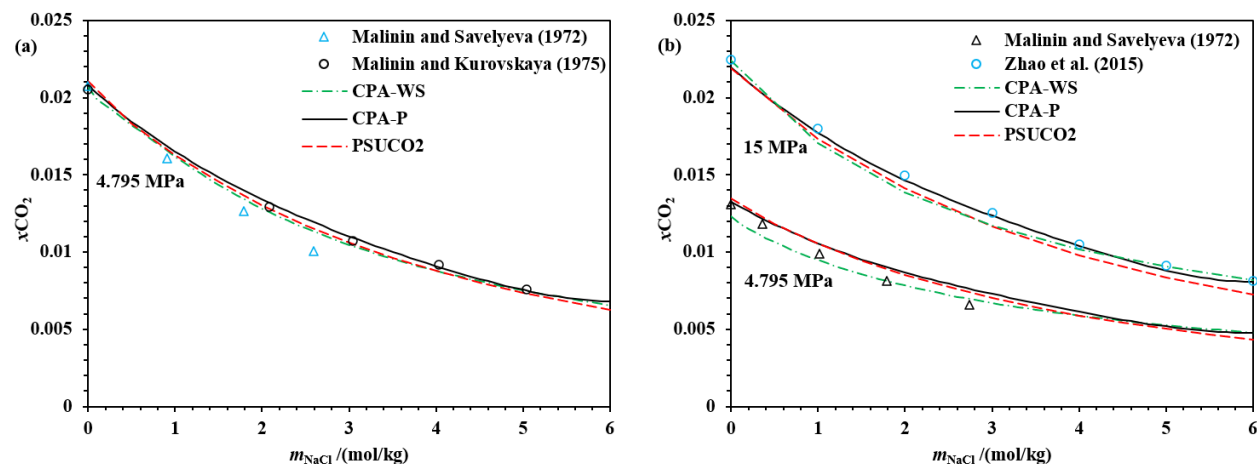


Fig. 9 CO₂-H₂O-NaCl VLE at 313.15 K (a), 323.15 K (b), 353.15 K (c), 373.15 K (d), 393.15 K (e), 423.15 K (f), 473.15 K (g) and 523.15 K (h). The experimental data points were taken from Takenouchi and Kennedy (1965); Hou et al. (2013b); Kiepe et al. (2002); Koschel et al. (2006); Nighswander et al. (1989); Rumpf et al. (1994); Yan et al. (2011).

Fig. 10 shows that the calculations of CPA-P, PSUCO2, and CPA-WS models for carbon dioxide solubility in brine are accurate at 298.15–423.15 K, 4.795–15.000 MPa, and NaCl molalities of 0–6 mol·kg⁻¹. Fig. 11 shows that the proposed CPA-P model exactly predicts carbon dioxide solubility in aqueous sodium chloride solutions at 273.15–473.15 K, 10–40 MPa, and salinities up to 5 mol·kg⁻¹. Figs. 11 (a–c) show that the accuracy of predictions of the CPA-P model is slightly influenced by

pressure, especially at 273.15 to 313.15 K. Fig. 12 indicates that the predictions of the CPA-P model for the CO₂-H₂O-NaCl system are consistent with experimental data at 303.15–423.15 K, 0.1–30 MPa, and 0–6 mol·kg⁻¹. However, the predictions of this model are above the experimental data at low temperatures in Figs. 12 (a) and (b). Table 3 shows that the AARDs of CPA-P, PSUCO2, and CPA-WS models for CO₂ solubility in brine are 3.50%, 4.41%, and 8.38%, respectively.



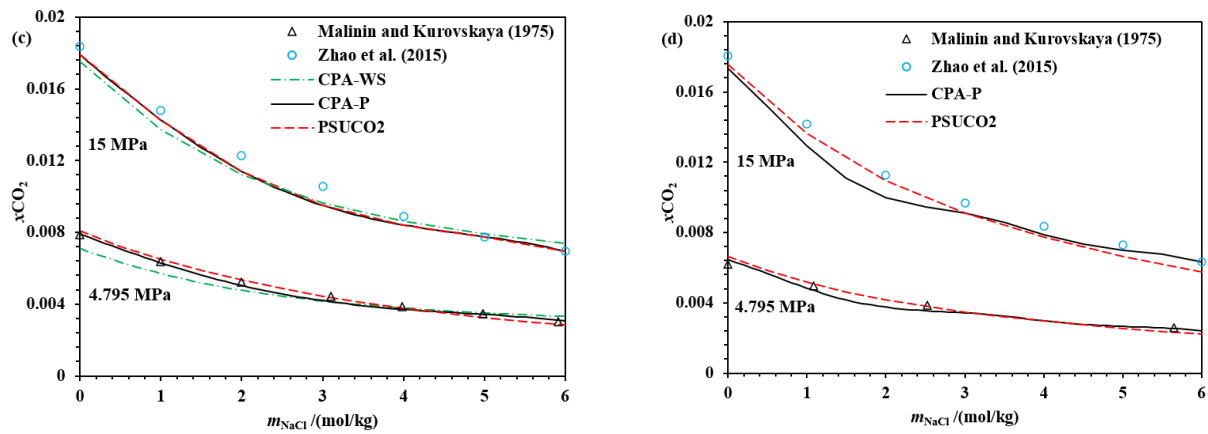


Fig. 10. CO₂-H₂O-NaCl VLE at 298.15 K (a), 323.15 K (b), 373.15 K (c), and 423.15 K (d). The experimental data points were taken from Malinin and Kurovskaya (1972); Malinin and Kurovskaya (1975); Zhao et al. (2015).

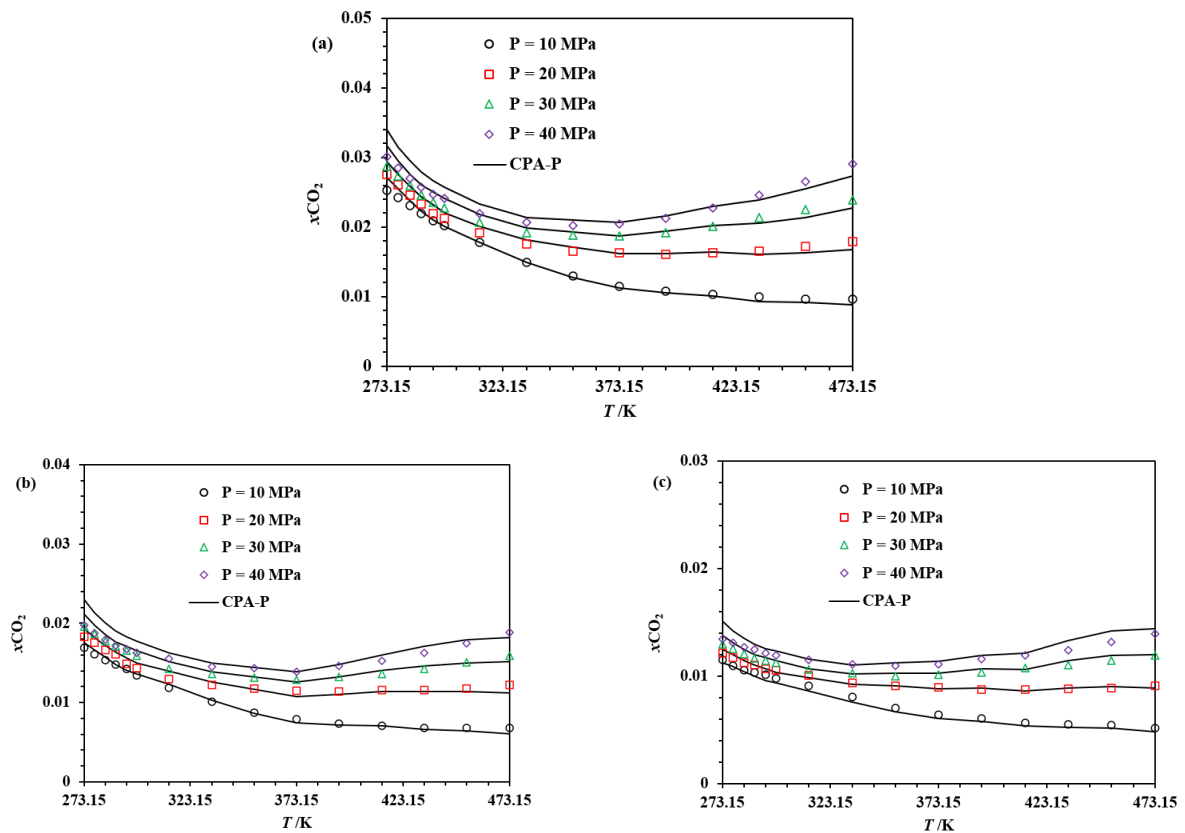
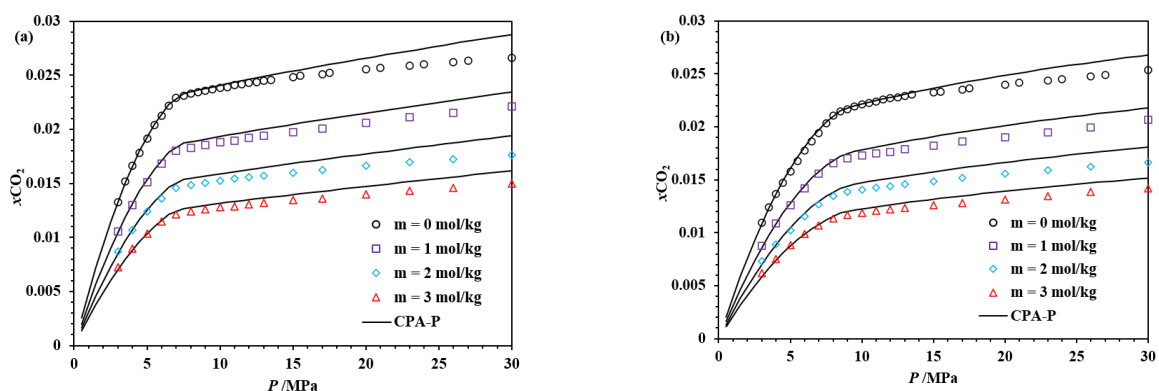


Fig. 11. CO₂-H₂O-NaCl VLE at salinities 1 mol·kg⁻¹ (a), 3 mol·kg⁻¹ (b), and 5 mol·kg⁻¹ (c). CPA-P predictions (black lines). The experimental data points were taken from Guo et al. (2016).



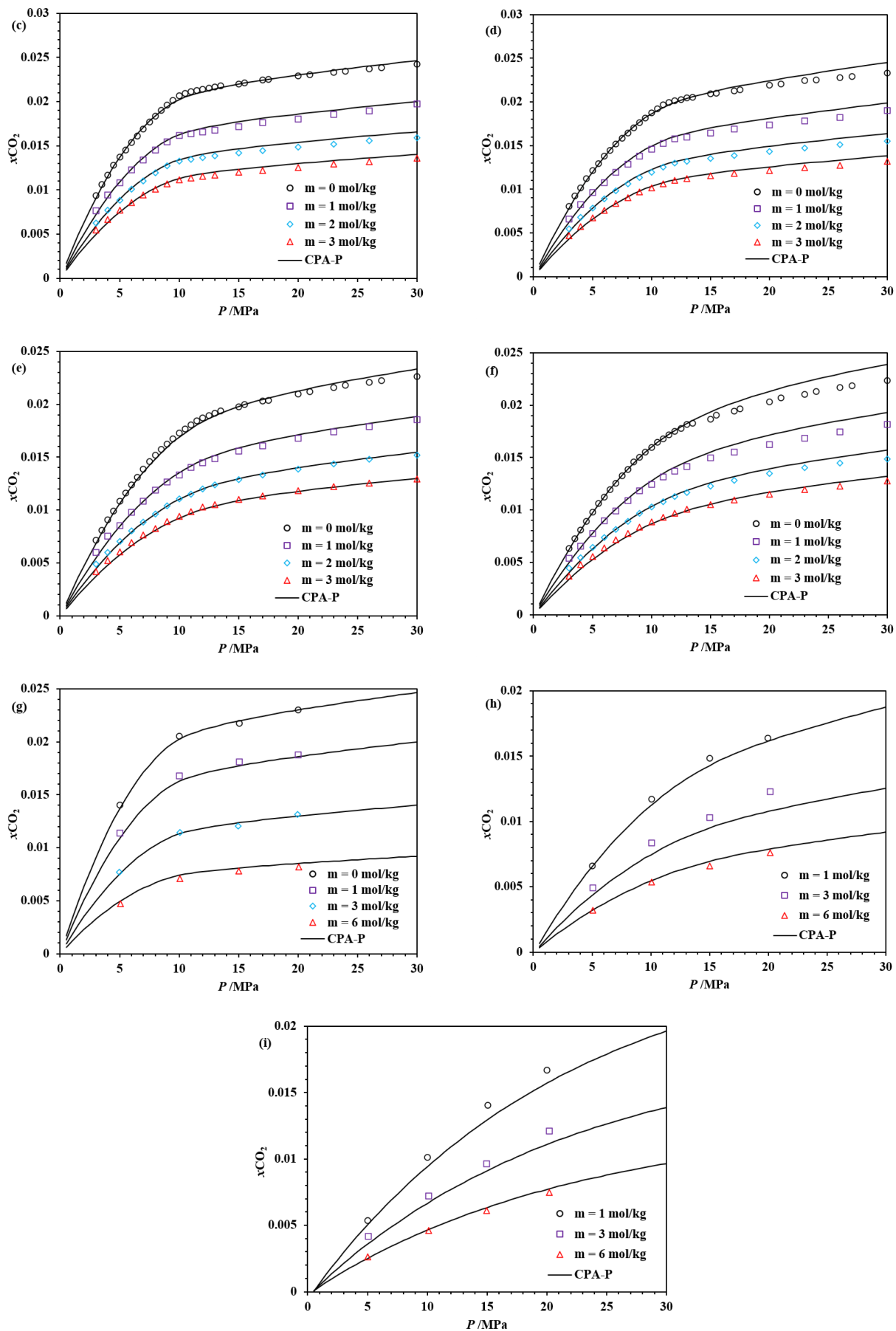


Fig. 12 CO₂-H₂O-NaCl VLE 303.15 K (a), 313.15 K (b), 323.15 K (c and g), 333.15 K (d), 343.15 K (e), 353.15 K (f), 373.15 K (h) and 423.15 K (i). CPA-P predictions (black lines). The experimental data points were taken from Messaieb et al. (2016) and Wang et al. (2019).

The present CPA-P model is parameterized and evaluated for NaCl solutions. Since the aqueous-phase non-ideality is described using Pitzer's activity model, the framework can be extended to other electrolyte and mixed-electrolyte systems, such as those containing KCl, CaCl₂, and MgCl₂, by introducing the corresponding electrolyte interaction parameters. Such an extension requires sufficient experimental data for parameter determination and model evaluation and will be considered in future work.

5. Conclusions

A thermodynamic model (CPA-P) based on the CPA EoS and Pitzer's activity model was constructed to study the phase behavior of the CO₂-H₂O and CO₂-H₂O-NaCl systems over a calculation range of 273.15–573.15 K and 0.1–350 MPa, with NaCl molalities up to 6 mol·kg⁻¹ for the brine system. Experimental data for the CO₂-H₂O system extend to 573.15 K and 350 MPa, while those available for the CO₂-H₂O-NaCl system extend to 523.15 K and 140 MPa, with NaCl molalities up to 6 mol·kg⁻¹. The carbon dioxide is considered a pseudo-associating component, and H₂O is modeled using the 4C association scheme. There are five adjustable parameters (i.e., $\bar{v}_{\text{CO}_2}$, $k_{\text{CO}_2-\text{H}_2\text{O}}$, $k_{\text{H}_2\text{O}-\text{CO}_2}$, F , and ξ_{nea}) for the CPA-P model, and they are empirically evaluated by fitting experimental data listed in Tables 1–3. Meanwhile, the effect of these parameters was analyzed.

The PSUCO2 and CPA-WS models are utilized for comparison with the CPA-P model. The results of calculations of the CPA-P, PSUCO2, and CPA-WS models for CO₂ solubility in pure H₂O liquid phase are accurate, and the AARDs of them are 3.53%, 5.07%, and 5.14%, respectively. However, the accuracies of the CPA-P and CPA-WS models for water content in the gas phase are above the PSUCO2 model, because the CPA-P and CPA-WS models take into account the interaction of hydrogen bonds between H₂O and CO₂ molecules. And the AARDs of the CPA-P, PSUCO2, and CPA-WS models for water solubility in carbon dioxide gas phase are 5.83%, 8.77%, and 6.65%, respectively.

The calculations of the CPA-P model for CO₂ solubility in brine are accurate at 273.15–523.15 K, 0.1–140 MPa, and 0–6 mol·kg⁻¹. The 376 experimental data points are utilized for correlating the parameter of the CPA-P model, and the AARD of calculations of the CPA-P, PSUCO2, and CPA-WS models for these data are 4.41%, 6.92%, and 7.30%, respectively. Meanwhile, the 724 experimental data points are used to verify the CPA-P model, and the predictions of the CPA-P model are in accordance with these experimental data. The AARD of the predictions of CPA-P, PSUCO2, and CPA-WS models are 3.02%, 3.04%, and 8.87%, respectively. The overall AARD of CPA-P, PSUCO2, and CPA-WS models for CO₂ solubility in brine are 3.50%, 4.41%, and 8.38%, respectively.

Supplementary Materials

The following are available online at: <https://serc.yandypress.com/index.php/3104-977X/article/view/142>

Author Contributions

W.X., Y.-L.Z., L.-H.Z., S.-M.W., Y.H., H.-B.L., X.H., Y.-C.W.: conceptualization, methodology, software, data curation, writing—original draft preparation, investigation, supervision; X.-Y.L., C.C., T.Z.: software, validation, writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Data will be made available on request.

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Conflict of interest

The authors declare no conflict of interest.

Use of AI and AI-assisted Technologies

No AI tools were utilized for this paper.

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