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The speciation equilibrium coupling with phase equilibrium in the H_2O–CO_2–NaCl system from 0 to 250 °C, from 0 to 1000 bar, and from 0 to 5 molality of NaCl

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Abstract

A model is developed for the calculation of the speciation equilibrium of H^+, OH^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ in aqueous solutions coupled with liquid-vapor phase equilibrium in the CO_2–H_2O–NaCl system from 273 to 523 K, from 0 to 1000 bar (possibly to 2000 bar) , and from 0 to 5.0 molality (m) of NaCl. The first and second ionization constants of carbonic acid, pH values in aqueous solutions, and their dependence on temperature (T), pressure (P) and NaCl concentrations can be calculated with accuracy close to those of experiments in the stated T–P–m range. Using the specific ion-interaction equations of Pitzer to calculate activity coefficients, the model is also able to accurately predict the difference between dissociation constants and apparent dissociation constants, and the concentrations of H^+, OH^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ at a given T–P–m condition. Compared to previous models, this model covers larger T–P–m space and much more closely reproduces experimental results, especially in the elevated pressure region. Even without fitting to the experimental data for pH values, dissociation constants and apparent dissociation constants at pressures above the saturation pressures of pure water, this model can accurately predicted these properties up to high pressures. A computer program based on this model is developed and online calculation is made available at: www.geochem-model.org/models.htm.

Keywords: CO_2; Aqueous carbonate system; pH; Speciation equilibrium; Ionization constant; CO_2-H_2O; CO_2-H_20-NaCl

1. Introduction

Natural occurring CO_2-bearing fluids can generally be described by the binary CO_2–H_2O system and the ternary CO_2–H_2O–NaCl system. Knowledge of thermodynamic and chemical properties of these fluids is essential because of their ubiquitous occurrence in and around the Earth and their active involvement in anthropological and geochemical processes, especially in the study of CO_2 sequestration and fluid-rock interactions. The equation of state (Duan et al., 1992) or CO_2 solubility model (Duan and Sun, 2006) can be used to calculate the distribution of CO_2 between liquid solution and vapor phase or the maximum concentration of CO_2 in aqueous solutions, $CO_{2(aq)}$. Once CO_2 being dissolved in water, $CO_{2(aq)}$ will be partially dissociated into H^+, HCO_3^-, and CO_3^{2-}, and H_2O will also be

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Table 1
Measurements of first and second dissociation constants of carbonic acid

References	T(K)	P(bar)	N^a K_1	N^a K_2
(Hastings and Sendroy, 1925)	311	1	16	16
(MacInnes and Belcher, 1933; MacInnes and Belcher, 1935; Shedlovsky and MacInnes, 1935)	273–311	1	37	24
(Übersicht, 1935)	273–291	1	–	16
(Harned et al., 1941; Harned and Raymond Davis, 1943; Harned and Bonner, 1945)	273–323	1	77	11
(Nasanen, 1946, 1947)	273–318	1	25	–
(Cuta and Strafelda, 1954)	333–363	1	–	20
(Ellis, 1959)	298–338	1–3000	117	–
(Khitarov et al., 1963)	373–491	P_s	3	3
(Nakayama, 1970, 1971)	273–323	1	17	19
(Dyrssen and Hansson, 1973)	283–303	1	14	14
(Read, 1975)	298–523	1–2000	88	–
(Park et al., 1998, 1999)	298–448	P_s	28	7

[a] Number of measurements, P_s is saturation pressure of water.

partially dissociated into H^+ and OH^-. Adding NaCl to the CO_2-bearing solutions will further complicate these dissociation or speciation reactions, dramatically altering the chemistry of solutions by lowering pH value and increasing the availability of CO_3^{2-}, which in turn affecting fluid–rock interactions. All these speciation changes are complex functions of temperature, pressure, and the concentration of salts. Therefore, quantitative modeling of all the speciation reactions, together with liquid-vapor equilibrium, is a great challenge.

Both experimentalists and theorists have devoted much effort in the study of the speciation equilibrium in the CO_2–H_2O and CO_2–H_2O–NaCl systems. Over the last half-century more than ten experimental data sets on the dissociation constants of carbonate acid were published (Table 1). However, these data covers only part of a T–P range from 273 to 523 K and from 1 to 2000 bar, with much of the T–P space without any data. Due to the lack of data in much of the T–P space, empirical fitting to the existing experimental data cannot yield a comprehensive model to accurately predict the properties of these solutions in the whole T–P range from 273 to 523 K up to high pressures. Therefore, models need to be developed for not only interpolating between data points but also extrapolating beyond experimental T–P range.

In the past, several models were reported for calculating the first and second dissociation constants (K_1 and K_2, respectively) of aqueous $CO_{2(aq)}$, and have been widely cited for geochemical applications. The model of Patterson and co-workers (Patterson et al., 1982, 1984) is quite accurate for $T < 400$ K and $P < 100$ bar in NaCl free solutions. However, it has three shortcomings: (1) it deviates considerably from experimental measurements at elevated pressures, as demonstrated in Section 3; (2) the calculated results for K_2 are not accurate for $T > 400$ K; (3) it does not take the salt effects into account. Park et al. (1999) and Plummer and Busenberg (1982) presented a temperature-dependent model of K_1 and K_2 , but they ignored the effects of pressure and salts, which are generally substantial. Many models (Roy et al., 1993; Lee and Millero, 1995; Millero, 1995; Javier et al., 2002; Millero et al., 2002, 2006) were presented for studying carbonate equilibria in seawater system, but their applications are restricted in a relatively small range of temperature (0–50 °C). The revised equations of Helgeson, Kirkham, and Flowers (HKF) (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock et al., 1989; Shock and Helgeson, 1990; Shock et al., 1992), as embodied in the SUPCRT92 software (Johnson et al., 1992), are well-known equations for these thermodynamic properties, but the results from SUPCRT92 in certain T–P regions display large deviations from experimental data. These models generally do not consider the dramatic effects of dissolved salts. Another common defect in these models is that they did not couple the speciation equilibrium with the CO_2 solubility (or liquid-vapor phase equilibrium) for a given temperature and pressure, thus not able to calculate the concentrations of H^+, OH^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ accurately at a given temperature and pressure and molality of $NaCl_{(aq)}$. There is no previous model that can accurately calculate K_1 and K_2 as a function of temperature, pressure, and system composition in a large T–P–m region.

In this report, we present a model to calculate the CO_2 solubility and the concentrations of equilibrium species, H^+, OH^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ in the CO_2–H_2O and CO_2–H_2O–NaCl systems from 273 to 523 K and from 0 to 1000 bar (possibly to 2000 bar), such that at a given temperature, pressure, and NaCl concentration, the first and second dissociation constants, the pH value, and concentrations of all equilibrium species can be accurately calculated. In the next Section, we will present the phenomenological model and the related equations. In Section 3, we discuss the parameterization and the validation of the model. Subsequently, an algorithm is developed to calculate the speciation equilibrium, pH value, the dissociation constants and apparent dissociation constants before conclusions are drawn.

2. Phenomenological description of liquid-vapor phase equilibrium and speciation equilibrium as a function of pressure, temperature and composition

In the H_2O–CO_2 and H_2O–CO_2–NaCl systems, there are two kinds of physico-chemical changes, phase change and chemical change. These changes are complicated functions of temperature, pressure, and molality of salt components. At a given T–P–m condition, the various changes will approach dynamic equilibrium states, though microscopically components still move from one phase to another and from one species to another through dissociation or association. Therefore, there are two kinds of equilibrium, phase equilibrium and chemical speciation equilibrium, need to be described in order to fully understand the H_2O–CO_2 and H_2O–CO_2–NaCl systems.

Phase equilibrium involves halite solubility equilibrium, liquid–liquid equilibrium (below 304.21 K of CO_2 critical temperature), liquid-vapor-hydrate equlibrium, liquid-hydrate equilibrium, and liquid-vapor equilibrium. The liquid-vapor equilibrium or liquid–liquid equilibrium is well described by solubility models. The liquid-vapor-hydrate equilibrium can be accurately predicted with an ab initio method by Sun and Duan (2005) and the model of Duan and Sun (2006). These models will be used to calculate the phase boundaries of the ternary system in this study. Since the chemical speciation of CO_2 depends on the available amount of $CO_{2(aq)}$ in the aqueous solution, the liquid-vapor phase equilibria (Eq. (1)) or CO_2 solubility is very important in the study of speciation equilibrium.

$$CO_{2(vapor)} \leftrightarrow CO_{2(aq)} \tag{1}$$

In the CO_2–H_2O–NaCl system, there are seven aqueous species, H^+, Na^+, OH^-, Cl^-, HCO_3^-, CO_3^{2-} and $CO_{2(aq)}$, involve in the speciation reactions:

$$H_2O + CO_{2(aq)} \leftrightarrow HCO_3^- + H^+ \tag{2}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{3}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{4}$$

Corresponding to the above reactions, three equilibrium constants can be defined,

$$K_1 = \frac{(m_{H^+}\gamma_{H^+}) \cdot \left(m_{HCO_3^-}\gamma_{HCO_3^-}\right)}{a_{CO_2} \cdot a_{H_2O}} \tag{5}$$

$$K_2 = \frac{(m_{H^+}\gamma_{H^+}) \cdot \left(m_{CO_3^{2-}}\gamma_{CO_3^{2-}}\right)}{\left(m_{HCO_3^-}\gamma_{HCO_3^-}\right)} \tag{6}$$

$$K_3 = \frac{(m_{H^+}\gamma_{H^+}) \cdot (m_{OH^-}\gamma_{OH^-})}{a_{H_2O}} \tag{7}$$

where K, m, a, and γ represent the equilibrium constant, molality, molal activity and molal activity coefficient of the subscripted reaction or aqueous species, respectively.

The vapor-liquid equilibrium (Eq. (1)) or the solubility of CO_2 is a complicated function of temperature, pressure, and the concentration of NaCl, and has been accurately modeled by Duan and coworkers (Duan and Sun, 2003; Duan et al., 2006). Marshall and Franck (1981), Quist (1970), and Tanger and Pitzer (1989) studied the dissociation constant of pure water (K_3) and established models valid in a wide range of temperature and pressure. In this study, we employ the model of Marshall and Franck (1981) to compute dissociation constants of water (K_3) because it is more reliable in the investigated T–P range and accepted by many researchers. For the calculation of activity coefficients, we use Pitzer model to account for the effects of $NaCl_{(aq)}$ and $CO_{2(aq)}$.

2.1. The temperature effect on the equilibrium constants of K_1 and K_2

The equilibrium constants K of a speciation reaction (such as Eq. (2) or (3)) is related to the standard free energy change by $\Delta G^o = -RT\ln K$. Considering

$$\left(\frac{\partial(\Delta G^0/T)}{\partial T}\right)_P = -\frac{\Delta H^0}{T^2} \tag{8}$$

we have the van't Hoff equation,

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^0}{RT^2} \tag{9}$$

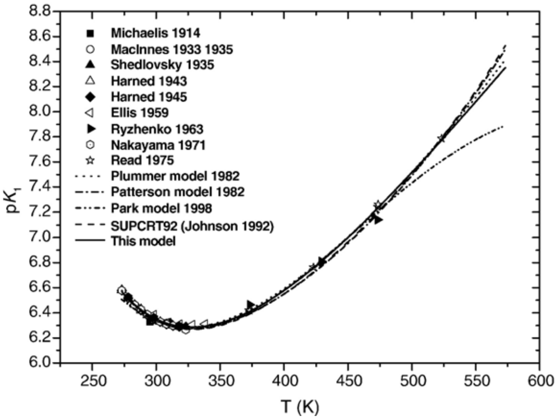

Fig. 1. The dissociation constant, pK_1, as a function of temperature in pure water (the model of this study vs. experimental data at pressures close to water saturation pressures, where $pK_1 = -\log_{10}(K_1)$.

where R is gas constant and H is the enthalpy of chemical reaction. The heat capacity of species i is a function of temperature at a given pressure and is generally expressed as (Maier and Kelley, 1932):

$$C_p^0 = a_i + b_i T + c_i T^{-2} \tag{10}$$

From $\Delta C_p^0 = \frac{d\Delta H^0}{dT}$, we can derive the following equation:

$$\frac{d\Delta H^0}{dT} = \Delta C_p^0 = \Delta a + \Delta b T + \Delta c T^{-2} \tag{11}$$

Integration of Eqs. (11) and (9) yields

$$\ln K = B + \frac{\Delta b}{2R} T - \frac{A}{R} T^{-1} + \frac{\Delta c}{2R} T^{-2} + \frac{\Delta a}{R} \ln T \tag{12}$$

where A and B are integral constants of Eqs. (9) and (11), respectively, and $\Delta a = \sum_i \nu_i a_i$ for reactions (2) and (3), and so on. Therefore, the temperature-dependent equation for the equilibrium constant of a reaction is determined by adjusting selected constants in the following equation:

$$\ln K = a_1 + a_2 T + a_3 T^{-1} + a_4 T^{-2} + a_5 \ln T \tag{13}$$

where the parameters, a_1–a_5, are obtained by fitting experimental data of dissociation constants of $CO_{2(aq)}$.

2.2. The pressure effect on the equilibrium constants

In a multi-component system, we have

$$\left(\frac{\partial \mu_i^o}{\partial P}\right)_T = \overline{V}_i^o \tag{14}$$

$$\left(\frac{\partial \overline{V}_i^o}{\partial P}\right)_T = -\overline{\kappa}_i^o \tag{15}$$

where $\overline{V}_i^o$ is the partial molar volumes of species i at the standard state, and $\overline{\kappa}_i^o$ is the standard partial molar compressibility. The variation of the thermodynamic equilibrium constant with respect to pressure is given by

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^o}{RT} \tag{16}$$

where ΔV^o is the change in the molar volume of the reaction in standard state. If $\Delta\kappa_i^o$ is assumed to be independent of pressure, then

$$\ln K_p = -\frac{1}{RT}\left[\Delta V^0 (P - P_s) - \frac{1}{2}\Delta\kappa^0 (P - P_s)^2\right] + \ln K_s \tag{17}$$

where K_p is the equilibrium constant at various pressures, $\Delta V^o = \sum_i \nu_i \overline{V}_i^o$, $\Delta\kappa^o = \Sigma_i \nu_i \overline{\kappa}_i^o$, P_s is saturation pressure of water at any temperature above 373.15 K or 1 bar below 373.15 K, K_s is equilibrium constant of reaction at saturation pressures of water

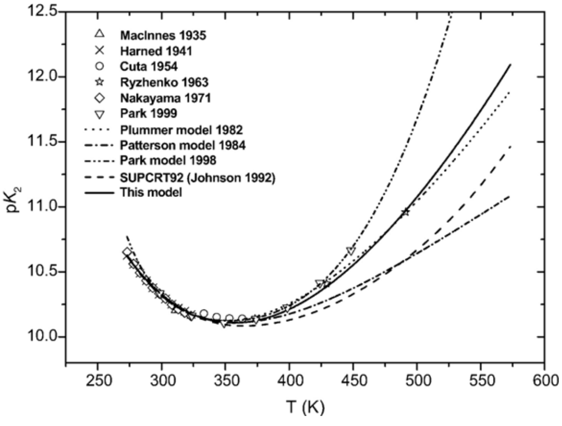

Fig. 2. The dissociation constant, pK_2, as a function of temperature in pure water (the model of this study vs. experimental data at pressures close to water saturation pressures, where $pK_2 = -\log_{10}(K_2)$.

above 373.15 K and at 1 bar below 373.15 K. It follows that the effect of pressure on equilibrium constant can be calculated from previously reported partial molar volumes and partial molar compressibility. The formula, $\bar{V}^o = b_1 + b_2T^{-1} + b_3 \ln T$ and $\bar{\kappa}^o = c_1 + c_2T^{-1} + c_3 \ln T$ are used in this study to calculate the partial molar volume and compressibility of species i for a wide range of temperature. For reactions (2) and (3), ΔV^o (cm^3/mol) and $\Delta\kappa^o$ (10^3 cm^3 mol^{-1} bar^{-1}) are independent of pressure, so their functions can be expressed as

$$\Delta V^o = b_1 + b_2T^{-1} + b_3 \ln T \tag{18}$$

$$\Delta\kappa^o = c_1 + c_2T^{-1} + c_3 \ln T \tag{19}$$

where b_1–b_3 and c_1–c_3 are parameters, T is temperature in K. Substituting Eqs. (13), (18), and (19) into Eq. (17) yields:

$$\begin{aligned}\ln K = {} & a_1 + a_2T + a_3T^{-1} + a_4T^{-2} + a_5 \ln T \\ & + \left(a_6T^{-1} + a_7T^{-2} + a_8T^{-1} \ln T\right)(P - P_s) \\ & + \left(a_9T^{-1} + a_{10}T^{-2} + a_{11}T^{-1} \ln T\right)(P - P_s)^2\end{aligned} \tag{20}$$

where a_1–a_{11} are parameters, which will be evaluated in Section 3, P_s is 1 bar at temperatures below 373.15 K or saturation pressure of water at temperatures above 373.15 K, which can be calculated by IAPWS-IF97 (Wagner and Kruse, 1998) (Appendix B).

2.3. The effect of NaCl on the speciation equilibria

In order to calculate speciation equilibrium in aqueous NaCl solutions, we need to compute the activity coefficients in electrolytic solutions. In this study, we use the specific interaction model of Pitzer (1973) to calculate the activity coefficients of species in electrolytic solutions:

$$\begin{aligned}(\phi - 1) = {} & \left(2/\sum_i m_i\right)\left[-A^\varphi I^{3/2}/\left(1 + 1.2I^{1/2}\right)\right] \\ & + \sum_{c=1}^{Nc}\sum_{a=1}^{Na} m_c m_a \left(B^\varphi_{ca} + ZC_{ca}\right) \\ & + \sum_{c=1}^{Nc-1}\sum_{c'=c+1}^{Nc} m_c m_{c'} \left(\Phi^\varphi_{cc'} + \sum_{a=1}^{Na} m_a \psi_{cc'a}\right) \\ & + \sum_{a=1}^{Na-1}\sum_{a'=a+1}^{Na} m_a m_{a'} \left(\Phi^\varphi_{aa'} + \sum_{c=1}^{Nc} m_c \psi_{aa'c}\right) \\ & + \sum_{n=1}^{Nn}\sum_{c=1}^{Nc} m_n m_c \lambda_{nc} + \sum_{n=1}^{Nn}\sum_{a=1}^{Na} m_n m_a \lambda_{na} \\ & + \sum_{n=1}^{Nn}\sum_{c=1}^{Nc}\sum_{a=1}^{Na} m_n m_c m_a \zeta_{nca}\end{aligned} \tag{21}$$

$$a_{H_2O} = \exp\left(-\frac{M_{H_2O} \cdot \phi}{1000} \cdot \sum_j m_j\right) \tag{22}$$

$$\begin{aligned}\ln\gamma_M = {} & z_M^2 F + \sum_{a=1}^{Na} m_a \left(2B_{Ma} + ZC_{Ma}\right) \\ & + \sum_{c=1}^{Nc} m_c \left(2\Phi_{Mc} + \sum_{a=1}^{Na} m_a \psi_{Mca}\right) \\ & + \sum_{a=1}^{Na-1}\sum_{a'=a+1}^{Na} m_a m_{a'} \psi_{aa'M} \\ & + |z_M| \sum_{c=1}^{Nc}\sum_{a=1}^{Na} m_c m_a C_{ca} + 2\sum_{n=1}^{Nn} m_n \lambda_{nM} \\ & + 6\sum_{n=1}^{Nn}\sum_{a=1}^{Na} m_n m_a \zeta_{Mna}\end{aligned} \tag{23}$$

Table 2
The parameters of Eqs. (18) and (19)

	ΔV_1^o	ΔV_2^o
b_1	3748.1678	2453.97326
b_2	−177207.90885	−115489.29266
b_3	−558.25496	−367.46855
	$\Delta\kappa_1^o$	$\Delta\kappa_2^o$
c_1	1395.81946	535.45092
c_2	−66772.55024	−27345.82051
c_3	−206.23006	−78.76586

Table 3
The parameters of Eq. (20)

	$\ln K_1$	$\ln K_2$
a_1	233.5159304	−151.1815202
a_2	0.0	−0.088695577
a_3	−11974.38348	−1362.259146
a_4	0.0	0.0
a_5	−36.50633536	27.79798156
a_6	−450.8004597	−295.1448102
a_7	21313.18848	13890.15354
a_8	67.14256299	44.19625804
a_9	83.93915212	32.19993525
a_{10}	−4015.441404	−1644.471261
a_{11}	−12.40187350	−4.736672395

$$\begin{aligned}\ln \gamma_X = {} & z_X^2 F + \sum_{c=1}^{Nc} m_c (2B_{cX} + ZC_{cX}) \\ & + \sum_{a=1}^{Na} m_a \left(2\Phi_{Xa} + \sum_{c=1}^{Nc} m_c \psi_{Xac} \right) \\ & + \sum_{c=1}^{Nc-1} \sum_{c'=c+1}^{Nc} m_c m_{c'} \psi_{cc'X} \\ & + |z_X| \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a C_{ca} + 2\sum_{n=1}^{Nn} m_n \lambda_{nX} \\ & + 6 \sum_{n=1}^{Nn} \sum_{c=1}^{Nc} m_n m_c \zeta_{ncX} \qquad (24)\end{aligned}$$

$$\begin{aligned}\ln \gamma_N = {} & 2\sum_{n=1}^{Nn} m_n \lambda_{Nn} + 2\sum_{c}^{Nc} m_c \lambda_{Nc} + 2\sum_{a}^{Na} m_a \lambda_{Na} \\ & + \sum_{c}^{Nc} \sum_{a}^{Na} m_c m_a \zeta_{Nca} \qquad (25)\end{aligned}$$

where ϕ is the osmotic coefficient of the solvent (water). Φ is the second virial coefficient. λ and ζ are second-order and third-order interaction parameters, respectively. m_c and z_c are the molality and charge of cation c. N_c is the total number of cations. Similar definitions apply for anions, a, and neutrals, n. The subscripts M, X and N refer to cations, anions, and neutrals, respectively. F is defined by

$$\begin{aligned}F = {} & -A^{\phi} \left(\frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln \left(1 + 1.2 I^{1/2} \right) \right) \qquad (26) \\ & + \sum_{c=1}^{Nc} \sum_{a=1}^{Na} m_c m_a B'_{ca} + \sum_{c=1}^{Nc-1} \sum_{c'=c+1}^{Nc} m_c m_{c'} \Phi'_{cc'} \\ & + \sum_{a=1}^{Na-1} \sum_{a'=a+1}^{Na} m_a m_{a'} \Phi'_{aa'}\end{aligned}$$

where A^{Φ} is one third the Debye–Hückel limiting slope; $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, C^{φ}_{MX} are virial parameters for each cation–anion pair, MX; θ_{ij} for each cation–cation or anion–anion pair; ψ_{ijk} for each cation–cation–anion and anion–anion–cation triplet; λ_{ni} for ion-neutral pairs; and ζ_{nij} for neutral–anion–cation triplet. The virial parameters for each cation–anion pair are functions of temperature and pressure. In order to calculate the activity coefficient, we need to evaluate the parameters in the equations above. Fortunately most of the Pitzer parameters of the H_2O–CO_2–NaCl system are available from previous publications, and only a small number of parameters need to be evaluated for the H_2O–CO_2–NaCl system.

3. Parameterization of the CO_2–H_2O–NaCl model

3.1. CO_2–H_2O binary system

The equilibrium of carbonate systems has been studied since early last century. The equilibrium constants of reactions (2) and (3) have been measured from 273 K to 523 K and from 1 to 3000 bar (Table 1), but most of the data were measured at 1 bar or at saturated pressures of water. The only high-pressure data were reported by Ellis (1959) and Read (1975), who measured the first dissociation constant up to 3000 bar. However, for many high-pressure conditions, there is still no data available. The most extensive studies of second dissociation constants, K_2, are reported by Cuta and Strafelda (1954), Dyrssen and Hansson (1973), and Nakayama (1971), at 1 atm or at saturated pressures of water, and there are no data available at higher pressures. The existing data are sufficient to construct a temperature-dependent model for the calculation of the dissociation constants and the speciation of the system, but not sufficient for building a

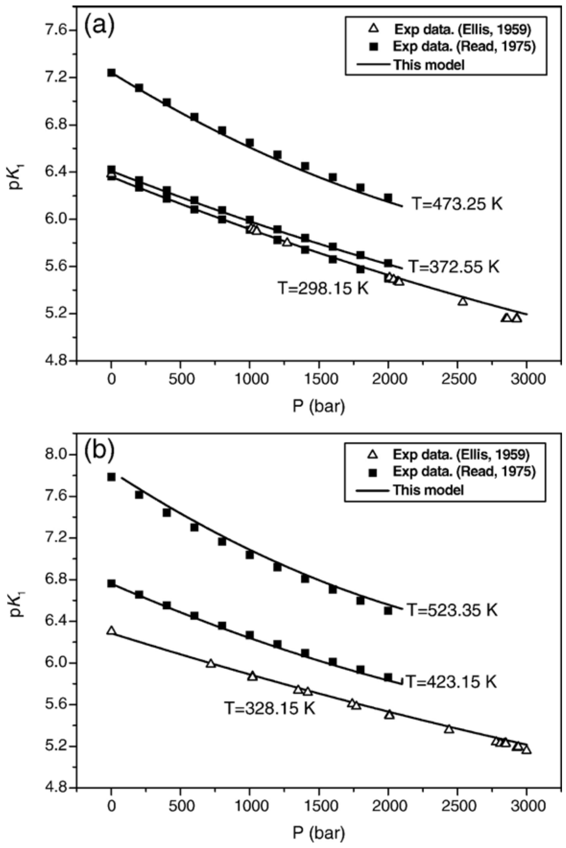

Fig. 3. Comparison of the calculated values of pK_1 as a function of pressure at different temperatures with experimental data.

temperature-pressure dependence model for pressures above the saturation pressures of water.

In this study, we first take the temperature-dependence into account, as previous researchers did. In order to do this, we fit the parameters, a_1 to a_5 in Eq. (20) to the experimental data (close to the water saturation pressures) to account for the temperature dependence. As can be seen from Figs. 1 and 2, all the experimental data at low pressures (close to 1 bar below 373 K, and water boiling pressures above 373.15 K) can be accurately reproduced by our model. These data are also partially reproduced by some previous models (Plummer and Busenberg, 1982; Patterson et al., 1982, 1984; Park et al., 1998, 1999), except for the model of Patterson for K_1 above 500 K, the SUPCRT92 (Johnson et al., 1992) and Park et al. (1999) for K_2 above 373 K. Note that the data at elevated pressures are not plotted in these two figures. It is obvious that the model of this study is the most reliable one with deviations from experimental data of less 3% in K values.

Now the question is how to model the dissociation constants as a function of both temperature and pressure. Due to the lack of data for the dissociation constants at elevated pressures, we cannot directly fit the parameters a_6–a_{11} in Eq. (20). In this study, we turn to experimental data of partial molar volumes and compressibility (Disteche and Disteche, 1967; Hershey et al., 1983; Polya et al., 2001) to account for the effect of pressure.

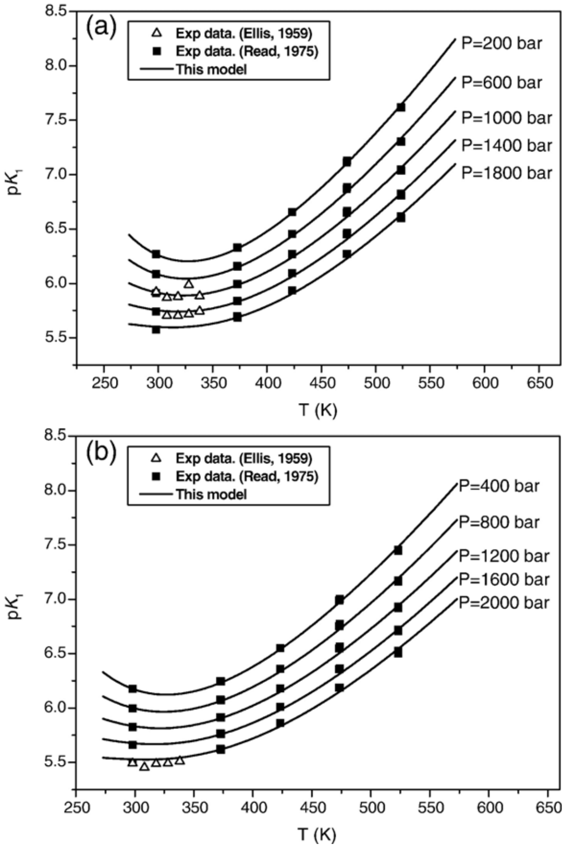

Fig. 4. Comparison of the calculated values of pK_1 as a function of temperature at different pressures with experimental data.

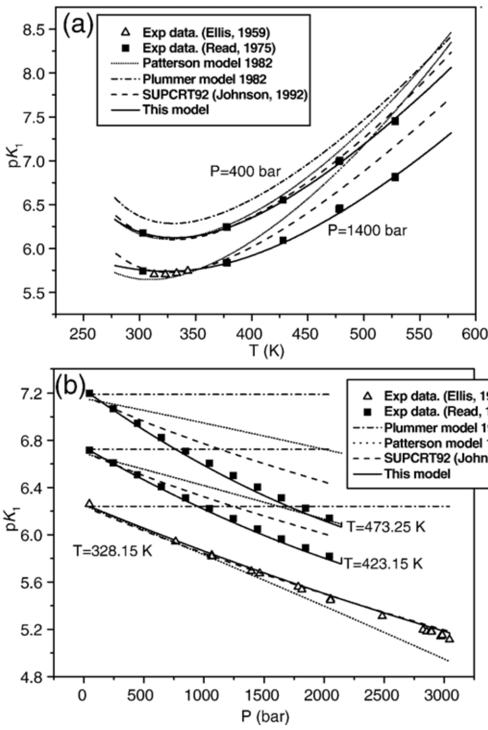

Fig. 5. pK_1 as a function of temperature and pressure (the model of this study vs. experimental data and other models).

The changes of partial molar volumes and compressibility (ΔV and $\Delta\kappa$) for reactions (2) and (3) are from previous papers (Ellis, 1959; Read, 1975; Hershey et al., 1983; Polya et al., 2001). The parameters b_1, b_2, b_3, c_1, c_2, and c_3 in Eqs. (18) and (19) were fitted to the data of ΔV and $\Delta\kappa$ simultaneously by least square method for the reactions (2) and (3), respectively (see Table 2). Substituting Eqs. (18) and (19) into Eq. (17) yields the parameters a_6–a_{11}, and the temperature and pressure dependent parameters of Eq. (20) can be obtained (see Table 3).

By substituting the parameters of Table 3 into Eq. (20), the K_1 and K_2 can be calculated at various temperatures and pressures. Fig. 3 shows the prediction of the value of pK_1 as a function of pressure where $pK_1 = -\log_{10}(K_1)$. It is remarkable that the dissociation constant data are accurately predicted, considering the pressure-dependence function is not fitted from the dissociation data but from volume and compressibility changes. It demonstrates that a sound thermodynamic

Table 4
All Pitzer parameters for the H_2O–CO_2–NaCl system

$\beta^{(0)}_{H-OH}$	$\beta^{(1)}_{H-OH}$	C^{ϕ}_{H-OH}	–
$\beta^{(0)}_{H-Cl}$	$\beta^{(1)}_{H-Cl}$	C^{ϕ}_{H-Cl}	298 K[6,23]; 273–323 K[11]; 273–523 K[16]; 273–523 K 400 bar[19, a]
$\beta^{(0)}_{H-HCO_3}$	$\beta^{(1)}_{H-HCO_3}$	$C^{\phi}_{H-HCO_3}$	–
$\beta^{(0)}_{H-CO_3}$	$\beta^{(1)}_{H-CO_3}$	$C^{\phi}_{H-CO_3}$	–
$\beta^{(0)}_{Na-OH}$	$\beta^{(1)}_{Na-OH}$	C^{ϕ}_{Na-OH}	298 K[5,6,23]; 298–524 K 400 bar[1]; 273–323 K[11]; 273–523 K[16];273–623 K 400 bar[14, a]
$\beta^{(0)}_{Na-Cl}$	$\beta^{(1)}_{Na-Cl}$	C^{ϕ}_{Na-Cl}	298 K[5,6,23]; 298–523 K[9]; 228–298 K[10]; 233–298 K[22]; 273–573 K 1000 bar[13, a]
$\beta^{(0)}_{Na-HCO_3}$	$\beta^{(1)}_{Na-HCO_3}$	$C^{\phi}_{Na-HCO_3}$	298 K[3,6]; 298–323 K[18]; 273–363 K[17]; 298–523 K 400 bar[15, a]
$\beta^{(0)}_{Na-CO_3}$	$\beta^{(1)}_{Na-CO_3}$	$C^{\phi}_{Na-CO_3}$	298 K[3,7,6]; 298–323 K[18]; 273–363 K[17]; 298–523 K 400 bar[15, a]
		θ_{H-Na}	298 K[4,6]; 273–370 K[16, a]
		θ_{OH-Cl}	298 K[4,6]; 273–523 K[16, a]
		θ_{OH-HCO_3}	–
		θ_{OH-CO_3}	298 K[6, a]
		θ_{Cl-HCO_3}	298 K[3, a,6]
		θ_{Cl-CO_3}	298 K[3, a,6]
		$\theta_{HCO_3-CO_3}$	298 K[2,6, a]
		$\psi_{H-Na-OH}$	–
		$\psi_{H-Na-Cl}$	298 K[4]; 273–360 K[16, a]
		$\psi_{H-Na-HCO_3}$	–
		$\psi_{H-Na-CO_3}$	–
		$\psi_{OH-Cl-H}$	–
		$\psi_{OH-Cl-Na}$	298 K[4,6]; 273–523 K[16, a]
		ψ_{OH-HCO_3-H}	–
		ψ_{OH-HCO_3-Na}	–
		ψ_{OH-CO_3-H}	–
		ψ_{OH-CO_3-Na}	298 K[6, a]
		ψ_{Cl-HCO_3-H}	–
		ψ_{Cl-HCO_3-Na}	298 K[6, a]; 273–323 K[11]
		ψ_{Cl-CO_3-H}	–
		ψ_{Cl-CO_3-Na}	298 K[6,20, a]; 273–323 K[11]
		$\psi_{HCO_3-CO_3-H}$	
		$\psi_{HCO_3-CO_3-Na}$	298 K[3, a,6]
		$\lambda_{CO_2-CO_2}$	278–298 K[12]; 273–523 K 2000 bar[24, a]
		λ_{CO_2-H}	–
		λ_{CO_2-OH}	–
		$\lambda_{CO_2-HCO_3}$	278–298 K[8]; 273–403 K 580 bar[24, a]
		$\lambda_{CO_2-CO_3}$	–
		λ_{CO_2-Na}	298 K[18]; 273–363 K[17]; 273–523 K 2000 bar[21,24, a]
		λ_{CO_2-Cl}	278–298 K[8]; 273–363 K[17]; 273–523 K 2000 bar[21,24, a]
		$\zeta_{CO_2-Na-Cl}$	298 K[18]; 273–363 K[17]; 273–523 K 2000 bar[21,24, a]

Ref 1: (Simonson et al., 1989); 2: (Roy et al., 1984); 3: (Peiper and Pitzer, 1982); 4: (Pitzer and Kim, 1974); 5: (Pitzer and Mayorga, 1973); 6: (Harvie et al., 1984); 7: (Robinson and Macaskill, 1979); 8: (Wong et al., 2005b); 9: (Møller, 1988); 10: (Spencer et al., 1990); 11: (Marion, 2001); 12: (Wong et al., 2005a); 13: (Pitzer et al., 1984); 14: (Pabalan and Pitzer, 1987b); 15: (Polya et al., 2001); 16: (Christov and Møller, 2004); 17: (He and Morse, 1993); 18: (Millero et al., 2007); 19: (Holmes et al., 1987); 20: (Thurmond and Millero, 1982); 21: (Duan and Sun, 2003); 22: (Thurmond and Brass, 1988); 23: (Kim and Frederick, 1988); 24: This study.

[a] Which value will be used in our model.

approach can be used for reliable predictions as shown in Fig. 4. However, experimental data are not available to test the accuracy of our calculated K_2 values at higher pressures. Comparison of the previous models with experimental data (Fig. 5) indicates that these models have poor predictions at elevated pressures.

3.2. CO_2–H_2O–NaCl ternary system

In terms of speciation reactions, the difference between the CO_2–H_2O system and the CO_2–H_2O–NaCl system is on how NaCl affects the activities of the species in the ternary system. When carbon dioxide dissolves in aqueous NaCl solutions, it forms H^+, Na^+, OH^-, Cl^-, HCO_3^-, CO_3^{2-} and $CO_{2(aq)}$ species. In this study, we use Pitzer model (Pitzer, 1973; Harvie et al., 1984) to calculate the activity coefficient of these species in the system. This calculation involves the parameters, $\beta^{(0)}_{c-a}$, $\beta^{(1)}_{c-a}$, C^{ϕ}_{c-a}, θ_{c-c}, θ_{a-a}, ψ_{c-c-a}, ψ_{a-a-c}, λ_{n-c}, λ_{n-a} and ζ_{n-c-a}, where c is cation (H^+ and Na^+), a is anion (OH^-, Cl^-, HCO_3^- and CO_3^{2-}) and n is neutral solute (CO_2). All these parameters are listed in Table 4.

Table 5
Pitzer parameters

	$\theta_{\text{OH,Cl}}$	$\theta_{\text{H,Na}}$	$\psi_{\text{OH,Cl,Na}}$	$\psi_{\text{H,Na,Cl}}$
c_1	1.10485703e−01	4.81363462e−02	1.27601977e+01	−1.45623335e−02
c_2	0.0	0.0	3.66503385e−03	0.0
c_3	−4.93613455e+01	−4.05430635	−3.55227032e+02	3.59308925
c_4	0.0	0.0	−2.21051220	0.0
c_5	0.0	0.0	3.23085637e−03	0.0
c_6	0.0	0.0	0.0	0.0
c_7	0.0	0.0	−2.71988632e+01	0.0
c_8	0.	0.	0.0	0.0

Parameter$(T)=c_1+c_2T+c_3/T+c_4\ln T+c_5/(T-263)+c_6T^2+c_7/(680-T)+c_8/(T-227)$.
Note: the parameters are from (Christov and Møller, 2004).

Many of the parameters in Table 4 are available from previous literature, but some parameters need to be evaluated. The previously published Pitzer parameters of this system are listed in Tables 5–9.

The second virial constants (β's) of H^+–OH^-, H^+–$CO_3^{2-}$and H^+–HCO_3^- in Eqs. (21)–(26) contribute very little to the activity coefficient, because their concentration is generally less than 0.001 m and their contribution to the activity coefficients is very small (Table 10). Therefore, we can set these parameters to zero. This practice was also taken by previous researchers (Harvie et al., 1984). The third virial coefficients, θ's and ψ's, are in general little dependent on pressure (e.g., Pabalan and Pitzer, 1987a). According to Eqs. (23) and (24), the θ's and ψ's associated with H^+, OH^-, HCO_3^-, CO_3^{2-},can be set to zero because their contribution to free energy is very small due to their low concentrations (<0.001 m). Some important cation–anion parameters for Na^+–OH^-, Na^+–$CO_3^{2-}$and Na^+–HCO_3^- were reported to cover pressures up to 400 bar, but there are no data to test if these parameters can be extended to higher pressures. However, we believe these parameters can be roughly extended to higher pressures from thermodynamic point of view, because these parameters has a dimension of free energy and should be directly proportional to partial volume of aqueous species, which changes little with pressure. Therefore, we only need to evaluate the Pitzer parameters associated with the neutral species $CO_{2(aq)}$.

Table 6
Pitzer second virial parameters for $HCl_{(aq)}$

	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}
c_1	0.17690	0.2973	0.724e−3
c_2	−9.140e−2	16.147	0
c_3	0	−1.7631e−2	0
c_4	−4.034e−4	0	−6.072e−5
c_5	6.20e−6	7.20e−5	0

Parameter$(T, P)=c_1+c_2\ln(\rho/997)+c_3(\rho-997)+c_4(T-298.15)+c_5(P-1)$.
Note: ρ is the density in kg/m^3 of pure water at the particular T and P. The parameters are from (Holmes et al., 1987).

Table 7
Pitzer second virial parameters for $NaCl_{(aq)}$

	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}
c_1	−6.5681518E+02	1.1931966E+02	−6.1084589E+00
c_2	2.4869130E+01	−4.8309327E−01	4.0217793E−01
c_3	5.3812753E−05	0	2.2902837E−05
c_4	−5.5887470E−08	0	0
c_5	6.5893263E−12	0	0
c_6	−4.4640952E+00	0	−7.5354649E−02
c_7	1.1109914E−02	1.4068095E−03	1.5317673E−04
c_8	−2.6573399E−07	0	−9.0550901E−08
c_9	1.7460070E−10	0	0
c_{10}	1.0462619E−14	0	0
c_{11}	−5.3070129E−06	0	−1.5386008E−08
c_{12}	8.6340233E−10	0	8.6926600E−11
c_{13}	−4.1785962E−13	0	0
c_{14}	−1.5793660E+00	−4.2345814E+00	3.5310414E−01
c_{15}	2.2022821E−03	0	−4.3314252E−04
c_{16}	−1.3105503E−07	0	0
c_{17}	−6.3813683E−11	0	0
c_{18}	9.7065780E+00	0	−9.1871455E−02
c_{19}	−2.6860396E−02	0	5.1904777E−04
c_{20}	1.5344744E−05	0	0
c_{21}	−3.2153983E−09	0	0

Parameter$(T,\ P)=\mathrm{c}_1/T+c_2+c_3P+c_4P^2+c_5P^3+c_6\ln(T)+(c_7+c_8P+c_9P^2+c_{10}P^3)T+(c_{11}+c_{12}P+c_{13}P^2)T^2+(c_{14}+c_{15}P+c_{16}P^2+c_{17}P^3)/(T-227)+(c_{18}+c_{19}P+c_{20}P^2+c_{21}P^3)/(680-T)$.
Note: the parameters are from (Pitzer et al., 1984).

Duan and Sun (2003) presented an accurate CO_2 solubility model and evaluated the parameter λ_{CO_2-Na} in a range of temperature 273–533 K, but they used a

Table 8
Pitzer second virial parameters for $NaOH_{(aq)}$

	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}
c_1	2.7682478E+02	4.6286977E+02	−1.6686897E+01
c_2	−2.8141778E−03	0	4.0534778E−04
c_3	−7.3755443E+03	−1.0294181E+04	4.5364961E+02
c_4	3.7012540E−01	0	−5.1714017E−02
c_5	−4.9359970E+01	−8.5960581E+01	2.9680772E+00
c_6	1.0945106E−01	2.3905969E−01	−6.5161667E−03
c_7	7.1788733E−06	0	−1.0553037E−06
c_8	−4.0218506E−05	−1.0795894E−04	2.3765786E−06
c_9	−5.8847404E−09	0	8.9893405E−10
c_{10}	1.1931122E+01	0	−6.8923899E−01
c_{11}	2.4824963E+00	0	−8.1156286E−02
c_{12}	−4.8217410E−03	0	0

Parameter$(T,\ P)=c_1+c_2P+(c_3+c_4P)/T+c_5\ln(T)+(c_6+c_7P)T+(c_8+c_9P)T^2+c_{10}/(T-227)+(c_{11}+c_{12}P)/(647-T)$.
Note: the parameters are from (Pabalan and Pitzer, 1987b).

Table 9
The third virial Pitzer parameters

$\theta_{OH,\ HCO3}$	–
$\theta_{OH,CO3}$	0.1 [a]
$\theta_{Cl,HCO3}$	0.0359 [b]
$\theta_{Cl,CO3}$	−0.053 [b]
$\theta_{HCO3,CO3}$	−0.04 [a]
$\psi_{H,Na,OH}$	–
$\psi_{H,Na,HCO3}$	–
$\psi_{H,Na,CO3}$	–
$\psi_{OH,Cl,H}$	–
$\psi_{OH,HCO3,H}$	–
$\psi_{OH,HCO3,Na}$	0.002 [a]
$\psi_{OH,CO3,H}$	–
$\psi_{OH,HCO3,Na}$	−0.017 [a]
$\psi_{Cl,HCO3,H}$	–
$\psi_{Cl,HCO3,Na}$	−0.0143 [b]
$\psi_{Cl,CO3,H}$	–
$\psi_{Cl,CO3,Na}$	0.016 [c]
$\psi_{HCO3,CO3,H}$	–
$\psi_{HCO3,CO3,Na}$	–

[a] Harvie et al. (1984).
[b] Peiper and Pitzer (1982).
[c] Thurmond and Millero (1982).

reference state as the H_2O–CO_2 binary system instead of pure H_2O. So the interaction between CO_2 and CO_2 was neglected and the activity coefficient of $CO_{2(aq)}$ is set to be unit in the binary system. Due to the deviation between mixture and pure substance, the activity coefficient of $CO_{2(aq)}$ is not unit. Although such a reference would not affect the accuracy of solubility, it will change the calculation of speciation equilibrium. We now redefine the infinite dilution solution (Henry's law constant) as the reference state for activity coefficient of $CO_{2(aq)}$ and rewrite the D-S solubility model as

$$\ln \frac{y_{CO_2} P}{m_{CO_2}} = \ln k_H + PF - \ln \varphi_{CO_2}(T,P,y) + \ln \gamma_{CO_2}(T,P,m) \tag{27}$$

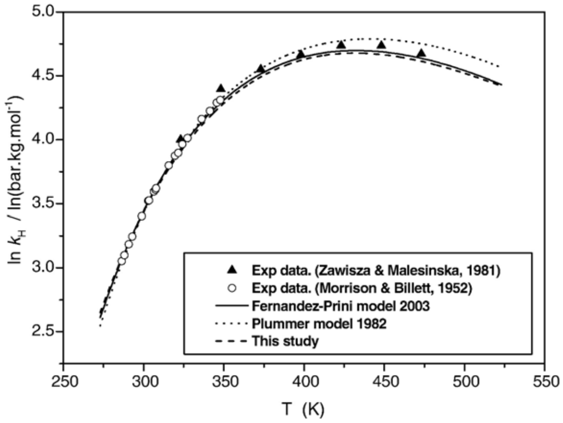

Fig. 6. Henry's law constant of CO_2 in H_2O.

where y_{CO_2} is the molar fraction of CO_2 in the gas phase, P is total pressure in bar. k_H is the Henry's constant which is defined by $k_H = \lim_{m_{CO_2} \to 0}(f_{CO_2}/m_{CO_2})$, where f_{CO_2} and m_{CO_2} are the liquid-phase fugacity in bar and molality of the solute, respectively. k_H is a function of temperature only along the saturation curve of water. In the Eq. (27), PF is Poynting Factor defined by $PF = \int_{P_s}^{P} \widetilde{V}_m dP/RT$, where R is the gas constant, T is temperature in Kelvin, $\widetilde{V}_m$ is partial molar volume of $CO_{2(aq)}$. φ_{CO_2} and γ_{CO_2} are the fugacity coefficient and activity coefficient of CO_2, respectively. φ_{CO_2} can be calculated from the EOS of Duan et al. (1992) because there is little difference in fugacity coefficients between pure and binary system in the vapor phase. γ_{CO_2}, which is referenced to Henry's law (molality scale), can be calculated by

$$\ln \gamma_{CO_2} = 2m_{CO_2}\lambda_{CO_2-CO_2} + 2\sum_c m_c \lambda_{CO_2-c} + 2\sum_a m_a \lambda_{CO_2-a} + \sum_c \sum_a m_c m_a \zeta_{CO_2-c-a} \tag{28}$$

Due to the amount of CO_2 dissolved in solution, m_{CO_2}, is large at elevated pressures, neutral component will affect the activity of ions, so the neutral-ion parameters of CO_2 is important for calculating ion activities. Using CO_2 solubility in pure water (Duan and Sun, 2003), $m_{CO_2}(T, P)$, we can obtain Henry's constant from following equation.

$$k_H = \lim_{P \to P_s} P/m_{CO_2}(T,P) \tag{29}$$

where P_s is saturated pressures of water in bar at various temperatures. The result is shown in Fig. 6, showing the

Table 10
Pitzer second virial parameters of Na,CO_3 and Na,HCO_3

	$\beta^{(0)}$ (Na,CO_3)	$\beta^{(1)}$ (Na,CO_3)	C^{φ} (Na,CO_3)	$\beta^{(0)}$ (Na,HCO_3)	$\beta^{(1)}$ (Na,HCO_3)
c_1	5.153E−01	2.044E+00	−9.140E−02	6.61E−02	−4.116E+00
c_2	−5.991E−04	−4.303E−03	0	0	6.309E−03
c_3	0	0	0	0	9.240E+02
c_4	−2.581E+01	−2.545E+01	6.482E+00	0	−5.202E+01
c_5	−2.659E+00	3.618E+02	8.048E+00	0	−8.026E+01
c_6	0	0	0	3.75951E −08	0
c_7	8.750E−05	0	−2.890E−05	0	1.634E−04
c_8	−2.660E−08	0	0	0	−1.390E−07

Parameter(T, P)$=c_1+c_2T+c_3/T+c_4/(T-210)+c_5/(647-T)+c_6(T-443)^3/3+c_7(P-1)+c_8(P-1)^2/2$.
Note: the parameters are from (Polya et al., 2001).

Table 11
Henry's law constant for CO_2 in water

a_1	1.3999520898E+01
a_2	−1.3340507000E−02
a_3	−5.5897820016E+02
a_4	−4.2257732219E+05

$\ln k_H/\ln(\mathrm{bar\ mol^{-1}\ kg^{-1}}) = a_1 + a_2T + a_3/T + a_4/T^2$.
T is temperature in K.

agreement of our values with the experimental data (Morrison and Billett, 1952; Zawisza and Malesinska, 1981) and those predicted from other models (Plummer and Busenberg, 1982; Fernandez-Prini et al., 2003). We fit such result with a polynomial formula with correlative coefficient $R_2 = 0.9999$ (Table 11). Partial molar volume of CO_2 ($\mathrm{cm^3/mole}$), $\widetilde{V}_m$, can be calculated by following equation (Garcia, 2001):

$$\widetilde{V}_m = 35.663 - 0.05960t + 0.0006308t^2 \tag{30}$$

where t is temperature in °C Eq.(30) is effective in the range from 273 to 523 K. Based on D-S model (Duan and Sun, 2003), $\mu^{1(0)}_{CO_2}/RT$ can be rewritten as,

$$\begin{aligned}\mu^{l(0)}_{CO_2}/RT &= \ln k_H + PF + \ln \gamma_{CO_2} \\ &= \ln k_H + PF + 2m_{CO_2}\lambda_{CO_2-CO_2}\end{aligned} \tag{31}$$

From the above equation, we obtain $\lambda_{CO_2-CO_2}$ at various temperature and pressure as listed in Table 12. Based on Eqs. (27) and (28), we can derive the following equation,

$$\begin{aligned}&2m_{NaCl}(\lambda_{CO_2-Na} + \lambda_{CO_2-Cl}) + m^2_{NaCl}\zeta_{CO_2-Na-Cl} \\ &\quad = \ln(y_{CO_2}P) + \ln\varphi_{CO_2} - \ln k_H - PF \\ &\quad\quad - \ln m_{CO_2} - 2m_{CO_2}\lambda_{CO_2-CO_2}\end{aligned} \tag{32}$$

From the D-S solubility model, a series of values for the terms in the right side of Eq. (32) can be calculated for different T–P–m_{NaCl} conditions (273–523 K, 0–2000 bar and 0–5 m). Using these series of data obtained from the D-S model, λ_{CO_2-Na} and $\zeta_{CO_2-Na-Cl}$ can be evaluated by Levenberg–Marquardt method (Press et al., 1992), which are also listed in Table 12.

Table 12
The neutral-ion parameters of CO_2

	$\lambda_{CO_2-CO_2}$	λ_{CO_2-Na}	$\zeta_{CO_2-Na-Cl}$
c_1	−8.603471564E−01	−2.739092216E−01	−1.665719188E−02
c_2	3.297141654E−03	7.399855859E−04	1.391618600E−06
c_3	6.309267405E+01	5.552132850E+01	0
c_4	−4.098960500E−06	0	0
c_5	1.529493614E+01	0	0
c_6	6.506644253E−03	0	0
c_7	−9.637977140E−04	0	0
c_8	−3.238222665E−01	5.683638727E−03	−1.873812115E−03
c_9	1.599113719E−02	−8.009093476E−04	−1.577400757E−03
c_{10}	0	0	0
c_{11}	−1.886733300E−05	−1.745620270E−05	0

$\mathrm{Parameter}(T,\ P) = c_1 + c_2T + c_3/T + c_4T^2 + c_5/(630-T) + c_6P + c_7P\ln T + c_8P/T + c_9P/(630-T) + c_{10}P^2/(630-T)^2 + c_{11}T\ln P$.
Note: in this study, we set $\lambda_{CO_2-Cl} = 0$.

Table 13
The neutral-ion parameters of CO_2

	$\lambda_{CO_2-Na} + \lambda_{CO_2-HCO_3}$
c_1	0.35284
c_2	−27.85446
c_3	19.56109

$\mathrm{Parameter}(T, P) = c_1 + c_2/(T-210) + c_3/(P-100)$.
Note: in this study, we set $\lambda_{CO_2-CO_3} = 2\lambda_{CO_2-HCO_3}$.

In order to account for the effect of $CO_{2(aq)}$, $\lambda_{CO_2-HCO_3}$ and $\lambda_{CO_2-CO_3}$ need to be evaluated in a wide T–P range. Wong et al. (2005a,b) presented such parameters, but the T–P range is very small (278–298 K and 1 bar). Similar to Eq. (32), we can obtain Eq. (33):

$$\begin{aligned}&2m_{NaHCO_3}(\lambda_{CO_2-Na} + \lambda_{CO_2-HCO_3}) + m^2_{NaHCO_3}\zeta_{CO_2-Na-HCO_3} \\ &\quad = \ln(y_{CO_2}P) + \ln\varphi_{CO_2} - \ln k_H - PF - \ln m_{CO_2} \\ &\quad\quad -2m_{CO_2}\lambda_{CO_2-CO_2}\end{aligned} \tag{33}$$

where y_{CO_2} and m_{CO_2} are the molar fraction of CO_2 in the gas phase and CO_2 solubilities in aqueous $NaHCO_3$ solutions, respectively, and their values can be obtained from experimental data (Gao et al., 1997; Wong et al., 2005b) at various temperatures, pressures, and molality of $NaHCO_3$. Because the third virial contribution is small, we can set $\zeta_{CO_2-Na-HCO_3} = 0$, and therefore, values for $\lambda_{CO_2-HCO_3}$ as a function of temperature and pressure can be calculated from Eq. (30) and the λ_{CO_2-Na} values listed in Table 12 (see Table 13).

4. Calculation, prediction, and application

4.1. A simple algorithm for calculating the speciation equilibrium of H^+, OH^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ in the CO_2–H_2O–NaCl system

There are many algorithms available for calculating speciation equilibrium and phase equilibrium. One of the

Table 14
The molalities and activity coefficients of species in aqueous solutions

	H^+	OH^-	CO_3^{2-}	HCO_3^-	$CO_{2(aq)}$
Initial molality	m_1	m_2	m_3	m_4	m_5
Change of molality	$x_1+x_2+x_3$	x_3	x_2	x_1-x_2	$-x_1$
Equilibrium molality	$m_1+x_1+x_2+x_3$	m_2+x_3	m_3+x_2	$m_4+x_1-x_2$	m_5-x_1
Activity coefficient	γ_1	γ_2	γ_3	γ_4	γ_5

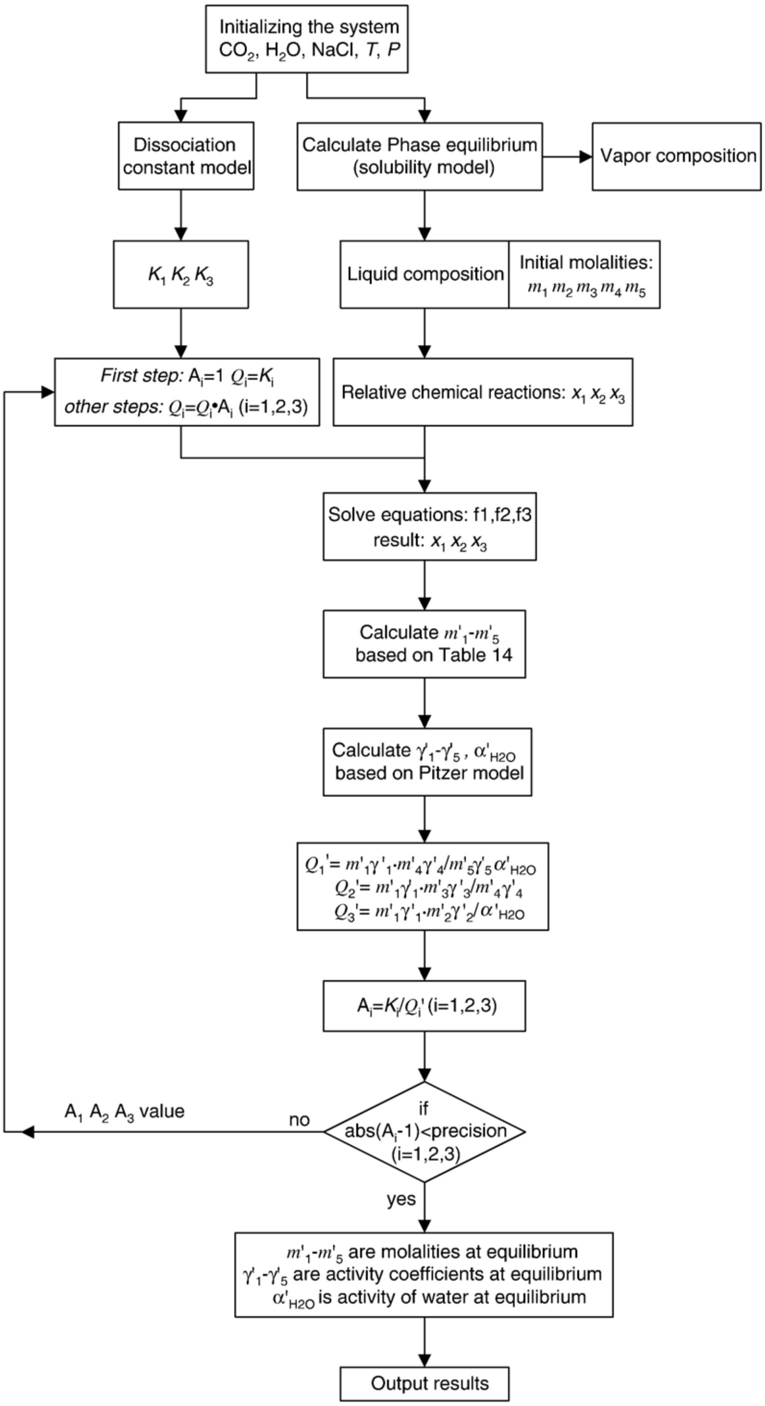

Fig. 7. The flow diagram of the algorithm to calculate the speciation equilibrium in the H_2O–CO_2–NaCl system.

most widely used approaches is free energy minimization (Harvie et al., 1987; Eriksson and Hack, 1990; Makkuni et al., 2002). Several software packages, such as ChemSage, were developed for such calculations (Eriksson and Hack, 1990; Bale et al., 2002). Although these algorithms and softwares are useful in multifarious fields of studying those equilibriums, they are quite complex for simple applications. In this work we propose a concise method for the computing of the speciation equilibrium in aqueous system of CO_2–H_2O–

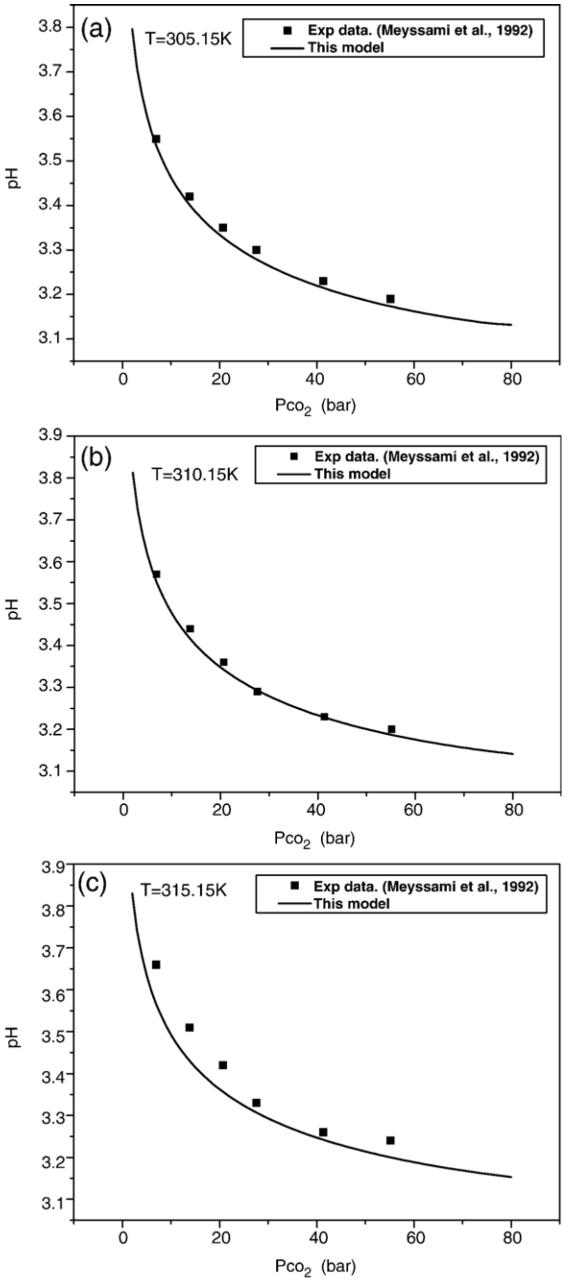

Fig. 8. pH values of CO_2–H_2O system at various temperatures and pressures.

NaCl. We first define vectors, Γ and M, representing activity coefficients (include activity of water, a_{H_2O}) and molalities of all interested components, respectively

$$\Gamma = (\gamma_{H^+}, \gamma_{OH^-}, \gamma_{HCO_3^-}, \gamma_{CO_3^{2-}}, \gamma_{CO_{2(aq)}}, \gamma_{Na^+}, \gamma_{Cl^-}, a_{H_2O}) \quad (34)$$

$$M = (m_{H^+}, m_{OH^-}, m_{HCO_3^-}, m_{CO_3^{2-}}, m_{CO_{2(aq)}}, m_{Na^+}, m_{Cl^-}) \quad (35)$$

M is constrained by carbon equilibrium and electric charge equilibrium

$$m_{HCO_3^-} + m_{CO_3^{2-}} + m_{CO_{2(aq)}} - C_T = 0 \quad (36)$$

$$m_{H^+} + m_{Na^+} - m_{OH^-} - m_{HCO_3^-} - 2m_{CO_3^{2-}} - m_{Cl^-} = 0 \quad (37)$$

where C_T is total carbon in solution and can be obtained from CO_2 solubility model, m_{Na^+} and m_{Cl^-} are equal to molality of NaCl. The relation between Γ and M is

$$\Gamma = pz(T, P, M) \quad (38)$$

where pz function were shown in Eq. (21) to Eq. (25), We define vector K=(K_1, K_2, K_3), for the equlibrium constants in Eqs. (5)–(7)

$$K = g(\Gamma, M) \quad (39)$$

Based on K_1 and K_2 models in Eq. (20) and ion product of water, K_3, (Appendix A), we define the following:

$$K = f(T, P) \quad (40)$$

Based on Eqs. (39) and (40), the speciation equlibrium condition is

$$f(T, P) - g(\Gamma, M) = 0 \quad (41)$$

By solving the Eq. (41) with Eq. (38), we can obtain the molality vector, M.

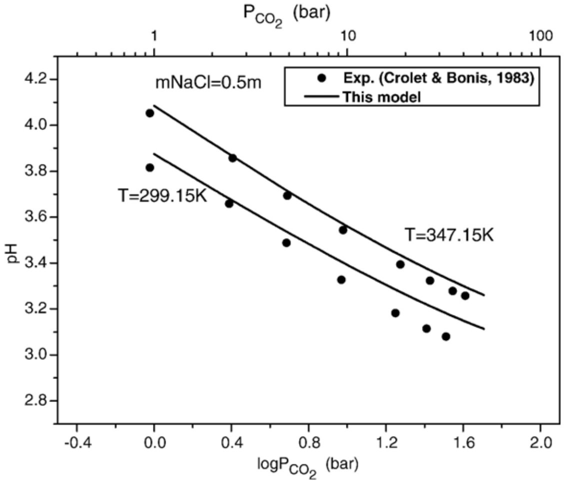

Fig. 9. A comparison of pH values as a function of pressure at different temperatures with experimental data in the H_2O–CO_2–NaCl solutions.

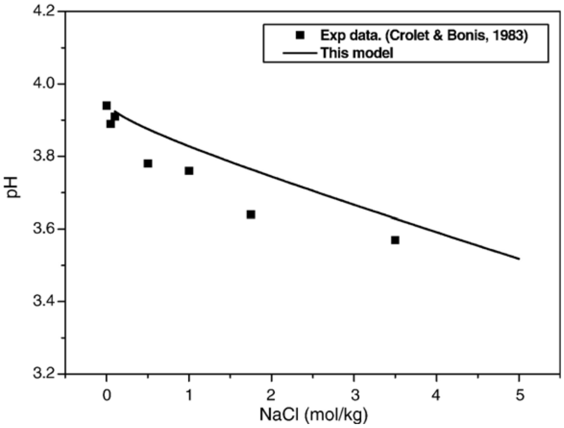

Fig. 10. Comparison of the pH values as a function of molality of NaCl with experimental data in the H_2O–CO_2–NaCl solutions (1 bar, 25 °C).

In order to solve Eq. (41), we define the change of molality for the reactions (2), (3) and (4) as x_1, x_2 and x_3, respectively. The initial molalities of these species (H^+, OH^-, CO_3^{2-}, HCO_3^-, and $CO_{2(aq)}$) are defined as m_1–m_5, respectively, and the equilibrium molalities are shown in Table 14. We can derive the following functions based on Table 14:

$$f1 : (m_1 + x_1 + x_2 + x_3) \cdot (m_4 + x_1 - x_2) - Q_1 \cdot (m_5 - x_1) = 0 \tag{42}$$

$$f2 : (m_1 + x_1 + x_2 + x_3) \cdot (m_3 + x_2) - Q_2 \cdot (m_4 + x_1 - x_2) = 0 \tag{43}$$

$$f3 : (m_1 + x_1 + x_2 + x_3) \cdot (m_2 + x_3) - Q_3 = 0 \tag{44}$$

where Q_1, Q_2, and Q_3 are ion molality products of three reactions 2, 3, and 4, respectively, which are defined by Eqs. (42)–(44). x_1, x_2 and x_3 are independent variables and others are constants. When m_1–m_5 and Q_1–Q_3 are specified, this array of functions can be worked out using Newton–Raphson Method (Press et al., 1992):

$$Q_1 = [H^+]\left[HCO_3^-\right]/\left[CO_{2(aq)}\right] \tag{45}$$

$$Q_2 = [H^+]\left[CO_3^{2-}\right]/\left[HCO_3^-\right] \tag{46}$$

$$Q_3 = [H^+][OH^-] \tag{47}$$

The activity coefficients of species (H^+, OH^-, CO_3^{2-}, HCO_3^-, and $CO_{2(aq)}$) are defined as γ_1–γ_5, respectively.

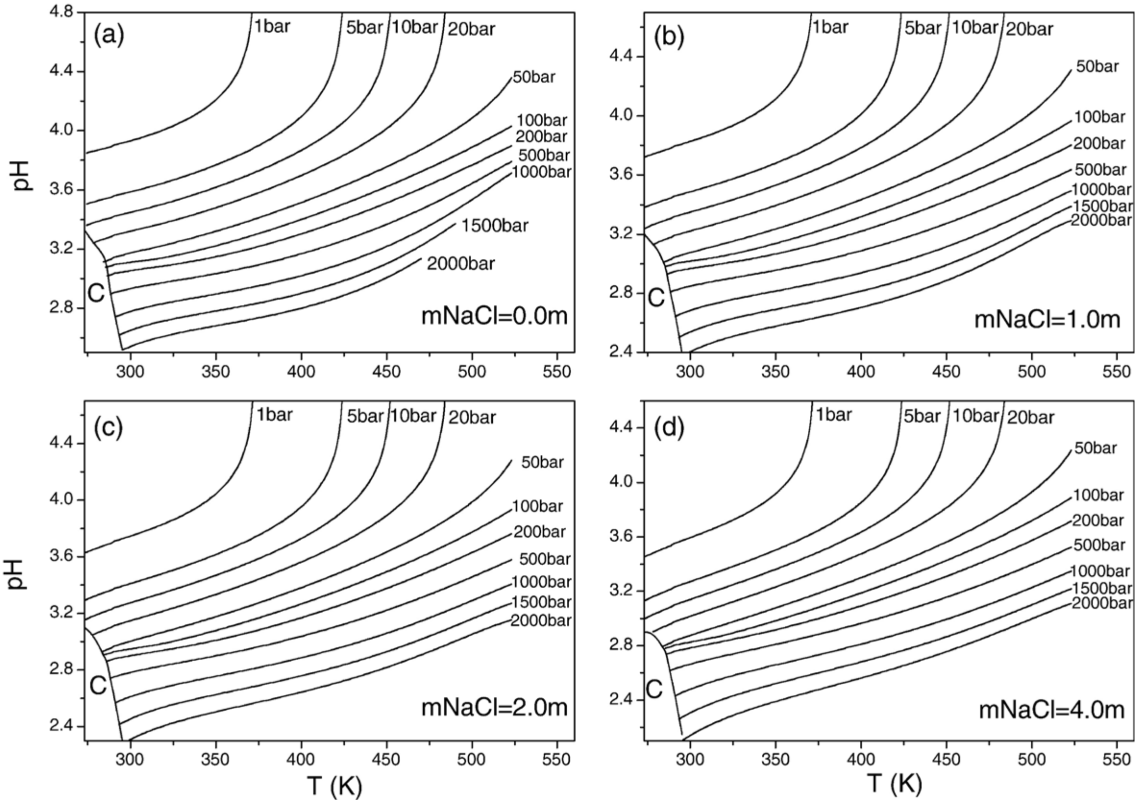

Fig. 11. Calculated pH values of aqueous CO_2–NaCl solutions at various temperatures and pressures, where C denotes clathrate hydrate field. For a given salinity solution, the pH values will increase with temperature, but will decrease as pressure increases.

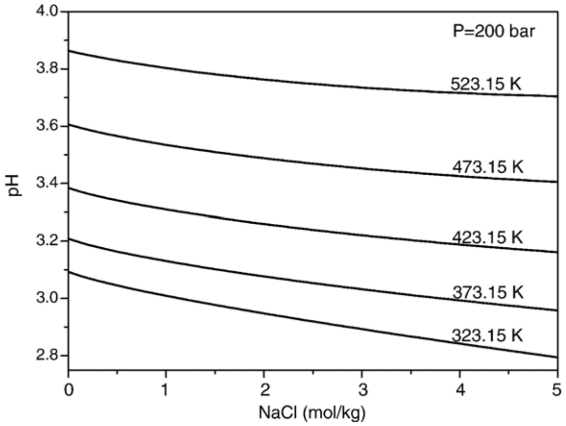

Fig. 12. pH values of aqueous solutions as a function of the molality of NaCl at 200 bar CO_2. At any temperature, the pH values will decrease as the molality of NaCl increases.

Ions products (Q_1–Q_3) are equal to activity coefficients and a_{H_2O} multiplied by dissociation constants (K_1–K_3) when system is in equilibrium,

$$Q_1 = \frac{\gamma_5 \cdot a_{H_2O}}{\gamma_1 \cdot \gamma_4} K_1 \tag{48}$$

$$Q_2 = \frac{\gamma_4}{\gamma_1 \cdot \gamma_3} K_2 \tag{49}$$

$$Q_3 = \frac{a_{H_2O}}{\gamma_1 \cdot \gamma_2} K_3 \tag{50}$$

In order to illuminate the calculating method explicitly, we make a flow chart as shown in Fig. 7. This method can be applied to similar systems for calculating the molality or activity coefficient of ions in aqueous solutions.

4.2. Application and prediction of this model

4.2.1. Predicting pH value of the solutions

In aqueous H_2O–CO_2–NaCl solutions, pH is a dominant factor for the dissolution and precipitation of many minerals at various temperatures and pressures. Using this model, the pH values in a wide *T*–*P*–*m* range can be calculated. Although there are not many pH data being reported, the comparison of the model predictions with measurements of Crolet and Bonis (1983) and Meyssami et al. (1992) shows the remarkable agreement. Note that Schaef and McGrail (2004) also did pH measurements in those solutions, but their results are confusing and difficult to use. As shown in Figs. 8–10, our model prediction are consistent with the experimental data in the aqueous H_2O–CO_2 solutions with maximum deviations of $\Delta pH < 0.05$, and in the aqueous H_2O–CO_2–NaCl solutions with maximum deviation of $\Delta pH < 0.2$.

Figs. 11–13 show the pH variation with temperature, pressure, and NaCl concentration, and they are ready to be used for many geochemical applications.

4.2.2. Predicting apparent dissociation constants of carbonic acid

Apparent (stoichiometric) dissociation constants for carbonic acid are very important for the study of fluid–mineral interactions and for the CO_2 sequestration. They are defined as:

$$K_1^* = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} \tag{51}$$

$$K_2^* = \frac{[H^+][CO_3^{2-}]}{[HCO_3^{2-}]} \tag{52}$$

where the squared brackets represent the concentrations of the ions in molality (m/kg). He and Morse (1993), Patterson et al. (1984, 1982) measured K_1^* and K_2^* at various temperatures and salinities. Recently, Millero et al. (2007) reported a series of experimental data for K_1^* and K_2^* from 0 to 50 °C, and molality of NaCl from 0.05 to 6.0 mol/kg. These data can be accurately predicted by our model (Fig. 14), even though the model was not fitted to any data of apparent dissociation constant.

4.2.3. Predicting concentrations of bicarbonate and carbonate in aqueous NaCl solutions

The values of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) concentrations in liquid phase are important

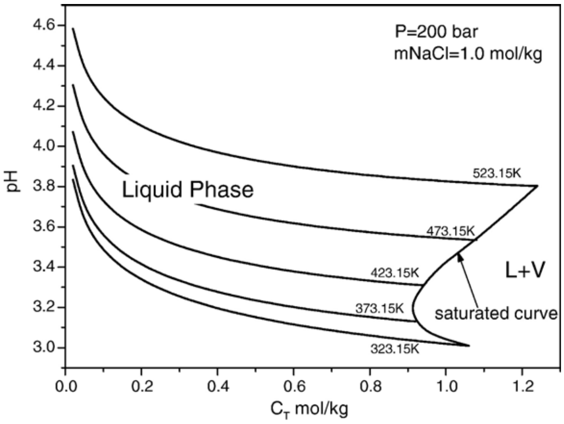

Fig. 13. pH values of aqueous solutions as a function of the molality of CO_2 at 200 bar CO_2. L+V denotes liquid phase and vapor phase coexisting field. In liquid-phase field, the pH values will decrease as the dissolved CO_2 increases.

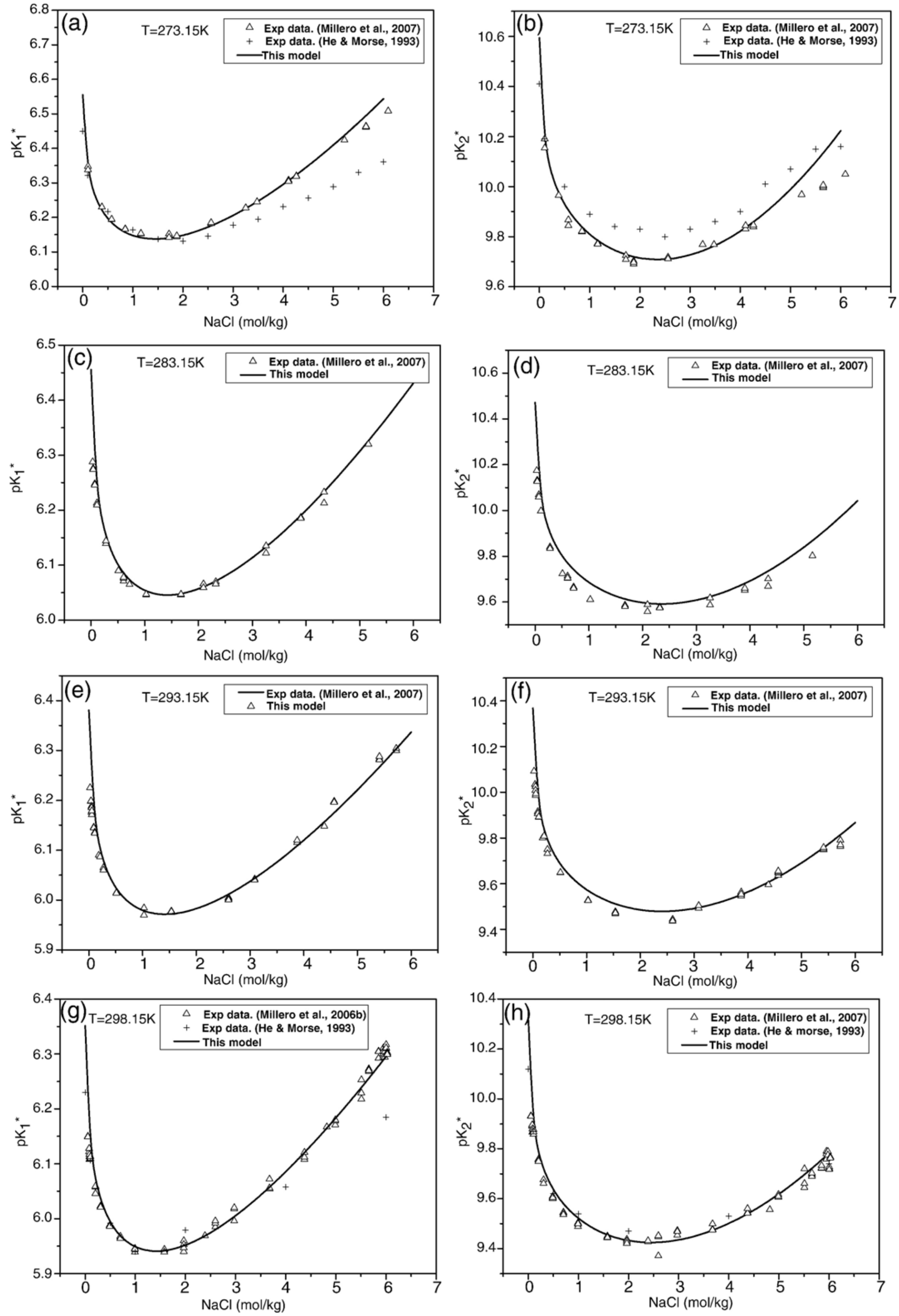

Fig. 14. The values of the apparent dissociation constants, pK_1^* and pK_2^*, for carbonic acid in aqueous NaCl solutions as a function of molality. The solid curves are calculated using this study model; the scatters are experimental data.

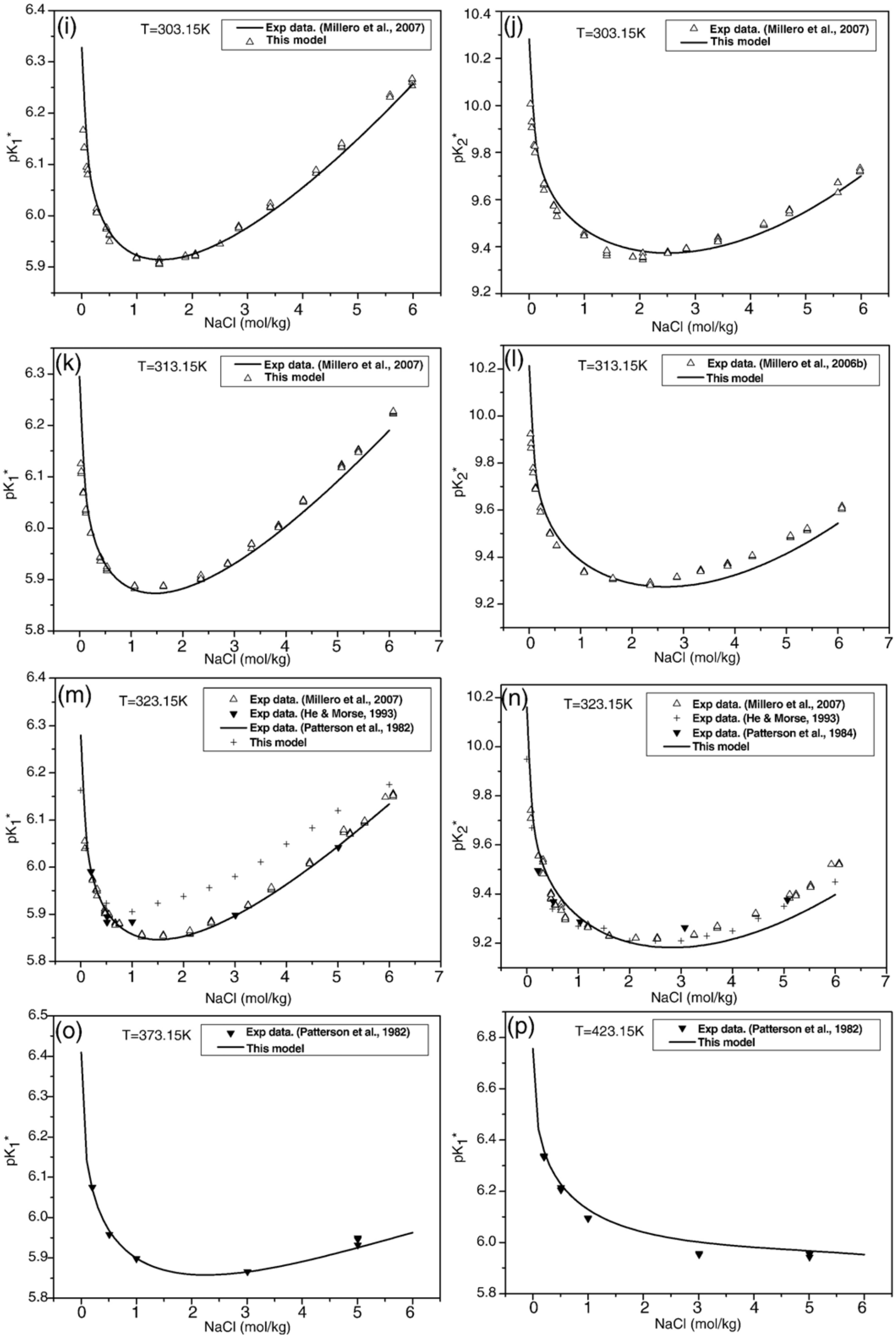

Fig. 14 (*continued*).

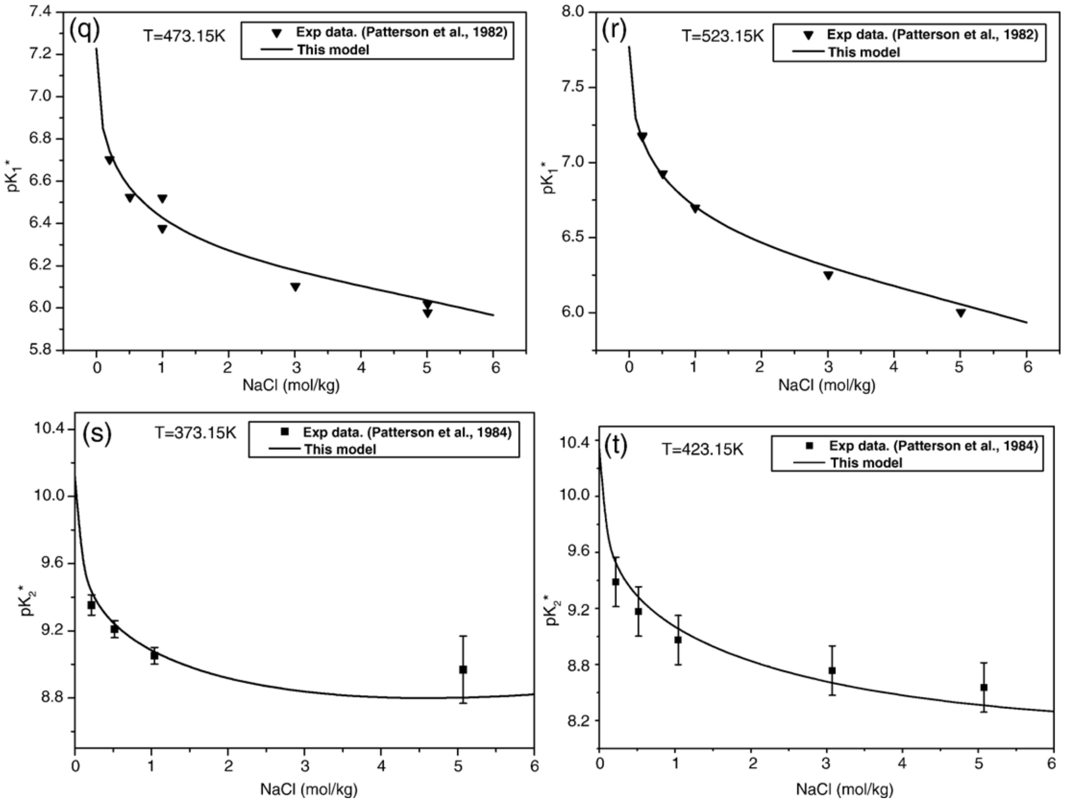

Fig. 14 (*continued*).

information for studying the interaction of carbonate minerals and rocks (such as calcite, aragonite, etc.) with geologic fluids. It is also useful for many other geochemical and chemical engineering applications. With this model and the algorithm presented in Section 4.1, the molalities of these species in a wider *T–P–m* range (273–523 K, 0–1000 bar (possibly to 2000 bar) and 0–5.0 m) are calculated, and some results are shown in Fig. 15 for convenient applications.

5. Conclusion

A thermodynamic model is developed to calculate the speciation equilibrium for the species H^+, OH^-, Na^+, Cl^-, HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$ coupled with the liquid-vapor phase equilibrium in aqueous solutions of CO_2–H_2O–NaCl system from 273 to 523 K, 0 to 1000 bar (possibly to 2000 bar), and 0 to 5.0 molality of NaCl, with accuracy close to those of experiments. Using the data of volume and compressibility instead of high-pressure dissociation data, the model accurately predicts carbonate dissociation constants at high pressures. Also, by using Pitzer's approach to calculate the activity coefficients instead of fitting measured apparent dissociation constants data, our model accurately reproduces the experimental data of apparent dissociation constants. With this model, one can calculate the concentrations of dissolved species (H^+, OH^-,HCO_3^-, CO_3^{2-}, and $CO_{2(aq)}$) in solutions at equilibrium, pH values, carbonate dissociation constants, and apparent dissociation constants in the stated *T–P–m* range (273 to 523 K, 0 to 1000 bar (possibly to 2000 bar) and 0 to 5.0 molality of NaCl). One of the advantage of this model is its coupling of the speciation equilibrium with liquid-vapor phase equilibrium, making it possible to calculate not only ionization constants, but also the concentrations and activities of each species. Compared to previous models, this model covers much larger *T–P–m* space and is more reliable, especially in the elevated pressure region. The merit of this model is its predictability. This model can accurately predict pH values, dissociation constants, and apparent dissociation constants at pressures above the saturation pressures of pure water, despite the fact that the model was not constructed by fitting these experimental data.

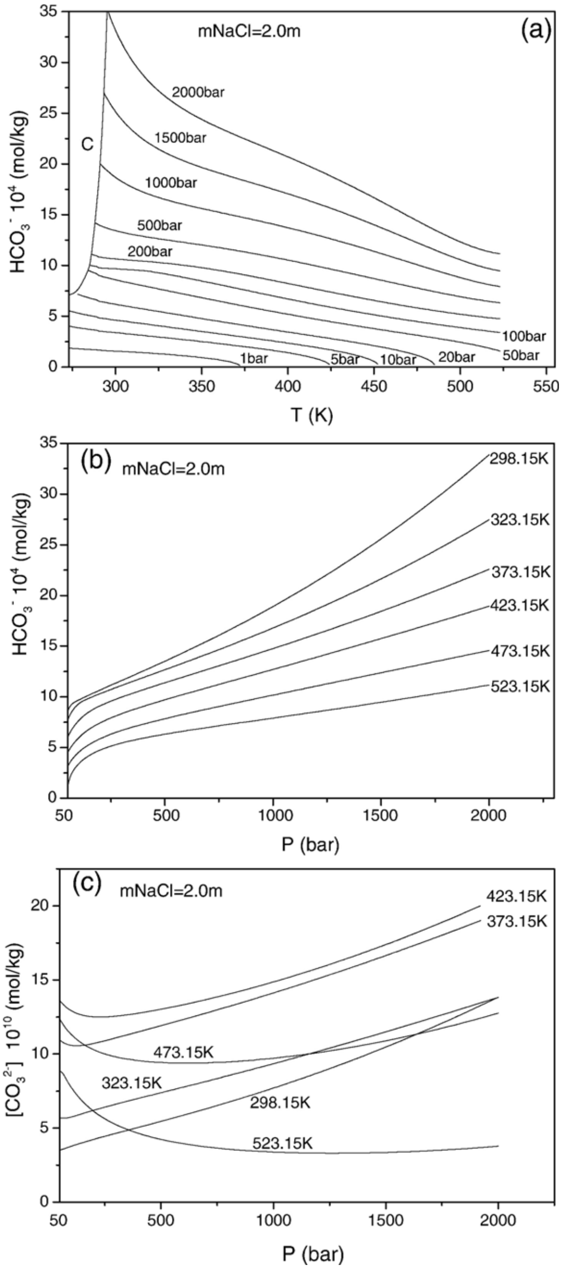

Fig. 15. The molality of HCO_3^- and CO_3^{2-} in 2.0 m NaCl aqueous solutions at various temperatures and pressures, where C denotes clathrate hydrate field.

In order to facilitate the application of the model, we developed a concise algorithm for the calculation of speciation equilibrium. A number of diagrams for geochemical applications are presented. A computer code is developed based on this model and online calculation is made available at www.geochem-model.org/models.htm.

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Appendix A. The ion product of water

The empirical model to calculate ion product of water developed by Marshall and Franck (1981) has the following form:

$$\log K_w = A + B/T + C/T^2 + D/T^3 + \left(E + F/T + G/T^2\right)\log\rho_w \tag{A1}$$

where K_w is ion product of water with the unit of (mol/kg)^2, ρ_w is the density of water (in g/cm^3), which can be deduced from the equation of state for H_2O developed by Wagner and Kruse (1998); and T is temperature in K. The parameters, A–G, are listed in Table A1.

Table A1
Parameters for Eq. (A1)

A	−4.098
B	−3245.2
C	2.2362e+5
D	−3.984e+7
E	13.957
F	−1262.3
G	8.5641e+5

Appendix B. Saturation pressure of water

The IAPWS-IF97 (Wagner and Kruse, 1998) functions to calculate saturation pressures of water has the following form:

$$p_s = \left[\frac{2C}{-B + (B^2 - 4AC)^{0.5}}\right]^4 \tag{B1}$$

$$A = \vartheta^2 + n_1\vartheta + n_2 \tag{B2}$$

$$B = n_3\vartheta^2 + n_4\vartheta + n_5 \tag{B3}$$

$$C = n_6\vartheta^2 + n_7\vartheta + n_8 \tag{B4}$$

$$\vartheta = T + n_9/(T - n_{10}) \tag{B5}$$

where p_s is saturation pressure of water in bar, T is temperature in K. The parameters, n_1–n_{10}, are listed in Table B1.

Table B1
Parameters for Eqs. (B1)–(B5)

n_1	0.11670521452767e+04
n_2	−0.72421316703206e+06
n_3	−0.17073846940092e+02
n_4	0.12020824702470e+05
n_5	−0.32325550322333e+07
n_6	0.14915108613530e+02
n_7	−0.48232657361591e+04
n_8	0.40511340542057e+06
n_9	−0.23855557567849e+00
n_{10}	0.65017534844798e+03

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