A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from 1 to 2000 bar

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Abstract

A thermodynamic model is presented to calculate methane solubility, liquid phase density and gas phase composition of the H_2O–CH_4 and H_2O–CH_4–$NaCl$ systems from 273 to 523 K (possibly up to 573 K), from 1 to 2000 bar and from 0 to 6 mol kg^{-1} of NaCl with experimental accuracy. By a more strict theoretical approach and using updated experimental data, this model made substantial improvements over previous models: (1) the accuracy of methane solubility in pure water in the temperature range between 273 and 283 K is increased from about 10% to about 5%, but confirms the accuracy of the Duan model [Duan Z., Moller N., Weare J.H., 1992a. Prediction of methane solubilities in natural waters to high ionic strength from 0 to 250 °C and from 0 to 1600 bar. *Geochim. Cosmochim. Acta* **56**, 1451–1460] above 283 K up to 2000 bar; (2) the accuracy of methane solubility in the NaCl aqueous solutions is increased from >12% to about 6% on average from 273 K and 1 bar to 523 K and 2000 bar; (3) this model is able to calculate water content in the gas phase and liquid phase density, which cannot be calculated by previous models; and (4) it covers a wider range of temperature and pressure space. With a simple approach, this model is extended to predict CH_4 solubility in other aqueous salt solutions containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}, such as seawater and geothermal brines, with excellent accuracy. This model is also able to calculate homogenization pressure of fluid inclusions (CH_4–H_2O–$NaCl$) and CH_4 solubility in water at gas–liquid–hydrate phase equilibrium. A computer code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.
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1. Introduction

CH_4, one of the most important gases in nature, has been found in gas hydrate, natural gases, coalbed gas and fluid inclusions. Accurate prediction of CH_4 solubility in pure water, NaCl solutions and other common aqueous salt solutions over a wide range of temperature, pressure and ionic strength, especially where data do not exist or where experimental data are of poor quality, is important for the above mentioned geochemical applications. There have been many experimental studies of the solubility of CH_4 in pure water and aqueous NaCl solutions. However, these data are very

scattered and cover only a limited temperature–pressure space, and are inconvenient to use. Therefore, theorists have devoted extensive efforts to modeling of CH_4 solubility in aqueous solutions so as to interpolate between the data points or extrapolate beyond the data range (Duan et al., 1992a; Soreide and Whitson, 1992; Carroll and Mather, 1997; Li et al., 1997; Li et al., 2001; Spivey et al., 2004). Among these models, the one by Duan et al. (1992a) has been widely cited for geochemical applications, including the analysis of fluid inclusions, the study of methane hydrates, calculating of the phase status and amount of methane in geothermal or geopressured-geothermal reservoirs. However, all of the published models, including the Duan model, are found to possess intolerable deficiencies, which lead to the motivation of this study.

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Nomenclature

List of symbols

m_i	Molality (mol kg^{-1}) of component i in liquid phase
P	Total pressure, that is $P_{CH_4} + P_{H_2O}$ in bar
Par	parameter
R	Universal gas constant (83.14472 bar cm^3 mol^{-1} K^{-1})
T	Absolute temperature in Kelvin
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in gas phase

Greek letters

α	Activity
φ	Fugacity coefficient
γ	Activity coefficient
μ	Chemical potential
ρ	Density
λ_{CH_4-ion}	Interaction parameter
$\xi_{CH_4-cation-anion}$	Interaction parameter

Subscripts

a	Anion
c	Cation
sol	Solution

Superscripts

v	Vapor
l	Liquid
(0)	Standard state

Over the last two decades, about 10 models have been reported to calculate CH_4 solubility in aqueous solutions. Li and Nghiem (1986) studied the phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry's Law, but the model is not reliable because they confused the molality with molarity of NaCl, which causes about 10% concentration deviation for a 4 M NaCl solution at 324.65 K and pressure between 100 and 600 bar. Harvey and Prausnitz (1989) used an equation of state to predict CH_4 solubility in aqueous salt solutions at high pressure, but the deviations are over 15% on average. Combining an EOS with a modified Debye-Hückel electrostatic term, Aasberg-Petersen et al. (1991) tried to predict CH_4 solubility in aqueous mixtures of electrolytes. The predicted solubility is in agreement with experimental data (O'Sullivan and Smith, 1970) (324.7–398.2 K, 100–600 atm and 0–4.4 mol kg^{-1}), but cannot be extended above 398 K. Zuo and Guo (1991) extended the Patel-Teja equation to predict the solubility of natural gas in formation water. The T–P–m space for CH_4–H_2O–NaCl is 324.7–398.2 K, 100–600 atm and 0–4.4 mol kg^{-1}, but the results are not satisfactory with the average deviation up to about 18% as compared with experimental data (O'Sullivan and Smith, 1970). Based on Pitzer phenomenology for the liquid phase and an equation of state (Duan et al., 1992b) for vapor phase, Duan et al. (1992a) developed a model (Duan model) to predict methane solubility in brines (273–523 K, 0–1600 bar, and 0–6 mol kg^{-1} NaCl). The new experimental data prove that the Duan model can predict CH_4 solubility in pure water within the experimental uncertainty except for the small temperature range (273–283 K), where the model deviates from the data by about 10%. However, it cannot accurately predict CH_4 solubility in aqueous NaCl solutions for a large portion of temperature–pressure range, with errors up to 20% at some temperatures. Soreide and Whitson (1992) developed a model to calculate CH_4 solubility in pure water and aqueous NaCl solutions, ranging from 298 to 444 K and from 14 to 690 bar. It is in good agreement with experimental data in pure water or in low NaCl concentration solutions in the stated temperature and pressure range, beyond which the deviations increase with temperatures and pressures. In addition, it is not accurate in aqueous NaCl solutions with m_{NaCl} above 2.5 mol kg^{-1}. For instance, the average deviation is about 15% at 374 K and 5.7 mol kg^{-1} compared with experimental data (Blount and Price, 1982) for $P < 700$ bar. Using Henry's law and Peng-Robinson EOS, Carroll and Mather (1997) modeled the solubility of light hydrocarbons in water (C-M model). The valid temperature range for the CH_4–H_2O system is 298–444 K, but the pressure is limited below 300 bar. Li et al. (2001, 1997) developed a model to predict the solubility and gas–liquid phase equilibrium in pure water and aqueous electrolyte systems using modified UNIFAC (Weidlich and Gmehling, 1987) and Soave-Redlich-Kwong EOS (Soave, 1972), covering a valid range of 479–589 K and pressure up to 2000 bar for the CH_4–H_2O system, and the range of 303–398 K, 14–616 bar and 0.5–4.0 mol kg^{-1} for CH_4–H_2O–NaCl system. However, this model cannot calculate CH_4 solubility at low temperature, e.g., the average solubility deviation in pure water is up to 20% at 324.65 K compared with experimental measurements (O'Sullivan and Smith, 1970). Wu and Prausnitz (1998) developed a model to predict phase equilibria for systems containing hydrocarbons, water and salt by using an extended Peng-Robinson equation of state, and the calculated CH_4 solubility results are no better than those of Zuo and Guo (1991). Vanderbeken et al. (1999) used MHV2 mixing rule to predict CH_4 solubility in brines at high temperature and high pressure. The fitted data are mainly calculated from the Duan model (1992), therefore the prediction accuracy is not better than Duan model.

With a cubic equation of state and the mixing rule of Huron and Vidal (1979), Sorensen et al. (2002) predicted gas solubility in brine. They tried to model CH_4 solubility in pure water (298.15–444.15 K and 40–608 atm) and aqueous NaCl solutions (283.15–398.15 K, 1–608 atm and 0.25–4.35 mol kg^{-1}). However, the average deviation of the calculated CH_4 solubility from experimental measurements is up to 26.4% in the CH_4–H_2O system and up to 25.4% in the CH_4–H_2O–NaCl system. Chapoy et al. (2004) used the Valderrama modification of the Patel-Teja equation (Valderrama, 1990) and non-density dependent mixing rules (Avlonitis et al., 1994) to model CH_4 solubility in water. The T–P range is very small (275–313 K and $P < 200$ bar) but the modeling results are in good agreement with experimental measurements. Spivey et al. (2004) presented an empirical model (S-M-N model) to model CH_4 solubility in aqueous NaCl solutions, and claimed that the model is valid in the range of 293–623 K, 9–2000 bar and 0–6 mol kg^{-1}. However, comparison with their fitting data (Sultanov et al., 1972) indicates that the calculated average absolute deviation from data is about 20% between 423 and 623 K. In the important low T–P regions (273–293 K and 1–9 bar), calculated solubilities are lower than experimental values by about 40% on average.

Trying to overcome the deficiencies of the previous models, in this article we present an improved model to calculate methane solubility, liquid phase density and gas phase composition of the H_2O–CH_4–NaCl system (273–523 K, 1–2000 bar and 0–6 molality of NaCl) by improving the theoretical approach and using updated experimental data including the corrected data of Blount and Price (1982) instead of their data published in 1979. The framework of the model is presented in Section 2 and the experimental data are reviewed in Section 3. Parameterization and comparison with experimental data are shown in Section 4. Then in Section 5, the model is extended to predict CH_4 solubility in other complicated systems like seawater and geothermal brines containing Na^+, K^+, Mg^{2+}, $Ca^{2+,}$ Cl^-, and SO_4^{2-}, to calculate homogenization pressure of fluid inclusions; to predicate CH_4 solubility in water at gas–liquid–hydrate equilibrium; and to calculate liquid phase density of CH_4–H_2O–NaCl system at equilibrium.

2. Phenomenological description of gas solubility as a function of pressure, temperature and composition

CH_4 solubility in aqueous solutions depends on the balance between the chemical potential of CH_4 in the liquid phase $\mu_{CH_4}^l$ and that in the vapor phase $\mu_{CH_4}^v$. The potential can be written in terms of fugacity in vapor phase and activity in the liquid phase:

$$
\begin{aligned}
\mu_{CH_4}^v(T,P,y) &= \mu_{CH_4}^{v(0)}(T) + RT \ln f_{CH_4}(T,P,y) \\
&= \mu_{CH_4}^{v(0)}(T) \\
&\quad + RT \ln y_{CH_4}P + RT \ln \varphi_{CH_4}(T,P,y_{CH_4})
\end{aligned}
\tag{1}
$$

$$
\begin{aligned}
\mu_{CH_4}^l(T,P,m) &= \mu_{CH_4}^{l(0)}(T,P) + RT \ln a_{CH_4}(T,P,m) \\
&= \mu_{CH_4}^{l(0)}(T,P) \\
&\quad + RT \ln m_{CH_4} + RT \ln \gamma_{CH_4}(T,P,m)
\end{aligned}
\tag{2}
$$

where $\mu_{CH_4}^{l(0)}$, the standard chemical potential of CH_4 in liquid, is defined as the chemical potential in hypothetically ideal solution of unit molality (Denbigh, 1971) and $\mu_{CH_4}^{v(0)}$, the standard chemical potential in vapor, is the hypothetical ideal gas chemical potential when the pressure is set to 1 bar.

At phase equilibrium $\mu_{CH_4}^l = \mu_{CH_4}^v$, and we obtain

$$
\begin{aligned}
\ln \frac{y_{CH4}P}{m_{CH_4}} &= \frac{\mu_{CH_4}^{l(0)}(T,P) - \mu_{CH_4}^{v(0)}(T)}{RT} - \ln \varphi_{CH_4}(T,P,y) \\
&\quad + \ln \gamma_{CH_4}(T,P,m).
\end{aligned}
\tag{3}
$$

In the parameterization, the reference value $\mu_{CH_4}^{v(0)}$ can be set to 0 for convenience, because only the difference between $\mu_{CH_4}^{l(0)}$ and $\mu_{CH_4}^{v(0)}$ is important. Since there is little water in the vapor phase, the fugacity coefficient of CH_4 in gaseous mixtures differs little from that of pure CH_4 at 273–565 K. Therefore, $\ln \varphi_{CH_4}$ can be approximated from the EOS for pure CH_4 (Duan et al., 1992b) (see Appendix A). y_{CH_4}, the mole fraction of CH_4 in the gas, is calculated from

$$
y_{CH_4} = 1 - y_{H_2O} = \frac{P - P_{H_2O}}{P},
\tag{4}
$$

where the partial pressure of water in vapor, P_{H_2O}, is approximated as the saturated pressure of pure water in our previous studies (Duan et al., 1992a; Duan and Sun, 2003; Mao et al., 2005), which will lead to errors (up to 5%) for $\mu_{CH_4}^{l(0)}/RT$ and $\ln \gamma_{CH_4}^l$. However, these errors can be cancelled to a large extent in the parameterization. In this study, the mole fraction of water, y_{H_2O} in the gas phase is estimated using the following semi-empirical equation:

$$
y_{H_2O} = \frac{x_{H_2O}P_{H_2O}^S}{\varphi_{H_2O}P} \exp\left(\frac{v_{H_2O}^l\left(P - P_{H_2O}^S\right)}{RT}\right),
\tag{5}
$$

where x_{H_2O} is the mole fraction of H_2O in the liquid, and is approximated as 1 for CH_4–H_2O system and $1 - 2x_{NaCl}$ for CH_4–H_2O–NaCl system; $P_{H_2O}^S$, the saturation pressure (bar) of water, is calculated from the recent correlation of Shibue (2003); $v_{H_2O}^l$, molar volume of liquid water (cm^3/mole), approximates saturated liquid phase volume of water and is calculated from the equation of Wagner and Pruss (1993).

The only remaining parameter of Eq. (5) for the calculation of water content in the gas phase, y_{H_2O}, is the fugacity coefficient of water (φ_{H_2O}) in the gas phase, which can be calculated from the following equation:

$$
\varphi_{H_2O} = \exp\left(a_1 + a_2P + a_3P^2 + a_4PT + \frac{a_5P}{T} + \frac{a_6P^2}{T}\right),
\tag{6}
$$

where $a_1 - a_6$ (Table 1) are obtained by regressing the water content data in the gas phase for the CH_4–H_2O sys-

Table 1
Parameters of Eq. (6)

Parameters	Values
a_1	−1.42006707D-02
a_2	1.08369910D-02
a_3	−1.59213160D-06
a_4	−1.10804676D-05
a_5	−3.14287155D00
a_6	1.06338095D-03

tem (Olds et al., 1942; Rigby and Prausnitz, 1968; Sultanov et al., 1972; Yarym-Agaev et al., 1985; Yokoyama et al., 1988; Chapoy et al., 2005a,b; Mohammadi et al., 2004a,b). The water content in the gas phase can be accurately calculated by Eqs. (5 and 6), as shown by Fig. 1.

$\ln \gamma_{CH_4}$ is expressed as a virial expansion of excess Gibbs energy (Pitzer, 1973).

$$\ln \gamma_{CH_4} = \sum_c 2\lambda_{CH_4-c} m_c + \sum_a 2\lambda_{CH_4-a} m_a + \sum_c \sum_a \xi_{CH_4-a-c} m_c m_a, \qquad (7)$$

where λ and ξ are second-order and third-order interaction parameters, respectively; c and a refer to cation and anion, respectively. Substituting Eq. (7) into Eq. (3) yields

$$\ln \frac{y_{CH_4} P}{m_{CH_4}} = \frac{\mu_{CH_4}^{l(0)}}{RT} - \ln \varphi_{CH_4} + \sum_c 2\lambda_{CH_4-c} m_c + \sum_a 2\lambda_{CH_4-a} m_a + \sum_c \sum_a \xi_{CH_4-c-a} m_c m_a. \qquad (8)$$
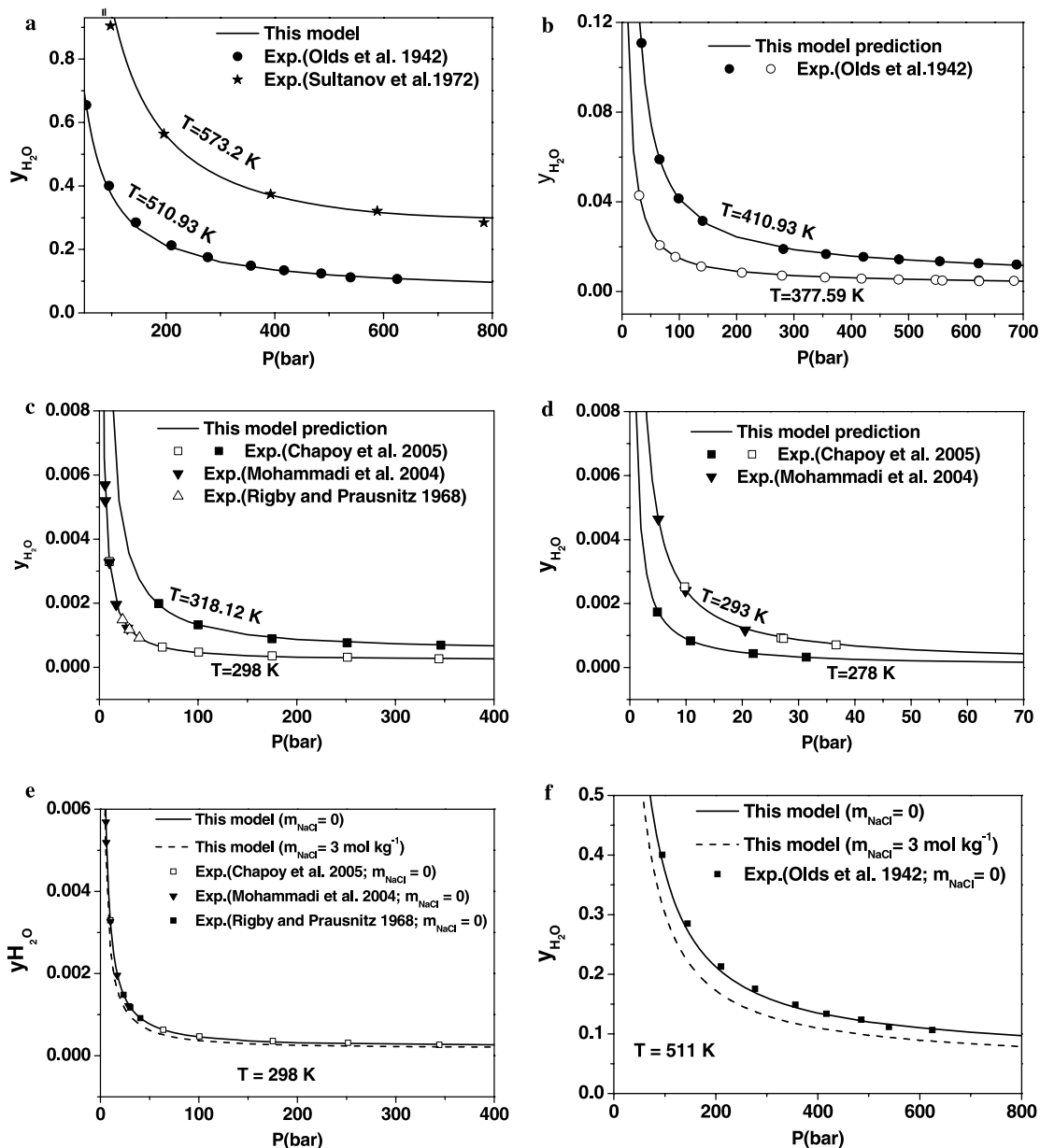

Fig. 1. The prediction of water content in the gas phase from this model (a–d is for CH₄–H₂O system and e–f is for CH₄–H₂O–NaCl system).

Table 2
Aqueous CH_4 solubility measurements

References	Solution	T (K)	P (bar)	N^{a}
Bunsen (1855)	Water	279.35–298.75	1[+]	5
Winkler (1901)	Water	273.38–353.17	1[+]	9
Michels et al. (1936)	Water	298.15–423.15	40.6–469.1	39
	1.01–6.59 m NaCl	298.15–423.15	41.8–456.0	97
	2.91–2.93 m CaCl₂	298.15	56.2–209.9	4
Dodson and Standing (1944)	0.0–0.6 m brine	311.15–394.15	35–345	96
Culberson et al. (1950)	Water	298.15	36.2–667.4	11
Eucken and Hertzberg (1950)	0–2.77 m NaCl	273.15–293.15	1[+]	7
Culberson and Mcketta (1951)	Water	298.2–444.3	22.3–689.1	71
Morrison and Billett (1952)	Water	285.1–348.4	1[+]	11
Claussen and Polglase (1952)	Water	274.8–312.8	1[+]	6
Lannung and Gjaldbaek (1960)	Water	291.15–310.15	1[+]	6
Duffy et al. (1961)	Water	298.15–303.15	3.17–51.71	17
	0.5–6.1 m NaCl	303.15	214.8–957.5	23
	0–7.35 M CaCl₂	298.15–303.15	3.2–74.8	47
	NaCl + CaCl₂	303.15	3.2–51.9	10
Namiot (1961)	Water	273.15–283.15	1[+]	2
Mishnina et al. (1962)	0–6.24 m NaCl	277.15–363.15	1[+]	45
Wetlaufer et al. (1964)	Water	278.2–318.2	1[+]	3
O'Sullivan and Smith (1970)	Water	324.65–398.15	101.3–616.1	18
	1.01–4.41 m NaCl	324.65–398.15	101.3–616.1	22
Wen and Hung (1970)	Water	278.15–308.15	1[+]	4
Amirijafari and Campbell (1972)	Water	310.93–344.26	41.4–344.7	8
Sultanov et al. (1972)	Water	423.2–633.2	98.1–1132.7	63
Ben-Naim et al. (1973)	Water	278.15–298.15	1[+]	5
Ben-Naim and Yaacobi (1974)	0–2.1 m NaCl	283.15–303.15	1[+]	25
Moudgil et al. (1974)	Water	298.15	1[+]	1
Yano et al. (1974)	0–1.55 m NaCl	298.15	1[+]	4
Yamamoto et al. (1976)	Water	273.91–302.70	1[+]	35
	Sea water	274–303	1	256
Blanco and Smith (1978)	1.0 m CaCl₂	298.2–398.2	101–608	30
Namiot et al. (1979)	0–1.54 m NaCl	323–623	295	14
Price (1979)	Water	427–627	35.4–1972.6	71
Wiesenburg and Guinasso (1979)	Water and seawater	271–303	1	185
Muccitelli and Wen (1980)	Water	278.15–298.15	1[+]	5
Cosgrove and Walkley (1981)	Water	278.15–318.15	1[+]	9
Rettich et al. (1981)	Water	275.46–328.15	1[+]	16
Blount and Price (1982)	0–5.9 m NaCl	372.15–513.15	75–1570	670
Byrne and Stoessell (1982)	Na–K–Mg–Ca–Cl–SO₄	298.15	37.9	12
Crovetto et al. (1982)	Water	297.5–518.3	13.27–64.51	7
Stoessell and Byrne (1982b)	Water	298.15	24.1–51.7	3
	Sea water	298.15	24.1–51.7	3
	0–4.0 m NaCl	298.15	24.1–51.7	15
	0–4.0 m KCl	298.15	24.1–51.7	15
	0–2.16 m MgCl₂	298.15	24.1–51.7	12
	0–2.0 m CaCl₂	298.15	24.1–51.7	12
	0–0.5 m K₂SO₄	298.15	24.1–51.7	9
	0–1.5 m MgSO₄	298.15	24.1–51.7	12
	0–1.0 m Na₂SO₄	298.15	24.1–51.7	9
Ashmayan et al. (1984)	Water	623	980	1
Cramer (1984)	Water	277.2–573.2	11–132	16
	0.81–4.7 m NaCl	273.7–574.3	19–124	60
Yarym-Agaev et al. (1985)	Water	298.2–338.2	25–125	15
Krader and Franck (1987)	0–2.0 m NaCl	638–799	400–2630	138
Yokoyama et al. (1988)	Water	298.15–323.15	30–80	6
Lekvam and Bishnoi (1997)	Water	274.19–285.68	5.67–90.82	18
Song et al. (1997)	Water	273.2–290.2	34.5	5

Table 2 (continued)

References	Solution	T (K)	P (bar)	N^a
Dhima et al. (1998)	Water	344	200–1000	4
Kiepe et al. (2003)	Water	313–473	3.4–93	26
	0.99-3.99 m KCl	313.51–373.19	4.2–97.9	86
Wang et al. (2003)	Water	283.2–303.2	20–400.3	17
Chapoy et al. (2004)	Water	275.11–313.11	9.7–180	16

Note. 1^+ denotes that partial pressure of methane is 1 atm.

[a] N, number of measurements.

Following Pitzer et al. (1984), we choose the following equation for the P–T dependence of λ's, ξ's, and $\mu_{CH_4}^{l(0)}/RT$:

$$Par(T,P) = c_1 + c_2 T + \frac{c_3}{T} + c_4 T^2 + \frac{c_5}{T^2} + c_6 P + c_7 PT$$

$$+ \frac{C_8 P}{T} + \frac{c_9 P}{T^2} + c_{10} P^2 T. \qquad (9)$$

Eqs. (8) and (9) form the basis of our model parameterization.

3. Review of the CH₄ solubility data

The solubility of CH₄ in pure water and aqueous NaCl solutions has been measured over a wide P–T–m range (Table 2). The measurements of CH₄ solubility in water are extensive. We find that most of the data sets are consistent with each other except for those reported by Michels et al. (1936), Song et al. (1997) and Winkler (1901), whose solubility data deviate from other data sets. Some data points of Duffy et al. (1961) are very scattered. The experimental data of Sultanov et al. (1972) below 523 K are compatible with data of Price (1979) below 523 K, but not above 523 K. Therefore, except for these small number of inconsistent data points (Winkler, 1901; Michels et al., 1936; Duffy et al., 1961; Song et al., 1997), the data points of Sultanov et al. (1972) above 523 K and those of Price (1979) above 565 K, most of experimental solubility measurements in water mentioned in Table 2 are used in the parameterization. The optimal T–P range of this model for CH₄-H₂O system is 273–565 K and 1–2000 bar.

Experimental CH₄ solubility data in aqueous NaCl solutions are not as extensive as in water. The data of Duffy et al. (1961) and Michels et al. (1936) are not accurate due to an inaccurate pressure decline technique as pointed out by O'Sullivan and Smith (1970). Experimental data of Cramer (1984) are not only internally inconsistent, but also inconsistent with other data sets. Therefore, all data points but those of Cramer (1984), Duffy et al. (1961) and Michels et al. (1936) are included in the parameterization which cover a wide T–P–m range (273–513 K, 1–1600 bar and 0–6 mol kg^{-1}) for the CH₄–H₂O–NaCl system.

CH₄ solubility data in aqueous solutions with salts other than NaCl are limited. Blanco and Smith (1978), Duffy et al. (1961) and Michels et al. (1936) measured the CH₄ solubility in aqueous CaCl₂ solutions and Stoessell and Byrne (1982b) measured CH₄ solubility in different aqueous salt solutions at 298 K and pressure below 52 bar. Kiepe et al. (2003) measured the CH₄ solubility in KCl solutions below 100 bar. Experimental data for CH₄ in aqueous CaCl₂ solutions from Duffy et al. (1961) and Michels et al. (1936) are unreliable, as are those in NaCl solutions, due to adopting the inaccurate pressure decline technique.

4. Parameterization and comparison with experimental data

Since measurements can only be made in electronically neutral solutions, one of the parameters in Eq. (8) must be assigned arbitrarily (Duan et al., 1992a). $\lambda_{CH_4–Cl}$ is set to zero and then the remaining parameters are fit to the experimental solubility data selected above, where $\mu_{CH_4}^{l(0)}/RT$ is evaluated from the CH₄ solubility data in pure water with a standard deviation of 3.35%; $\lambda_{CH_4–Na}$ and $\xi_{CH_4–Na–Cl}$ are then evaluated simultaneously to the solubility measurements in aqueous NaCl solutions with a standard deviation of 5.83%. Table 3 lists the optimized parameters.

With these parameters, the CH₄ solubility in pure water (Table 4) and aqueous NaCl solutions (Tables 5–8) can be calculated. It should be noted that the lower left blank region of Tables 4–8 is the CH₄–hydrate region where this model cannot be applied. Table 9 shows the deviation of our model from each data set for the CH₄ solubility in water and aqueous NaCl solutions. Other competitive models (C-M, S-M-N and Duan model) are also compared with experimental data. Figs. 2 and 3 show the comparisons between the experimental results and model predictions. As can be seen from the figures, the experimental

Table 3
Interaction parameters

T–P coefficient	$\mu_{CH_4}^{l(0)}/RT$	$\lambda_{CH_4–Na}$	$\xi_{CH_4–Na–C}$
C_1	0.83143711D+01	−0.81222036D+00	−0.29903571D−02
C_2	−0.72772168D−03	0.10635172D−02	
C_3	0.21489858D+04	0.18894036D+03	
C_4	−0.14019672D−04		
C_5	−0.66743449D+06		
C_6	0.76985890D−02	0.44105635D−04	
C_7	−0.50253331D−05		
C_8	−0.30092013D+01		
C_9	0.48468502D+03		
C_{10}		−0.46797718D−10	

Table 4
Calculated CH_4 solubility (mol kg^{-1}) in pure water

P (bar)	T (K)										
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15	573.15
1	0.00247	0.00126	0.00076	0.00025							
50		0.05642	0.04215	0.03837	0.03972	0.04423	0.04992	0.05194	0.03654		
100		0.09719	0.07520	0.07033	0.07492	0.08700	0.10606	0.13028	0.15141	0.14167	0.02009
150		0.12678	0.10121	0.09677	0.10498	0.12432	0.15577	0.20043	0.25509	0.30048	0.26908
200		0.14917	0.12221	0.11901	0.13096	0.15716	0.20009	0.26355	0.34902	0.44497	0.49583
300		0.18220	0.15492	0.15494	0.17401	0.21260	0.27593	0.37266	0.51254	0.69749	0.89159
400		0.20704	0.18048	0.18371	0.20905	0.25828	0.33899	0.46403	0.65015	0.91028	1.22285
500		0.22741	0.20192	0.20807	0.23886	0.29721	0.39281	0.54211	0.76778	1.09157	1.50152
600		0.24485	0.22063	0.22941	0.26493	0.33118	0.43965	0.60991	0.86962	1.24750	1.73671
700		0.26011	0.23732	0.24850	0.28818	0.36129	0.48098	0.66946	0.95866	1.38261	1.93547
800		0.27359	0.25240	0.26579	0.30914	0.38828	0.51777	0.72220	1.03709	1.50034	2.10333
900			0.26612	0.28157	0.32818	0.41262	0.55073	0.76918	1.10652	1.60338	2.24476
1000			0.27864	0.29603	0.34555	0.43466	0.58035	0.81115	1.16823	1.69388	2.36345
1100			0.29009	0.30931	0.36142	0.45464	0.60700	0.84871	1.22319	1.77357	2.46255
1200			0.30055	0.32150	0.37593	0.47275	0.63097	0.88231	1.27217	1.84389	2.54480
1300			0.31009	0.33269	0.38917	0.48914	0.65249	0.91230	1.31581	1.90603	2.61259
1400			0.31876	0.34293	0.40123	0.50392	0.67171	0.93897	1.35460	1.96099	2.66807
1500			0.32661	0.35228	0.41217	0.51718	0.68878	0.96255	1.38894	2.00961	2.71317
1600			0.33368	0.36077	0.42205	0.52902	0.70383	0.98321	1.41916	2.05258	2.74959
1700			0.34001	0.36845	0.43091	0.53949	0.71696	1.00112	1.44552	2.09046	2.77888
1800			0.34563	0.37536	0.43882	0.54866	0.72827	1.01641	1.46823	2.12372	2.80240
1900			0.35057	0.38152	0.44581	0.55660	0.73783	1.02920	1.48746	2.15272	2.82136
2000			0.35486	0.38696	0.45192	0.56337	0.74573	1.03960	1.50336	2.17774	2.83679

Table 5
Calculated CH_4 solubility (mol kg^{-1}) in 1 mol kg^{-1} NaCl solutions

P (bar)	T (K)										
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15	573.15
1	0.00177	0.00097	0.00062	0.00024							
50		0.04315	0.03384	0.03177	0.03348	0.03762	0.04275	0.04522	0.03507		
100		0.07402	0.06012	0.05797	0.06279	0.07341	0.08954	0.10982	0.12827	0.12548	0.04693
150		0.09616	0.08059	0.07943	0.08759	0.10437	0.13062	0.16718	0.21171	0.25080	0.23915
200		0.11270	0.09693	0.09730	0.10883	0.13137	0.16694	0.21838	0.28673	0.36400	0.41303
300		0.13664	0.12198	0.12576	0.14357	0.17640	0.22838	0.30593	0.41599	0.55994	0.71393
400		0.15421	0.14117	0.14815	0.17139	0.21294	0.27876	0.37829	0.52348	0.72327	0.96347
500		0.16832	0.15699	0.16683	0.19473	0.24370	0.32128	0.43952	0.61454	0.86136	1.17219
600		0.18020	0.17062	0.18300	0.21495	0.27031	0.35800	0.49233	0.69296	0.97968	1.34809
700		0.19045	0.18265	0.19735	0.23285	0.29378	0.39027	0.53861	0.76145	1.08226	1.49729
800		0.19941	0.19345	0.21030	0.24895	0.31479	0.41901	0.57967	0.82199	1.17216	1.62452
900		0.20731	0.20325	0.22210	0.26360	0.33379	0.44489	0.61650	0.87608	1.25176	1.73359
1000		0.21429	0.21219	0.23295	0.27703	0.35113	0.46839	0.64983	0.92487	1.32294	1.82757
1100			0.22041	0.24299	0.28942	0.36706	0.48987	0.68021	0.96926	1.38723	1.90903
1200			0.22798	0.25231	0.30092	0.38176	0.50961	0.70808	1.00998	1.44587	1.98016
1300			0.23497	0.26100	0.31163	0.39539	0.52785	0.73379	1.04760	1.49990	2.04284
1400			0.24144	0.26912	0.32163	0.40807	0.54475	0.75763	1.08259	1.55018	2.09873
1500			0.24744	0.27674	0.33100	0.41989	0.56047	0.77981	1.11533	1.59746	2.14929
1600			0.25301	0.28390	0.33980	0.43096	0.57512	0.80051	1.14613	1.64231	2.19584
1700			0.25819	0.29063	0.34808	0.44133	0.58881	0.81990	1.17524	1.68526	2.23953
1800			0.26300	0.29699	0.35590	0.45108	0.60164	0.83809	1.20284	1.72671	2.28143
1900			0.26749	0.30299	0.36330	0.46026	0.61367	0.85520	1.22912	1.76699	2.32247
2000			0.27167	0.30868	0.37031	0.46893	0.62500	0.87132	1.25419	1.80639	2.36348

data are accurately reproduced by this model and represent improvements over previous models.

Fig. 2(a–f) shows the experimental CH_4 solubility in water compared with the competitive models. It can be seen that this model and Duan model are apparently better than other models. S-M-N model cannot be applied in low-pressure and low-temperature regions (Fig. 2a and f). C-M model is only applicable in a small T–P range (<444 K and <300 bar) within experimental uncertainty. This model improves the prediction accuracy between 273 and 283 K over

Table 6
Calculated CH_4 solubility (mol kg^{-1}) in 2 mol kg^{-1} NaCl solutions

P (bar)	T (K)										
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15	573.15
1	0.00127	0.00075	0.00051	0.00023							
50		0.03320	0.02734	0.02646	0.02838	0.03218	0.03679	0.03945	0.03292		
100		0.05670	0.04835	0.04806	0.05294	0.06231	0.07601	0.09301	0.10894	0.11017	0.05986
150		0.07337	0.06455	0.06558	0.07352	0.08813	0.11015	0.14018	0.17646	0.20956	0.20893
200		0.08566	0.07734	0.08002	0.09098	0.11045	0.14009	0.18195	0.23670	0.29869	0.34288
300		0.10308	0.09663	0.10269	0.11915	0.14722	0.19013	0.25256	0.33941	0.45147	0.57266
400		0.11554	0.11108	0.12019	0.14134	0.17660	0.23057	0.31016	0.42377	0.57741	0.76142
500		0.12533	0.12279	0.13456	0.15970	0.20102	0.26431	0.35839	0.49460	0.68308	0.91838
600		0.13342	0.13273	0.14685	0.17543	0.22195	0.29322	0.39972	0.55526	0.77326	1.05048
700		0.14028	0.14141	0.15767	0.18927	0.24031	0.31853	0.43584	0.60819	0.85151	1.16294
800		0.14621	0.14916	0.16739	0.20168	0.25673	0.34110	0.46797	0.65517	0.92052	1.25984
900		0.15139	0.15616	0.17624	0.21299	0.27164	0.36152	0.49701	0.69755	0.98236	1.34434
1000		0.15596	0.16256	0.18441	0.22343	0.28535	0.38027	0.52363	0.73636	1.03867	1.41903
1100		0.16001	0.16847	0.19203	0.23316	0.29812	0.39768	0.54835	0.77242	1.09078	1.48603
1200		0.16362	0.17396	0.19919	0.24232	0.31012	0.41403	0.57158	0.80640	1.13978	1.54713
1300		0.16685	0.17912	0.20598	0.25103	0.32151	0.42955	0.59368	0.83884	1.18660	1.60385
1400		0.16975	0.18397	0.21247	0.25936	0.33242	0.44441	0.61490	0.87017	1.23200	1.65756
1500			0.18859	0.21870	0.26741	0.34294	0.45877	0.63548	0.90078	1.27666	1.70945
1600			0.19299	0.22474	0.27522	0.35317	0.47274	0.65561	0.93098	1.32115	1.76061
1700			0.19723	0.23062	0.28286	0.36319	0.48645	0.67545	0.96102	1.36598	1.81204
1800			0.20133	0.23639	0.29038	0.37307	0.49999	0.69515	0.99115	1.41158	1.86466
1900			0.20532	0.24208	0.29783	0.38287	0.51346	0.71483	1.02156	1.45835	1.91935
2000			0.20922	0.24772	0.30526	0.39266	0.52694	0.73462	1.05244	1.50663	1.97693

Table 7
Calculated CH_4 solubility (mol kg^{-1}) in 4 mol kg^{-1} NaCl solutions

P (bar)	T (K)										
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15	573.15
1	0.00067	0.00046	0.00035	0.00020							
50	0.02694	0.02001	0.01816	0.01869	0.02075	0.02394	0.02762	0.03020	0.02775		
100		0.03389	0.03184	0.03363	0.03829	0.04566	0.05567	0.06766	0.07918	0.08333	0.06309
150		0.04349	0.04217	0.04551	0.05272	0.06395	0.07966	0.10009	0.12411	0.14683	0.15401
200		0.05037	0.05013	0.05510	0.06472	0.07947	0.10034	0.12834	0.16357	0.20292	0.23459
300		0.05973	0.06173	0.06970	0.08355	0.10438	0.13406	0.17501	0.22942	0.29716	0.37034
400		0.06604	0.07002	0.08053	0.09786	0.12364	0.16051	0.21204	0.28214	0.37309	0.47969
500		0.07075	0.07648	0.08912	0.10935	0.13922	0.18204	0.24238	0.32557	0.43577	0.56952
600		0.07446	0.08178	0.09628	0.11896	0.15231	0.20019	0.26802	0.36236	0.48887	0.64490
700		0.07749	0.08630	0.10246	0.12731	0.16367	0.21596	0.29033	0.39443	0.53506	0.70962
800		0.08003	0.09028	0.10796	0.13475	0.17382	0.23004	0.31030	0.42317	0.57635	0.76657
900		0.08221	0.09385	0.11298	0.14157	0.18312	0.24296	0.32865	0.44962	0.61430	0.81798
1000		0.08411	0.09713	0.11766	0.14795	0.19183	0.25510	0.34593	0.47462	0.65013	0.86566
1100		0.08580	0.10020	0.12210	0.15405	0.20018	0.26676	0.36260	0.49883	0.68486	0.91110
1200		0.08733	0.10313	0.12640	0.15997	0.20833	0.27817	0.37900	0.52279	0.71933	0.95556
1300		0.08874	0.10597	0.13062	0.16584	0.21642	0.28955	0.39545	0.54698	0.75429	1.00017
1400		0.09008	0.10875	0.13482	0.17171	0.22457	0.30108	0.41220	0.57180	0.79041	1.04594
1500		0.09136	0.11153	0.13906	0.17768	0.23289	0.31289	0.42949	0.59764	0.82830	1.09384
1600		0.09261	0.11433	0.14339	0.18381	0.24147	0.32515	0.44754	0.62483	0.86857	1.14481
1700		0.09386	0.11718	0.14785	0.19016	0.25041	0.33799	0.46657	0.65373	0.91179	1.19978
1800		0.09512	0.12012	0.15247	0.19680	0.25980	0.35154	0.48676	0.68466	0.95855	1.25974
1900		0.09642	0.12316	0.15732	0.20379	0.26974	0.36593	0.50835	0.71798	1.00946	1.32572
2000		0.09776	0.12634	0.16241	0.21119	0.28030	0.38132	0.53153	0.75403	1.06518	1.39884

the Duan model. Note that the less competitive models discussed in the introduction are not compared here.

From Fig. 3(a–f) we can see that the present model is much more accurate than other models in aqueous NaCl solutions. S-W-N model cannot predict CH_4 solubility in both low and high T–P regions (Fig. 3a, b, d and f). Duan model deviates substantially from data in the low T–P regions (Fig. 3a, b and d).

The partial molar volume $(\overline{V}_{CH_4(l)})$, Henry's constant (k_H) and heat of solution (ΔH_m^s) of CH_4 in aqueous NaCl

Table 8
Calculated CH_4 solubility (mol kg^{-1}) in 6 mol kg^{-1} NaCl solutions

P (bar)	T (K)										
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	543.15	573.15
1	0.00036	0.00029	0.00025	0.00017							
50	0.01437	0.01235	0.01235	0.01351	0.01553	0.01819	0.02109	0.02324	0.02240		
100	0.02288	0.02074	0.02148	0.02409	0.02835	0.03422	0.04162	0.05004	0.05797	0.06171	0.05306
150	0.02776	0.02640	0.02821	0.03234	0.03870	0.04747	0.05887	0.07285	0.08854	0.10313	0.10958
200	0.03072	0.03034	0.03328	0.03886	0.04714	0.05851	0.07347	0.09239	0.11495	0.13916	0.15896
300		0.03545	0.04038	0.04845	0.05999	0.07574	0.09669	0.12389	0.15804	0.19844	0.24058
400		0.03866	0.04521	0.05526	0.06938	0.08860	0.11432	0.14816	0.19162	0.24505	0.30495
500		0.04090	0.04879	0.06045	0.07667	0.09870	0.12829	0.16758	0.21873	0.28288	0.35715
600		0.04256	0.05161	0.06464	0.08261	0.10700	0.13986	0.18376	0.24144	0.31468	0.40081
700		0.04384	0.05394	0.06819	0.08769	0.11413	0.14984	0.19778	0.26123	0.34245	0.43864
800		0.04486	0.05596	0.07132	0.09220	0.12049	0.15879	0.21043	0.27917	0.36766	0.47265
900		0.04572	0.05777	0.07418	0.09636	0.12639	0.16713	0.22228	0.29607	0.39145	0.50442
1000		0.04645	0.05944	0.07688	0.10033	0.13205	0.17517	0.23378	0.31256	0.41475	0.53523
1100		0.04712	0.06104	0.07951	0.10423	0.13764	0.18316	0.24529	0.32918	0.43832	0.56614
1200		0.04774	0.06262	0.08214	0.10816	0.14331	0.19132	0.25711	0.34637	0.46282	0.59811
1300		0.04835	0.06421	0.08483	0.11220	0.14918	0.19982	0.26952	0.36454	0.48888	0.63201
1400		0.04896	0.06584	0.08762	0.11643	0.15536	0.20882	0.28275	0.38408	0.51711	0.66870
1500		0.04960	0.06755	0.09056	0.12091	0.16196	0.21849	0.29705	0.40536	0.54809	0.70906
1600		0.05027	0.06936	0.09370	0.12573	0.16907	0.22898	0.31267	0.42878	0.58246	0.75402
1700		0.05101	0.07130	0.09707	0.13093	0.17681	0.24045	0.32986	0.45474	0.62090	0.80460
1800		0.05181	0.07340	0.10073	0.13660	0.18529	0.25308	0.34889	0.48369	0.66416	0.86195
1900		0.05269	0.07567	0.10471	0.14281	0.19462	0.26705	0.37007	0.51613	0.71310	0.92738
2000		0.05366	0.07814	0.10906	0.14964	0.20492	0.28257	0.39372	0.55263	0.76868	1.00244

solutions can also be derived form the above solubility model:

$$\frac{\overline{V}_{CH_4(l)}}{RT} = \frac{\partial}{\partial P}\left(\frac{\mu^{l(0)}}{RT}\right)_{T,m} + \left(\frac{\partial \ln \gamma_{CH_4}}{\partial P}\right)_{T,m}$$
$$= \frac{\partial}{\partial P}\left(\frac{\mu^{l(0)}}{RT}\right)_{T,m} + \sum_c 2m_c\left(\frac{\partial \lambda_{CH_4-c}}{\partial P}\right)_{T,m}$$
$$+ \sum_a 2m_a\left(\frac{\partial \lambda_{CH_4-a}}{\partial P}\right)_{T,m}$$
$$+ \sum_c \sum_a m_c m_a\left(\frac{\partial \lambda_{CH_4-c-a}}{\partial P}\right)_{T,m} \quad (10)$$

$$k_H(T) = \frac{y_{CH_4}\varphi_{CH_4}P}{x_{CH_4}}\exp\left(\frac{-\overline{V}_{CH_4(l)}\left(P - P^s_{H_2O}\right)}{RT}\right) \quad (11)$$

$$-\frac{\Delta H^s_m}{RT^2} = \frac{\partial}{\partial T}\left(\frac{\mu^{l(0)}}{RT}\right)_{P,m} + \left(\frac{\partial \ln \gamma_{CH_4}}{\partial T}\right)_{P,m}$$
$$= \frac{\partial}{\partial T}\left(\frac{\mu^{l(0)}}{RT}\right)_{P,m} + \sum_c 2m_c\left(\frac{\partial \lambda_{CH_4-c}}{\partial T}\right)_{P,m}$$
$$+ \sum_a 2m_a\left(\frac{\partial \lambda_{CH_4-a}}{\partial T}\right)_{P,m}$$
$$+ \sum_c \sum_a m_c m_a\left(\frac{\partial \lambda_{CH_4-c-a}}{\partial T}\right)_{P,m} \quad (12)$$

$$\left(\frac{\partial Par(T,P)}{\partial P}\right)_{T,m} = c_6 + c_7 T + \frac{c_8}{T} + \frac{c_9}{T^2} + 2c_{10}PT \quad (13)$$

$$\left(\frac{\partial Par(T,P)}{\partial T}\right)_{P,m} = c_2 - \frac{c_3}{T^2} + 2c_4 T - \frac{2c_5}{T^3} + c_7 P$$
$$- \frac{c_8 P}{T^2} - \frac{2c_9 P}{T^3} + c_{10}P^2. \quad (14)$$

The predicted molar heat of solution (Table 10) and Henry's constant of CH_4 in water (Table 11) are compared with some experimental or calculated results, which exhibit a good agreement. These, from another respective, prove the reliability of this model.

5. Applications of this model

5.1. Calculating CH_4 solubility in aqueous solutions with salts other than NaCl, such as seawater and geothermal brines

This model can be extrapolated to more complex aqueous solutions containing Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, and SO$_4^{2-}$. Because of the data limitations for aqueous solutions with salts other than NaCl, it is impossible to fit directly to experimental measurements as is possible with CH_4–H_2O–NaCl system. We therefore take a theoretically predictive approach to this problem. According to Duan et al. (1992a), CH_4–monovalent–cation interaction parameters have roughly the same value, and CH_4–bivalent cation interaction parameters are about twice as much as the CH_4–monovalent interaction parameters at various temperatures and pressures. The CH_4–anion interaction parameters are relatively small

Table 9
Calculated CH_4 solubility deviations from experimental data

References	System	T (K)	P (bar)	N[a]	AAD (%)	MAD (%)
Bunsen (1855)	Water	279.35–298.75	1[+]	5	1.18	2.23
Winkler (1901)	Water	273.38–353.17	1[+]	9	7.93	18.38
Culberson et al. (1950)	Water	298.15	36.2–667.4	10	6.94	14.38
Eucken and Hertzberg (1950)	0–2.77 m NaCl	273.15–293.15	1[+]	7	5.55	10.50
Culberson and Mcketta (1951)	Water	298.2–444.3	22.3–689.1	71	2.12	7.11
Morrison and Billett (1952)	Water	285.1–348.4	1[+]	11	5.00	6.28
Claussen and Polglase (1952)	Water	274.8–312.8	1[+]	6	1.13	2.65
Lannung and Gjaldbaek (1960)	Water	291.15–310.15	1[+]	6	1.83	3.33
Duffy et al. (1961)	Water	298.15–303.15	3.17–51.71	13	3.57	10.44
Namiot (1961)	Water	273.15–283.15	1[+]	2	0.75	1.31
Mishnina et al. (1962)	0–6.24 m NaCl	277.15–363.15	1[+]	45	4.73	16.19
O'Sullivan and Smith (1970)	Water	324.65–398.15	101.3–616.1	18	4.60	15.74
	1.01–4.41 m NaCl	324.65–398.15	101.3–616.1	22	8.90	20.94
Wen and Hung (1970)	Water	278.15–308.15	1[+]	4	1.63	3.28
Amirijafari and Campbell (1972)	Water	310.93–344.26	41.4–344.7	8	2.22	5.73
Ben-Naim et al. (1973)	Water	278.15–298.15	1[+]	5	0.78	1.25
Ben-Naim and Yaacobi (1974)	Water	283.15–303.15	1[+]	5	0.83	1.34
	0.25–2.09 m NaCl	283.15–303.15	1[+]	20	2.97	5.54
Moudgil et al. (1974)	Water	298.15	1[+]	1	0.48	0.48
Yano et al. (1974)	0–1.55 m NaCl	298.15	1[+]	4	12.20	19.92
Yamamoto et al. (1976)	Water	273.91–302.70	1[+]	35	1.23	2.72
Namiot et al. (1979)	0–1.54 m NaCl	323–573	295	14	4.83	14.24
Price (1979)	Water	427–589	35.4–1924.7	53	5.53	15.22
Muccitelli and Wen (1980)	Water	278.15–298.15	1[+]	5	1.33	3.05
Cosgrove and Walkley (1981)	Water	278.15–318.15	1[+]	9	3.16	5.77
Rettich et al. (1981)	Water	275.46–328.15	1[+]	16	0.88	3.12
Blount and Price (1982)	0–5.9 m NaCl	372.15–513.15	75–1570	654	5.97	21.28
Crovetto et al. (1982)	Water	297.5–518.3	13.27–64.51	7	3.31	9.44
Stoessell and Byrne (1982b)	Water	298.15	24.1–51.7	3	0.83	1.23
	0–4.0 m NaCl	298.15	24.1–51.7	15	2.08	4.21
Cramer (1984)	Water	277.2–573.2	11–132	12	5.79	13.58
Yarym-Agaev et al. (1985)	Water	298.2–338.2	25–125	15	2.63	4.84
Yokoyama et al. (1988)	Water	298.15–323.15	30–80	6	1.62	2.86
Lekvam and Bishnoi (1997)	Water	274.19–285.68	5.67–90.82	18	5.05	10.03
Dhima et al. (1998)	Water	344	200–1000	4	2.88	5.39
Kiepe et al. (2003)	Water	313–473	3.4–93	26	5.48	10.99
Wang et al. (2003)	Water	283.2–303.2	20–400.3	17	6.11	14.44
Chapoy et al. (2004)	Water	275.11–313.11	9.7–180	16	3.45	11.99

AAD, average absolute deviations calculated from this model; MAD, maximal absolute deviations calculated from this model; 1[+] denotes that partial pressure of methane is 1 atm.

[a] N, number of data points.

and contribute little to the calculation. Using the same approach, we approximate all CH_4–monovalent cation and CH_4–bivalent cation interaction parameters as $\lambda_{CH_4–Na^+}$ and $2\lambda_{CH_4–Na^+}$, respectively. The same treatment applies to the ternary parameters. With this simplification, Eq. (8) becomes

$$\ln m_{CH_4} = \ln \left(y_{CH_4} \varphi_{CH_4} P \right) - \frac{\mu_{CH_4}^{l(0)}}{RT}$$
$$- 2\lambda_{CH_4–Na^+} \left(m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} + 2m_{Mg^{2+}} \right)$$
$$- \xi_{CH_4–Na^+–Cl^-} \left(m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} + 2m_{Mg^{2+}} \right)$$
$$\times \left(m_{Cl^-} + 2m_{SO_4^{2-}} \right) - 4\lambda_{CH_4–SO_4^{2-}} m_{SO_4^{2-}}, \quad (15)$$

where $\lambda_{CH_4–SO_4^{2-}} = 0.0332$. In order to test this approximation, we compare the calculated results from

Eq. (15) with experimental data of CH_4 solubility in aqueous $CaCl_2$, KCl, and K_2SO_4 solutions (Fig. 4), seawater and brines (Table 12). It can be seen that the agreement between this approach and the experimental measurements is excellent.

5.2. Calculating homogenization pressure of fluid inclusions with CH_4–H_2O–NaCl

Fluid inclusions provide the most direct information on the formation conditions (such as temperature, pressure, and composition) of geological bodies. Phase relations in the CH_4–H_2O–NaCl system at high temperatures have been carefully studied by Lamb et al. (2002, 1996). Dubessy et al. (2001) and Thiéry (2006) have studied the methane-bearing aqueous fluid
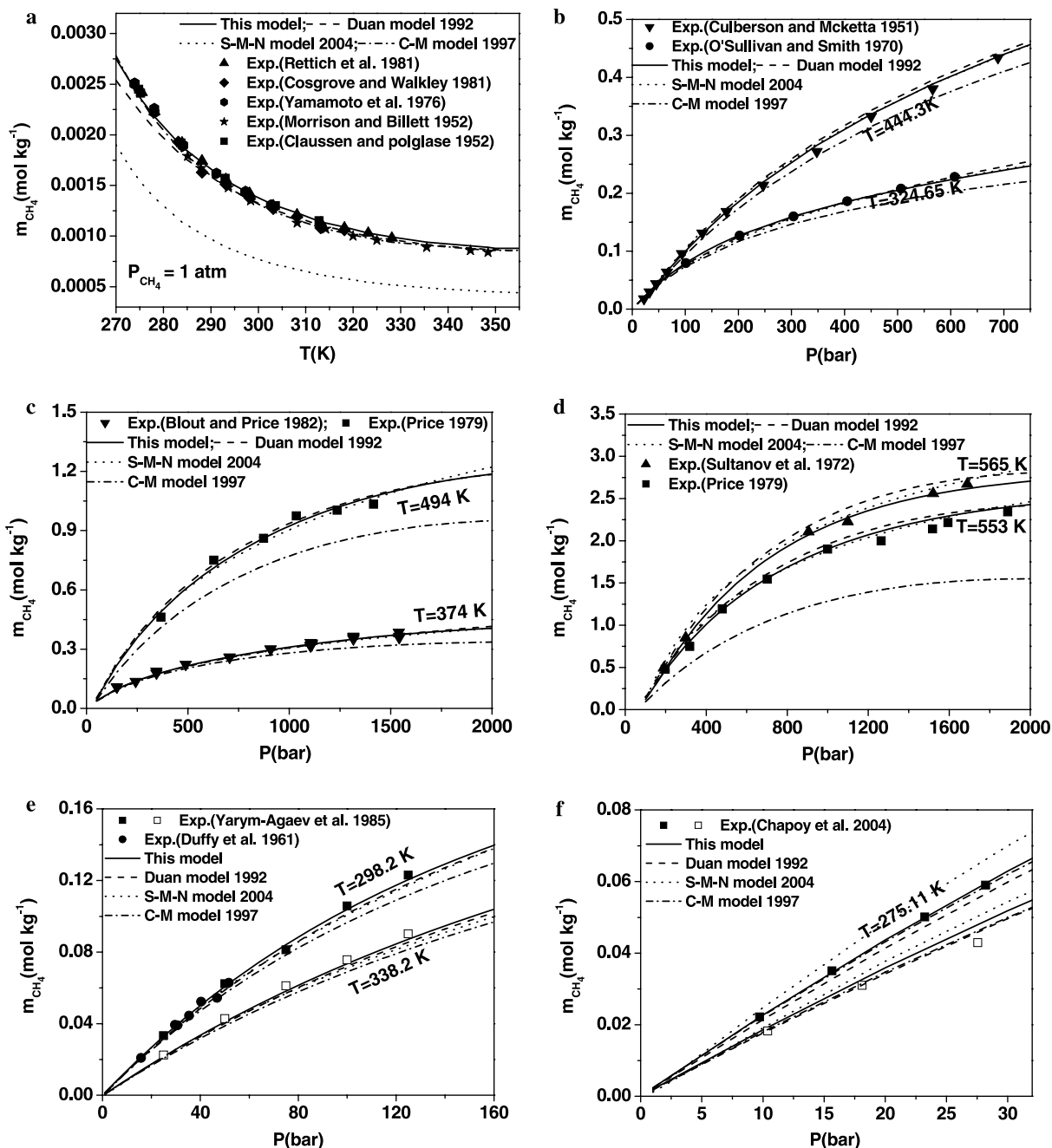
Fig. 2. CH₄ solubility in pure water (model predictions vs. experimental data).

inclusions. If the homogenization temperature and compositions of the fluid inclusions are known from microthermometric and spectroscopic techniques, the homogenization pressure of inclusions and the density at the homogenization can be determined from solubility models. Taking advantage of this approach, we calculate the trapping pressure of the quartz crystal from central alpine clefts (Table 13), using the fluid compositions in the H₂O–CH₄–NaCl system and homogenization temperatures of Mullis (1979). Mullis (1979) also calculated the trapping pressure using an alternative approach and the results are also shown in Table 13. They generally fall

within the range of pressure calculated from our model. At a given temperature, the uncertainty of pressure increases with molality of CH₄ and NaCl (Fig. 5) and the average uncertainty of pressure in the studied region is about 9.5%.

5.3. Calculating CH₄ solubility in liquid phase at gas–liquid–hydrate three phase equilibrium

CH₄ can form hydrate in pure water and aqueous NaCl solutions in the low-temperature and high-pressure region. Once the pressure of CH₄ at gas–liquid–hydrate
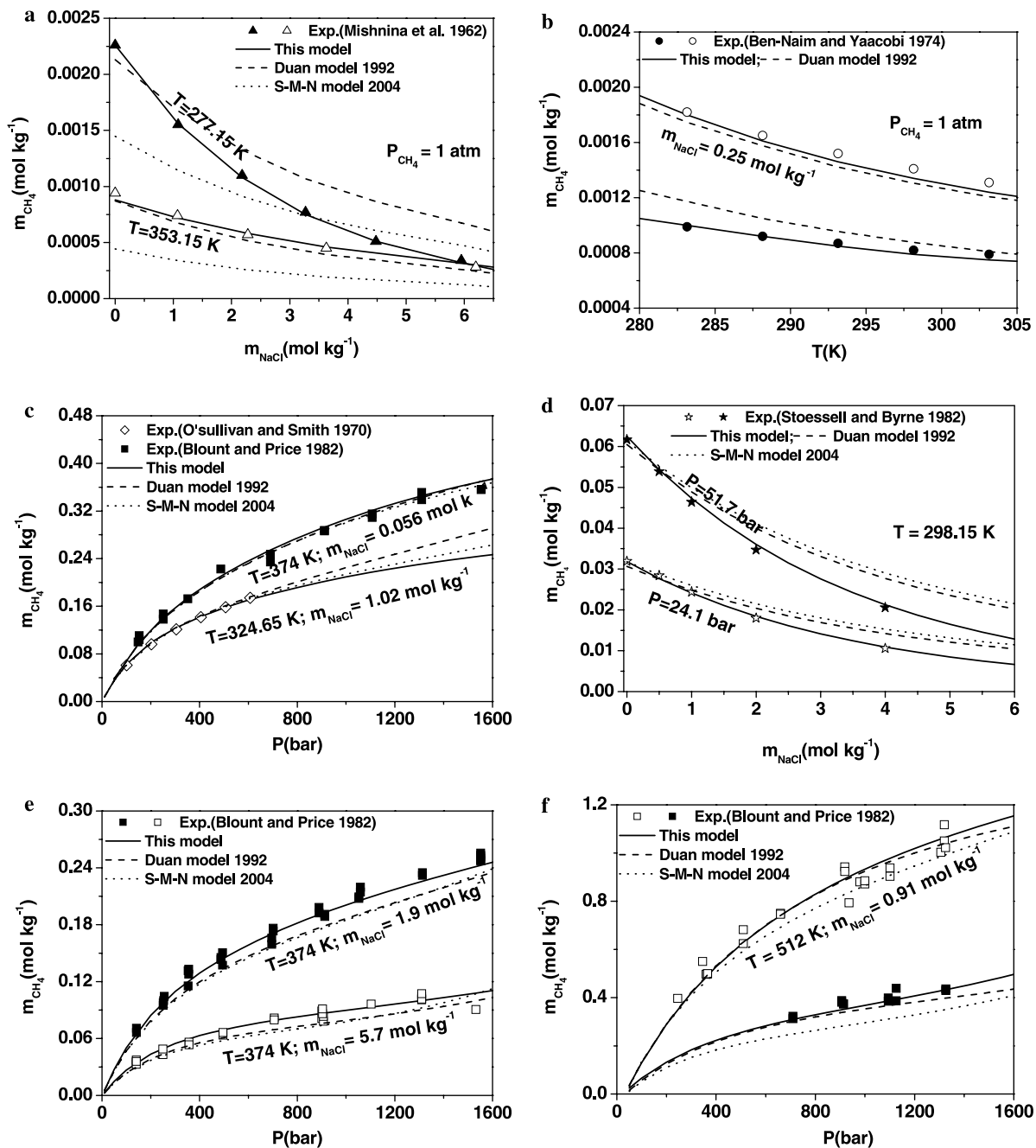
Fig. 3. CH$_4$ solubility in aqueous NaCl solutions (model predictions vs. experimental data).

equilibrium is determined for a given temperature, the CH$_4$ solubility in pure water and aqueous NaCl solutions can be calculated from this model. Recently, Sun and Duan (2005) developed a model that can predict the CH$_4$–hydrate and CO$_2$–hydrate formation pressure for a given temperature. With the temperature and pressure from the Sun and Duan (2005) model, we calculate the CH$_4$ solubility in pure water at gas–liquid–hydrate equilibrium (273.15–314.15 K and 26–2185 bar) (see Table 14).

5.4. Calculating liquid phase density of CH$_4$–H$_2$O–NaCl system at equilibrium

Liquid phase density of CH$_4$–H$_2$O–NaCl system at equilibrium can also be calculated from this model. In order to calculate the density of liquids in the CH$_4$–H$_2$O–NaCl system, an accurate density model for H$_2$O–NaCl system is required. There are two good density models for the H$_2$O–NaCl system covering a large T–P–m range. One was developed by Spivey et al. (2004) with valid T–P–m

Table 10
Molar heat of solution of CH$_4$ in water

T (K)	P (bar)	$-\Delta H_m^s$ (kJ mol^{-1})			
		a	b	c	d
288.15	1	15.45	15.53	15.60	14.56
298.15	1	13.18	13.06	13.19	12.64
308.15	1	11.09	10.70	10.87	10.75
313.15	1			9.75	9.82
323.15	1			7.59	7.97
333.15	1			5.54	6.15

a, Dec and Gill (1984, 1985); b, Olofsson et al. (1984); c, Rettich et al. (1981); d. This study.

Table 11
Henry's constants (k_H) of CH$_4$ in water

T (K)	k_{H1} (bar)	k_{H2} (bar)
273	22110	22804
298	38741	39381
300	40064	40690
350	62998	63016
400	59911	60169
450	42390	44294
500	24824	28128

k_{H1}, calculated from this model; k_{H2}, from Fernandez-Prini et al. (2003).

region (273–548 K, 1–2000 bar and 0–6 mol kg^{-1}). Another was presented by Rogers and Pitzer (1982) with a valid $T–P–m$ range (273–573 K, 1–1000 bar and 0–6 mol kg^{-1}). Here, we present a simple but reliable approach to calculate the liquid phase density of CH$_4$–H$_2$O–NaCl system at phase equilibrium:

$$m_{sol} = 1000 + m_{NaCl}M_{NaCl} + m_{CH_4}M_{CH_4}, \quad (16)$$

$$V_{sol} = \frac{1000 + m_{NaCl}M_{NaCl}}{\rho_{H_2O-NaCl}} + m_{CH_4}\overline{V}_{CH_4(l)}, \quad (17)$$

$$\rho_{sol} = \frac{m_{sol}}{V_{sol}}, \quad (18)$$

where the partial molar volume of CH$_4$, $\overline{V}_{CH_4(l)}$, can be obtained from Eqs. (10) and (13), the molar mass of NaCl $M_{NaCl} = 58.4428$ g mol^{-1} and the molar mass of CH$_4$ $M_{CH_4} = 16.042$ g mol^{-1}. $\rho_{H_2O-NaCl}$ is the liquid phase density of the H$_2$O–NaCl system, either calculated from the Spivey model or from Roger-Pitzer model. The calculated liquid phase density of CH$_4$–H$_2$O–NaCl system at phase equilibrium based on Roger-Pizer model and the Spivey model is compiled in Table 15. It can be seen that the calculated results by using two different density models of the H$_2$O–NaCl system are very close in the $T–P–m$ region where the studies overlap.
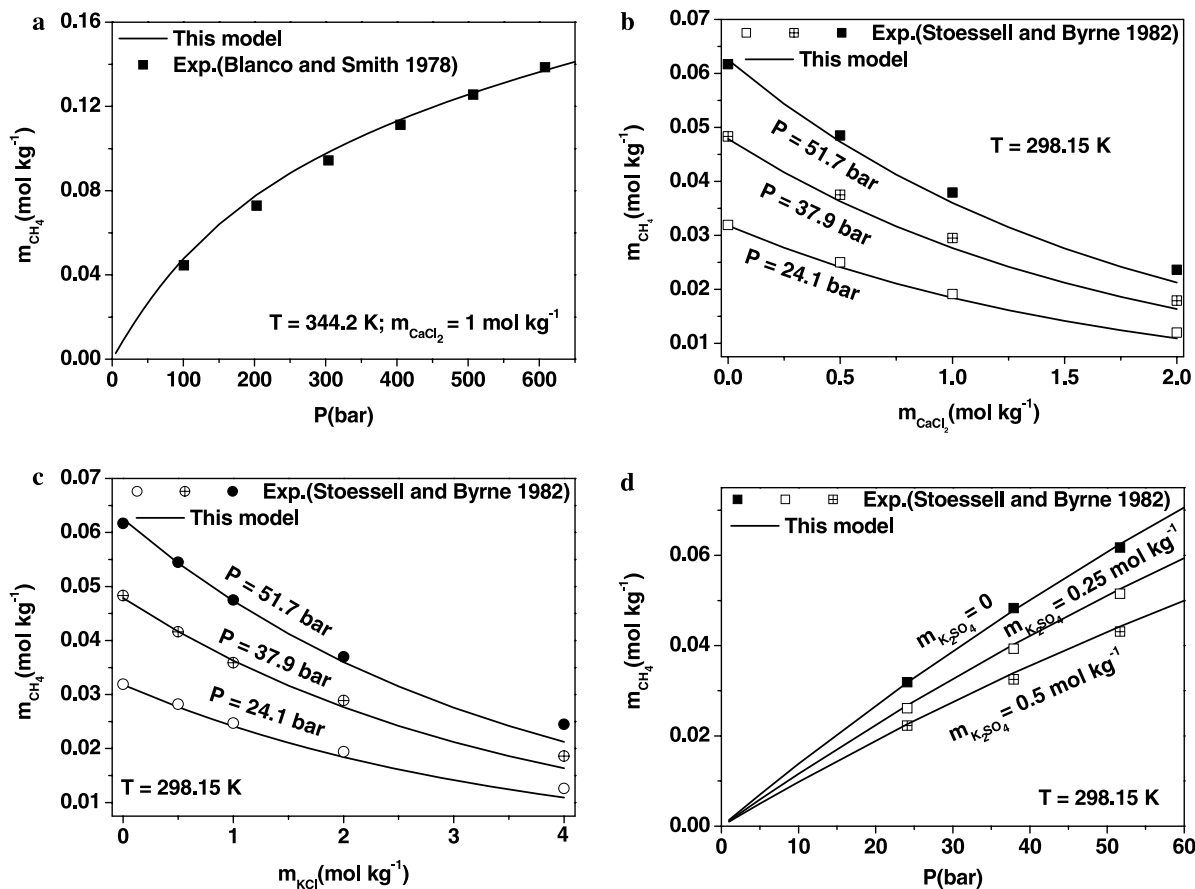

Fig. 4. CH$_4$ solubility predictions in aqueous CaCl$_2$, KCl and K$_2$SO$_4$ solutions (a–b is for CaCl$_2$(aq) solution, c is for KCl(aq) solution and d is for K$_2$SO$_4$(aq) solution).

Table 12
Solubility of CH_4 in seawater and Salton Sea geothermal brine

Solutions	T (K)	P (bar)	m_{CH_4} (exp) (mol kg^{-1})	m_{CH_4} (cal) (mol kg^{-1})
Seawater (Stoessell and Byrne, 1982b)	298.15	24.1	0.0263	0.02665
	298.15	37.9	0.0400	0.04008
	298.15	51.7	0.0514	0.05228
Salton Sea geothermal brine (Cramer, 1984)	277.65	26	0.01276	0.01047
	285.65	27	0.01261	0.01002
	289.15	27	0.01288	0.00974
	318.45	11	0.00388	0.00364
	333.35	11	0.00393	0.00356
	361.25	11	0.00373	0.00361
	394.85	11	0.00354	0.00375
	439.95	27	0.00812	0.01117
	477.45	53	0.01886	0.02720
	506.15	64	0.02733	0.03604
	541.15	105	0.06163	0.07323

Note. m_{CH_4} (exp) and m_{CH_4} cal denote experimental and calculated CH_4 solubility data from this model, respectively.

Table 13
The formation pressure of the 'Fadenquartz' in Central Alps

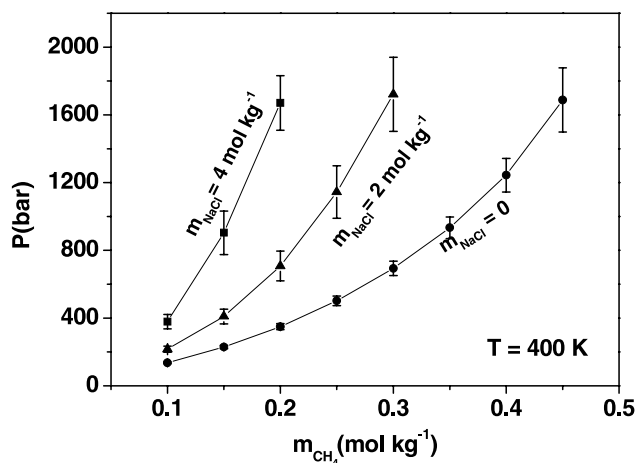| Locality	T (K)	x_{CH_4}	Formation pressure (bar)	
			This study	Mullis (1979)
Val d'lliez	522.15	0.022–0.030	915–2267	1570
Choex	515.15	0.017–0.023	674–1205	1370
Les Monte	514.15	0.016–0.022	624–1120	1120
Metholz	503.15	0.014–0.020	621–1223	1090
Jour De Duin	517.15	0.013–0.017	439–649	810

Fig. 5. The uncertainty of pressure vs. molality of CH_4 at a given temperature.

6. Conclusions

Based on a simple fugacity coefficient equation used to predict gas phase water content, and a highly accurate

Table 14
CH_4 solubility in pure water at CH_4 hydrate–liquid water–gas equilibrium

T (K)	P_{eq} (bar)	m_{CH_4} (mol kg^{-1})
273.15	26.17	0.05876
274.15	28.81	0.06229
275.15	31.73	0.06604
276.15	34.97	0.07003
277.15	38.56	0.07424
278.15	42.55	0.07871
279.15	47.00	0.08345
280.15	51.97	0.08846
281.15	57.54	0.09377
282.15	63.80	0.09937
283.15	70.87	0.10530
284.15	78.88	0.11154
285.15	88.01	0.11812
286.15	98.48	0.12504
287.15	110.53	0.13229
288.15	124.48	0.13986
289.15	140.71	0.14775
290.15	159.63	0.15592
291.15	181.69	0.16435
292.15	207.33	0.17300
293.15	236.97	0.18183
294.15	270.97	0.19081
295.15	309.57	0.19990
296.15	353.00	0.20907
297.15	401.36	0.21829
298.15	454.72	0.22755
299.15	513.20	0.23682
300.15	576.84	0.24609
301.15	645.81	0.25533
302.15	720.24	0.26453
303.15	800.31	0.27363
304.15	886.29	0.28262
305.15	978.54	0.29146
306.15	1077.35	0.30008
307.15	1183.27	0.30845
308.15	1296.74	0.31648
309.15	1418.56	0.32410
310.15	1549.39	0.33121
311.15	1690.25	0.33770
312.15	1842.33	0.34397
313.15	2006.92	0.34824
314.15	2185.40	0.35193

P_{eq}, equilibrium pressure for the CH_4 hydrate–liquid water–gas assemblage.

EOS (Duan et al., 1992b) for gas phase, and the electrolyte solution theory of Pitzer (1973) for liquid phase, an accurate model is presented here to calculate CH_4 solubility in pure water and aqueous NaCl solutions, gas phase compositions and liquid phase density with experimental accuracy from 273 to 523 K (possibly to 573 K), from 1 to 2000 bar and up to high salt concentrations (0–6 mol kg^{-1} of NaCl). With a simple approach, this model is extrapolated to predict the CH_4 solubility in other aqueous solutions containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} like seawater and geothermal brines with remarkable accuracy. In addition, this model can be used to calculate the homogenization pressure of fluid

Table 15
Calculated liquid phase density of CH_4–H_2O–NaCl system from this model at equilibrium

T (K)	P (bar)	m_{NaCl} (mol kg^{-1})	m_{CH_4} mol kg^{-1}	Method 1		Method 2	
				$\rho_{H_2O–NaCl}$ (g cm^{-3})	$\rho_{CH_4–H_2O–NaCl}$ (g cm^{-3})	$\rho_{H_2O–NaCl}$ (g cm^{-3})	$\rho_{CH_4–H_2O–NaCl}$ (g cm^{-3})
273.15	1	0	0.00247	0.99988	0.99982	0.99892	0.99886
	5	1	0.00873	1.04238	1.04214	1.04378	1.04353
	10	2	0.01228	1.08075	1.08036	1.08442	1.08403
	20	4	0.01231	1.14877	1.14831	1.15322	1.15276
	25	6	0.00806	1.20744	1.20710	1.20556	1.20521
323.15	10	0	0.00995	0.98843	0.98822	0.98866	0.98845
	100	1	0.06300	1.02998	1.02845	1.03060	1.02907
	500	2	0.12185	1.07955	1.07627	1.08146	1.07816
	1000	4	0.09203	1.15727	1.15460	1.16551	1.16279
	2000	6	0.06938	1.23796	1.23643		
373.15	10	0	0.00757	0.95879	0.95864	0.95809	0.95794
	100	1	0.05890	1.00041	0.99903	1.00001	0.99862
	500	2	0.14138	1.05065	1.04697	1.05196	1.04826
	1000	4	0.12652	1.12875	1.12530	1.13716	1.13364
	2000	6	0.12131	1.21014	1.20809		
423.15	100	0	0.08700	0.92231	0.92057	0.92149	0.91975
	100	1	0.07341	0.96154	0.95980	0.96108	0.95933
	500	2	0.20102	1.01540	1.01012	1.01723	1.01192
	1000	4	0.19183	1.09667	1.09152	1.10615	1.10090
	2000	6	0.20492	1.18069	1.17802		
473.15	100	0	0.12192	0.87091	0.86853	0.87055	0.86817
	100	1	0.10281	0.91395	0.91153	0.91369	0.91129
	500	2	0.32295	0.97456	0.96609	0.97653	0.96800
	1000	4	0.31199	1.06161	1.05341	1.07124	1.06285
	2000	6	0.35210	1.15004	1.14684		
523.15	100	0	0.15399	0.80574	0.80301	0.80677	0.80404
	100	1	0.13135	0.85615	0.85325	0.85496	0.85208
	500	2	0.55132	0.92829	0.91437	0.92801	0.91411
	1000	4	0.52769	1.02388	1.01070	1.03119	1.01777
	2000	6	0.61843	1.11781	1.11503		

Note. m_{CH_4} is the calculated solubility data from this model; Method 1, $\rho_{H_2O–NaCl}$ from Spivey et al. (2004) (273–548 K and 1–2000 bar); Method 2, ρ_{H_2O} calculated from Duan et al. (1992b) and $\rho_{H_2O–NaCl}$ from Rogers and Pitzer (1982) (273–573 K and saturation pressure $\leqslant P \leqslant 1000$ bar); $\rho_{CH_4–H_2O–NaCl}$ denotes liquid phase density of CH_4–H_2O–NaCl system at equilibrium.

inclusions (CH_4–H_2O–NaCl), to predict CH_4 solubility in liquid phase at gas–liquid–hydrate equilibria and the liquid phase density of CH_4–H_2O–NaCl system at phase equilibria. A FORTRAN code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.

Appendix A

The equation of state for CH_4

$$Z = \frac{P_r V_r}{T_r}$$

$$= 1 + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r} + \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{V_r^2}$$

$$+ \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{V_r^4} + \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{V_r^5}$$

$$+ \frac{a_{13}}{T_r^3 V_r^2}\left(a_{14} + \frac{a_{15}}{V_r^2}\right)\exp\left(-\frac{a_{15}}{V_r^2}\right) \tag{A1}$$

$$P_r = \frac{P}{P_c}; \qquad T_r = \frac{T}{T_c}, \tag{A2}$$

$$V_r = \frac{V}{V_c}; \qquad V_c = \frac{RT_c}{P_c}, \tag{A3}$$

where P_c and T_c are critical pressure and critical temperature, respectively; R is universal gas constant $(83.14472 \text{ bar cm}^3 \text{ K}^{-1} \text{ mol}^{-1})$; V is molar volume. Note that V_c is not the real critical volume. The parameters of the EOS are referred to Duan et al. (1992b). The critical properties of CH_4 are: $T_c = 190.6$ K; $P_c = 46.41$ bar. The fugacity coefficient of CH_4 can be derived from Eq. (A1):

$$
\begin{aligned}
\ln \varphi(T, P) = {} & Z - 1 - \ln Z + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r} \\
& + \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{2V_r^2} \\
& + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{4V_r^4} \\
& + \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{5V_r^5} + \frac{a_{13}}{2T_r^3 a_{15}} \\
& \times \left[a_{14} + 1 - \left(a_{14} + 1 + \frac{a_{15}}{V_r^2} \right) \times \exp\left(-\frac{a_{15}}{V_r^2} \right) \right].
\end{aligned}
$$
(A4)

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