Available online at www.sciencedirect.com

ScienceDirect

Fluid Phase Equilibria 248 (2006) 103–114

FLUID PHASE EQUILIBRIA

www.elsevier.com/locate/fluid

A thermodynamic model for calculating nitrogen solubility, gas phase composition and density of the N_2–H_2O–NaCl system

Shide Mao, Zhenhao Duan*

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

Received 19 April 2006; received in revised form 28 July 2006; accepted 29 July 2006
Available online 3 August 2006

Abstract

A thermodynamic model is presented to calculate N_2 solubility in pure water (273–590 K and 1–600 bar) and aqueous NaCl solutions (273–400 K, 1–600 bar and 0–6 mol kg^{-1}) with or close to experimental accuracy. This model is based on a semi-empirical equation used to calculate gas phase composition of the H_2O–N_2 system and a specific particle interaction theory for liquid phase. With the parameters evaluated from N_2–H_2O–NaCl system and using a simple approach, the model is extended to predict the N_2 solubility in seawater accurately. Liquid phase density of N_2–H_2O–NaCl system at phase equilibrium and the homogenization pressure of fluid inclusions containing N_2–H_2O–NaCl can be calculated from this model. A computer code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.

Keywords: N_2 solubility; Gas phase composition; Density; Water; Aqueous NaCl solutions

1. Introduction

N_2, one of the important natural gases, has been found in gas hydrate, oil fields and fluid inclusions. Accurate prediction of N_2 solubility in pure water, seawater and aqueous NaCl solutions over a wide range of temperature, pressure and ionic strength, especially where experimental data do not exist or where experimental data are of poor quality, is important for the geochemical and chemical engineering applications. There have been many experimental studies of the solubility of N_2 in pure water and some experimental studies in aqueous NaCl solutions. However, these data are very scattered and cover only a limited temperature–pressure space, which is inconvenient to use. Therefore, theorists have devoted extensive efforts to the modeling of N_2 solubility in aqueous solutions in order to interpolate between the data points or extrapolate beyond the data range [1–5]. However, all of the published models are found to possess intolerable deficiencies, which lead to the motivation of this study.

Battino et al. [5] developed a semi-empirical equation to predict N_2 solubility in water (350–590 K and 1–1000 bar) and claimed that the standard deviation is 5.6%. However, comparison with reliable experimental data [2,6,7] indicates that the average deviation is over 20% in the temperature range from 273 to 350 K and at 582.8 K. Li and Nghiem [4] (LN model) studied the phase equilibrium of oil, gas and water/brine mixtures from a cubic equation of state, but the model is not reliable because they confused the molality with molarity of NaCl, which causes about 10% concentration deviation for a 4 mol NaCl solution at 324.65 K between 100 and 600 bar. Overall the LN model has an average error increases from 6.77% in pure water to 12.94% in aqueous NaCl solutions in comparison with their fitting data [8]. Soreide and Whitson [3] developed a model (SW model) to calculate N_2 solubility in pure water and aqueous NaCl solutions, ranging from 298 to 400 K and from 14 to 1035 bar. In the temperature range between 298 and 323 K, the model can only predict N_2 solubility below 300 bar within experimental uncertainty and cause about 10% errors on average above 300 bar compared with their fitting data [6]. Using an equation of state [9] and Pitzer theory [10], Sun et al. [1] presented a model (SHD model) to predict the solubility of nitrogen in pure water (273–623 K and 0–600 bar) and aqueous NaCl solutions (0–4 M, 273–400 K and 0–600 bar). The model has two deficiencies: (1) the average deviation is over 10% at 298–323 K for pressures below 1000 bar as compared with their fitting data [6], and (2) the model cannot predict the solubility of N_2 in aqueous NaCl solu-

---

* Corresponding author. Tel.: +86 858 822 0281; fax: +86 858 484 3899.
E-mail address: duanzhenhao@yahoo.com (Z. Duan).

0378-3812/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2006.07.020

tions at low pressures. For example, the average deviation from experimental data [11] is about 10% between 283 and 343 K. It should be noted that the SW model and SHD model confused the molality with molarity of NaCl as the LN model did. Chapoy et al. [2] modeled the gas–liquid equilibrium of N_2–H_2O system (273–373 K and pressure up to 100 bar) by using a modified Patel–Teja equation of state and density-independent mixing rules. The calculated results are in agreement with experimental data in the small temperature–pressure range.

Trying to overcome the deficiencies of the previous models, we in this article present an improved model to calculate N_2 solubility in pure water (273–590 K and 1–600 bar) and aqueous NaCl solutions (273–400 K, 1–600 bar and 0–6 mol kg^{-1}), liquid phase density at equilibrium and gas phase composition of the H_2O–N_2–NaCl system by improving the theoretical approach and using updated experimental data. 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 N_2 solubility in other complicated systems like seawater, to calculate liquid phase density of the N_2–H_2O–NaCl system at phase equilibrium, and to evaluate homogenization pressure of fluid inclusions containing N_2–H_2O–NaCl.

2. Thermodynamic model

N_2 solubility in aqueous solutions depends on the balance between the chemical potential of N_2 in the liquid phase $\mu^{l}_{N_2}$ and that in the vapor phase $\mu^{v}_{N_2}$. The potential can be written in terms of fugacity in vapor phase and activity in the liquid phase:

$$\begin{aligned}\mu^{v}_{N_2}(T,P,y) &= \mu^{v(0)}_{N_2}(T) + RT\ln f_{N_2}(T,P,y)\\ &= \mu^{v(0)}_{N_2}(T) + RT\ln y_{N_2}P + RT\ln\varphi_{N_2}(T,P,y_{N_2})\end{aligned} \tag{1}$$

$$\begin{aligned}\mu^{l}_{N_2}(T,P,m) &= \mu^{l(0)}_{N_2}(T,P) + RT\ln a_{N_2}(T,P,m)\\ &= \mu^{l(0)}_{N_2}(T,P) + RT\ln m_{N_2} + RT\ln\gamma_{N_2}(T,P,m)\end{aligned} \tag{2}$$

where $\mu^{l(0)}_{N_2}$, the standard chemical potential of N_2 in liquid, is defined as the chemical potential in hypothetically ideal solution of unit molality [12] and $\mu^{v(0)}_{N_2}$, the standard chemical potential in vapor, is the hypothetical ideal gas chemical potential when the pressure is set to 1 bar.

At phase equilibrium $\mu^{l}_{N_2} = \mu^{v}_{N_2}$, and we obtain

$$\ln\frac{y_{N_2}P}{m_{N_2}} = \frac{\mu^{l(0)}_{N_2}(T,P) - \mu^{v(0)}_{N_2}(T)}{RT} - \ln\varphi_{N_2}(T,P,y) + \ln\gamma_{N_2}(T,P,m) \tag{3}$$

Table 1
Parameters of Eq. (5)

Parameters	Values
a_1	1.86357885E−03
a_2	1.17332094E−02
a_3	7.82682497E−07
a_4	−1.15662779E−05
a_5	−3.13619739E00
a_6	−1.29464029E−03

In the parameterization, the reference value $\mu^{v(0)}_{N_2}$ can be set to 0 for convenience, because only the difference between $\mu^{l(0)}_{N_2}$ and $\mu^{v(0)}_{N_2}$ is important. Since there is little water in the vapor phase, the fugacity coefficient of N_2 in gaseous mixtures differs little from that of pure N_2 in the studied region. Therefore, $\ln\varphi_{N_2}$ can be approximated from the EOS of pure N_2 [9] (see Appendix). y_{N_2}, the mole fraction of N_2 in the gas phase, is calculated using the following equation:

$$y_{H_2O} = \frac{\gamma_{H_2O}x_{H_2O}P^{S}_{H_2O}}{\varphi_{H_2O}P}\exp\left(\frac{v^{l}_{H_2O}(P - P^{S}_{H_2O})}{RT}\right) \tag{4}$$

where γ_{H_2O} is the activity coefficient of liquid phase H_2O and is approximated as 1 because dissolved N_2 is small and has little effect on the activity coefficient of H_2O; the same treatment is to x_{H_2O}, the mole fraction of H_2O in the liquid phase, which is approximated as 1 for the N_2–H_2O system and $1 - 2x_{NaCl}$ for the N_2–H_2O–NaCl system; $P^{S}_{H_2O}$, the saturation pressure (bar) of water, is calculated from the recent correlation of Shibue [13]; $v^{l}_{H_2O}$, molar volume of liquid water (cm^3/mol), approximates saturated liquid phase volume of water and is calculated from the equation of Wagner and Pruss [14].

The only remaining parameter of Eq. (4) 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 semi-empirical equation:

$$\varphi_{H_2O} = \exp\left(a_1 + a_2P + a_3P^2 + a_4PT + \frac{a_5P}{T} + \frac{a_6P^2}{T}\right) \tag{5}$$

where a_1–a_6 (Table 1) are obtained by regressing the water content data in the gas phase for the N_2–H_2O system [15–19]. The water content in the gas phase can be accurately calculated by Eqs. (4) and (5), as shown by Fig. 1.

$\ln\gamma_{N_2}$ is expressed as a virial expansion of excess Gibbs energy [10]

$$\ln\gamma_{N_2} = \sum_{c}2\lambda_{N_2-c}m_c + \sum_{a}2\lambda_{N_2-a}m_a + \sum_{c}\sum_{a}\xi_{N_2-a-c}m_cm_a \tag{6}$$

where λ and ξ are second-order and third-order interaction parameters, respectively; c and a refer to cation and anion, respectively. Substituting Eq. (6) into Eq. (3) yields

$$\ln\frac{y_{N_2}P}{m_{N_2}} = \frac{\mu^{l(0)}_{N_2}}{RT} - \ln\varphi_{N_2} + \sum_{c}2\lambda_{N_2-c}m_c + \sum_{a}2\lambda_{N_2-a}m_a + \sum_{c}\sum_{a}\xi_{N_2-c-a}m_cm_a \tag{7}$$

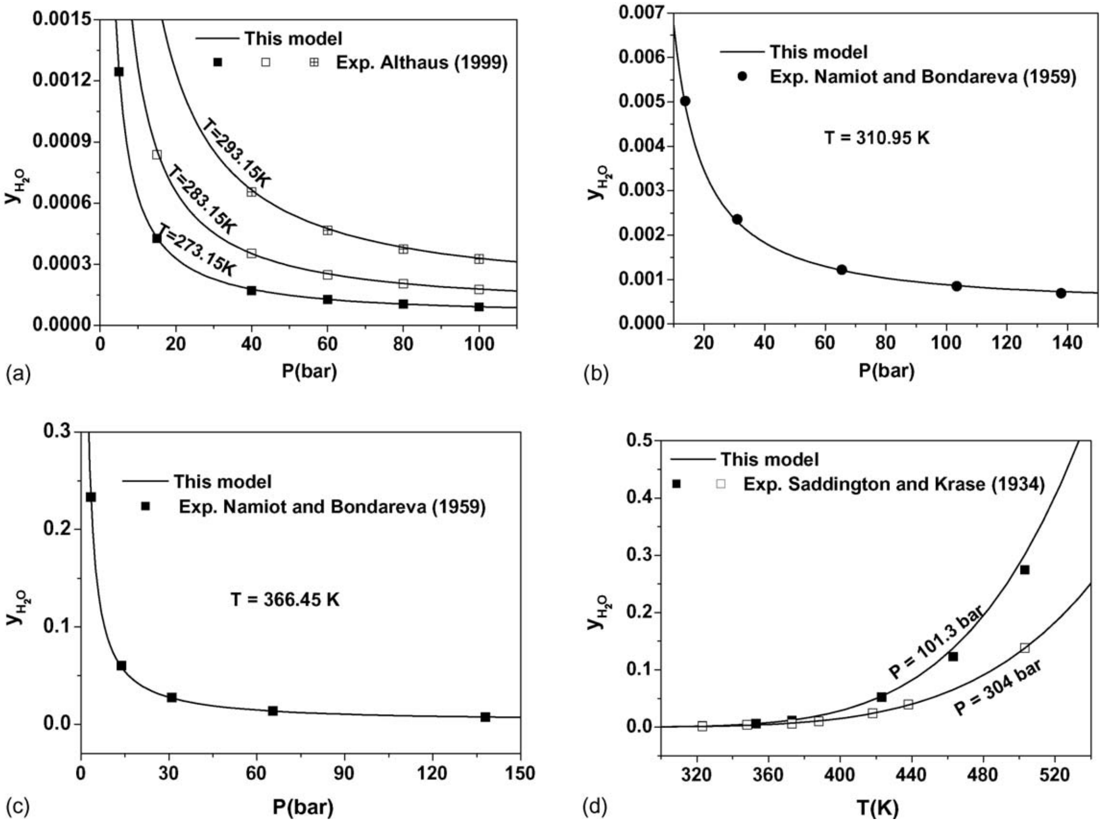

Fig. 1. Water content in the gas phase of the N_2–H_2O system.

Following Pitzer et al. [20], we choose the following equation for the *P*–*T* dependence of λ, ξ' and $\mu^{1(0)}_{N_2}/RT$:

$$\text{Par}(T, P) = c_1 + c_2T + \frac{c_3}{T} + c_4T^2 + \frac{c_5}{T^2} + c_6P + c_7PT + \frac{c_8P}{T} + \frac{c_9P^2}{T} \qquad (8)$$

Eqs. (7) and (8) form the basis of our model parameterization.

3. Review of the N_2 solubility data

The solubility of N_2 in pure water and aqueous NaCl solutions has been measured over a wide *P*–*T*–*m* range. The measurements of N_2 solubility and precision of every data set before 1981 can be seen from reference [21]. After 1981, the measurements of N_2 solubility in water included references [2,7,22,23] (Table 2). Rettich et al. [24] measured Henry's law constant of N_2 in water. Recently, Emerson et al. [25], Hamme and Emerson [26] measured the solubility of nitrogen in water and seawater using mass spectrometry methods, and the experimental results are reported as gas ratios, which are not listed in Table 2.

The measurements of N_2 solubility in water are extensive. We find that most of the data sets are consistent with each other except for those reports [27,28], whose solubility data deviate obviously from others' data sets by over 10%. Above 590 K, only a few data points exist. Experimental data at low pressures with high precision (standard deviation less than 2%) are reported by references [29–37], and at high pressures experimental data with high precision are those as reported in [2,6,8,22,38,39]. Therefore, all the experimental solubility data but those of Goodman and Krase [27] and Pray et al. [28] listed in Table 2 are used in the parameterization. The optimal *T*–*P* range of this model for N_2–H_2O system is 273–590 K and 1–600 bar. The Henry's law constants of Rettich et al. [24] are not used for parameterization, but instead used as a test of the model prediction.

Experimental N_2 solubility data in aqueous NaCl solutions are not as extensive as those in water. The data of Smith et al. [40] are scattered. The data of Braun [41] between 293.2 and 298.2 K at 1 atm is inconsistent with other data sets. So all the data points but those of Smith et al. [40] and Braun [41] above 293.2 K are included in the parameterization with the same weight, covering the *T*–*P*–*m* range (273–400 K, 1–600 bar and 0–6 mol kg^{-1}) for the N_2–H_2O–NaCl system.

4. Parameterization and comparison with experimental data

Since measurements can only be made in electronically neutral solutions, one of the parameters in Eq. (7) must be assigned arbitrarily. λ_{N_2-Cl} is set to zero and then the remaining parameters are fit to the experimental solubility data selected above, where $\mu^{1(0)}_{N_2}/RT$ is evaluated from the N_2 solubility data in pure water with a standard deviation of 2.96%; λ_{N_2-Na} and $\xi_{N_2-Na-Cl}$ are then evaluated simultaneously to the solubility measurements in aqueous NaCl solutions with a standard deviation of 3.85%. The optimized parameters are listed in Table 3.

Table 2
Experimental data for N_2 solubility in aqueous solutions

References	Solution	T (K)	P (bar)	N^a
Winkler [48]	Water	273.23–353.14	1^+	9
Braun [41]	0–2 m NaCl	278.2–298.2	1^+	65
Hufner [35]	Water	293.33	1^+	1
Fox [33]	Water	273.68–325.16	1^+	24
Bohr [32]	Water	294.35	1^+	1
Muller [49]	Water	289.35–290.35	1^+	2
Adeney and Becker [50]	Water	276.7–308.3	1^+	7
Goodman and Krase [27]	Water	273.15–442.15	101.3–303.9	28
Wiebe et al. [38]	Water	298.15	25.33–1013.25	7
Wiebe et al. [6]	Water	298.15–373.15	25.33–1013.25	32
Saddington and Krase [19]	Water	338.15–513.15	101.3–304	18
VansSlyke et al. [51]	0–0.16 m NaCl	298.15–311.15	1^+	14
Hawkins and Shilling [34]	Water	311.15	1^+	1
Morrison and Billett [31]	Water	285.65–345.65	1^+	12
Pray et al. [28]	Water	533.1–588.7	57.2–140.8	5
Eichelberger [52]	Water	338	70.88–203.25	6
Mishnina et al. [11]	0–6.3 m NaCl	283.15–343.15	1^+	156
Smith et al. [40]	0–6.2 m NaCl	303.15	11–72.6	57
Farhi et al. [29]	Water	276.25–310.2	1^+	6
Klots and Benson[30]	Water	275.01–300.16	1^+	33
Douglas [53]	Water	276.25–302.65	1^+	5
O'Sullivan and Smith [39]	0–1 m NaCl	324.65–375.65	101.3–607.9	18
Murray et al. [37]	Water	273.73–303.86	1^+	10
O'Sullivan and Smith [8]	0–4.6 m NaCl	324.65–398.15	101.3–616.1	50
Power and Stegall [54]	Water	310.15	1^+	1
Wilcock and Battino [55]	Water	298.15	1^+	2
Cosgrove and Walkley [56]	Water	278.15–313.15	1^+	8
Alvarez et al. [22]	Water	336.3–636.5	5.34–256	31
Kennan and Pollack [23]	Water	298.15	45.17–117.37	7
Alvarez and Fernandez-Prini [7]	Water	582.8–612.7	172.2–545.4	12
Chapoy et al. [2]	Water	274.19–363.02	9.71–70.43	52

Note: "1^+" denotes that partial pressure of nitrogen is 1 atm.

[a] N: number of measurements.

With these parameters, the N_2 solubility in pure water (Table 4) and aqueous NaCl solutions (Tables 5–7) can be calculated. It should be noted that the lower left blank region of Tables 4–7 is the N_2-hydrate region where there is no vapor–liquid equilibria and the upper right blank region of Tables 4–7 is due to total pressure below vapor pressure of the solutions. Table 8 shows the deviation of our model from each data set for the N_2 solubility in water and aqueous NaCl solutions. Other competitive models (SWD, SW, and LN model) are also compared with experimental data. Figs. 2 and 3 show the comparisons between the experimental results and the model predictions.

Fig. 2a–f shows the experimental N_2 solubility in water compared with the competitive models. It can be seen that this model is better than other previous models. SWD model and SW model cannot be applied in the region (298.15–323.15 K and 300–1000 bar) (Fig. 2c and d). From Fig. 2f, it can be seen that both SWD model and SW model deviate largely from the experimental data [7] at 582.8 K. From Fig. 3a–f, we can see that the present model is much more accurate than other mod-

Table 3
Interaction parameters for Eq. (7)

T–P coefficient	$\mu_{N_2}^{l(0)}/RT$	λ_{N_2-Na}	$\xi_{N_2-Na-Cl}$
C_1	−0.23093813E+02	−0.24434074E+01	−0.58071053E−02
C_2	0.56048525E−01	0.36351795E−02	
C_3	0.98808898E+04	0.44747364E+03	
C_4	−0.51091621E−04		
C_5	−0.13220298E+07		
C_6	−0.49542866E−03	−0.13711527E−04	
C_7	0.12698747E−05		
C_8	0.51411144E+00		
C_9	−0.64733978E−04	0.71037217E−05	

Table 4
Calculated N_2 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	0.001042	0.000578	0.000378	0.000134							
10	0.010275	0.005923	0.004575	0.004132	0.003867	0.003024					
50	0.047332	0.027874	0.022079	0.020985	0.022326	0.025285	0.028988	0.031016	0.023927		
100	0.085979	0.051729	0.041631	0.040160	0.043595	0.051150	0.062889	0.078466	0.094482	0.096686	0.036187
150	0.118105	0.072390	0.059029	0.057539	0.063111	0.075071	0.094386	0.122628	0.160087	0.199563	0.205717
200		0.090563	0.074675	0.073406	0.081111	0.097275	0.123717	0.163773	0.221074	0.294705	0.361085
250		0.106830	0.088908	0.088009	0.097805	0.117962	0.151091	0.202137	0.277729	0.382458	0.502688
300		0.121644	0.102011	0.101561	0.113377	0.137309	0.176695	0.237929	0.330290	0.463089	0.630759
350		0.135353	0.114213	0.114239	0.127987	0.155472	0.200690	0.271323	0.378943	0.536772	0.745349
400		0.148219	0.125696	0.126193	0.141768	0.172580	0.223209	0.302456	0.423817	0.603576	0.846292
450		0.160443	0.136606	0.137544	0.154832	0.188742	0.244358	0.331426	0.464976	0.663449	0.933170
500		0.172177	0.147056	0.148390	0.167268	0.204042	0.264211	0.358282	0.502403	0.716188	1.005256
550		0.183537	0.157137	0.158806	0.179144	0.218535	0.282807	0.383022	0.535989	0.761416	1.061450
600		0.194616	0.166918	0.168850	0.190503	0.232253	0.300145	0.405575	0.565511	0.798533	1.100193

Table 5
Calculated N_2 solubility (mol kg^{-1}) in 2 mol kg^{-1} NaCl solutions

P (bar)	*T* (K)										
	273.15	293.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	0.000504	0.000385	0.000316	0.000257	0.000177	0.000038					
10	0.004966	0.003861	0.003311	0.003017	0.002839	0.002692	0.002496	0.002159	0.001550	0.000479	
50	0.022919	0.018077	0.015712	0.014553	0.014052	0.013937	0.014040	0.014235	0.014391	0.014343	0.013851
100	0.041714	0.033404	0.029383	0.027489	0.026794	0.026846	0.027398	0.028294	0.029409	0.030609	0.031712
150	0.057383	0.046562	0.041384	0.039040	0.038321	0.038643	0.039701	0.041319	0.043382	0.045788	0.048408
200		0.058046	0.052046	0.049448	0.048822	0.049483	0.051080	0.053425	0.056413	0.059975	0.064029
250		0.068251	0.061647	0.058921	0.058463	0.059502	0.061650	0.064712	0.068594	0.073253	0.078652
300		0.077483	0.070410	0.067632	0.067382	0.068816	0.071514	0.075272	0.080006	0.085698	0.092348
350		0.085967	0.078506	0.075720	0.075698	0.077528	0.080760	0.085183	0.090721	0.097374	0.105174
400		0.093869	0.086071	0.083297	0.083506	0.085721	0.089464	0.094513	0.100799	0.108336	0.117181
450		0.101310	0.093203	0.090450	0.090883	0.093465	0.097686	0.103318	0.110290	0.118627	0.128402
500		0.108380	0.099981	0.097247	0.097890	0.100813	0.105477	0.111640	0.119231	0.128278	0.138861
550		0.115146	0.106463	0.103740	0.104574	0.107808	0.112873	0.119512	0.127647	0.137305	0.148562
600		0.121661	0.112694	0.109970	0.110970	0.114480	0.119898	0.126950	0.135546	0.145706	0.157490

Table 6
Calculated N_2 solubility (mol kg^{-1}) in 4 mol kg^{-1} NaCl solutions

P (bar)	*T* (K)										
	273.15	293.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	0.000255	0.000228	0.000209	0.000182	0.000136	0.000051					
10	0.002514	0.002286	0.002166	0.002083	0.001994	0.001869	0.001680	0.001401	0.001004	0.000462	
50	0.011625	0.010721	0.010291	0.010047	0.009841	0.009589	0.009243	0.008775	0.008166	0.007399	0.006457
100	0.021200	0.019850	0.019283	0.019014	0.018793	0.018487	0.018031	0.017396	0.016577	0.015574	0.014390
150	0.029206	0.027712	0.027202	0.027047	0.026920	0.026649	0.026156	0.025415	0.024435	0.023237	0.021840
200		0.034582	0.034249	0.034299	0.034340	0.034167	0.033690	0.032890	0.031788	0.030424	0.028837
250		0.040685	0.040596	0.040904	0.041158	0.041123	0.040700	0.039873	0.038677	0.037169	0.035409
300		0.046191	0.046378	0.046970	0.047462	0.047590	0.047244	0.046411	0.045139	0.043503	0.041579
350		0.051229	0.051701	0.052586	0.053327	0.053630	0.053373	0.052547	0.051209	0.049451	0.047368
400		0.055888	0.056646	0.057823	0.058813	0.059294	0.059130	0.058314	0.056915	0.055037	0.052792
450		0.060236	0.061272	0.062735	0.063968	0.064622	0.064550	0.063742	0.062279	0.060278	0.057865
500		0.064320	0.065627	0.067364	0.068831	0.069649	0.069660	0.068854	0.067319	0.065186	0.062593
550		0.068177	0.069743	0.071742	0.073429	0.074400	0.074481	0.073666	0.072047	0.069767	0.066978
600		0.071832	0.073646	0.075892	0.077784	0.078891	0.079027	0.078186	0.076465	0.074020	0.071014

Table 7
Calculated N_2 solubility (mol kg^{-1}) in 6 mol kg^{-1} NaCl solutions

P (bar)	*T* (K)										
	273.15	293.15	313.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15
1	0.000135	0.000142	0.000144	0.000134	0.000106	0.000052					
10	0.001333	0.001418	0.001484	0.001505	0.001465	0.001355	0.001177	0.000938	0.000652	0.000335	0.000005
50	0.006177	0.006660	0.007061	0.007266	0.007217	0.006907	0.006367	0.005655	0.004835	0.003971	0.003115
100	0.011287	0.012357	0.013257	0.013777	0.013806	0.013333	0.012424	0.011193	0.009770	0.008275	0.006805
150	0.015572	0.017277	0.018730	0.019628	0.019808	0.019247	0.018043	0.016364	0.014399	0.012327	0.010286
200		0.021582	0.023610	0.024922	0.025300	0.024708	0.023269	0.021198	0.018744	0.016139	0.013569
250		0.025405	0.028004	0.029745	0.030350	0.029768	0.028138	0.025722	0.022824	0.019727	0.016660
300		0.028846	0.032001	0.034170	0.035017	0.034471	0.032685	0.029962	0.026656	0.023101	0.019569
350		0.031979	0.035666	0.038255	0.039350	0.038856	0.036940	0.033938	0.030255	0.026273	0.022302
400		0.034857	0.039052	0.042046	0.043387	0.042956	0.040927	0.037671	0.033636	0.029251	0.024865
450		0.037517	0.042195	0.045579	0.047161	0.046796	0.044667	0.041174	0.036808	0.032042	0.027262
500		0.039987	0.045124	0.048880	0.050694	0.050397	0.048175	0.044459	0.039780	0.034651	0.029495
550		0.042286	0.047859	0.051969	0.054005	0.053773	0.051464	0.047535	0.042556	0.037080	0.031563
600		0.044428	0.050415	0.054860	0.057106	0.056934	0.054541	0.050406	0.045138	0.039328	0.033463

els for N_2 solubility in aqueous NaCl solutions. SWD model deviates apparently from experimental data at low-pressure region (Fig. 3a and c). At high temperature region (Fig. 3f), LN model deviates substantially from experimental data with over 12% errors on average. As can be seen from these figures, the experimental data are accurately reproduced by this model, which demonstrates the substantial improvements over previous models.

The partial molar volume ($\overline{V}_{N_2(l)}$) and Henry's constant (k_H) of N_2 in aqueous NaCl solutions can be derived form our

Table 8
The model deviations from experimental data

References	System	*T* (K)	*P* (bar)	*N*[a]	AAD (%)	MAD (%)
Winkler [48]	Water	273.23–353.14	1^+	9	2.62	3.74
Braun [41]	0–2 m NaCl	278.2–288.2	1^+	39	3.78	14.38
Hufner [35]	Water	293.33	1^+	1	0.44	0.44
Fox [33]	Water	273.68–325.16	1^+	24	1.11	2.46
Bohr [32]	Water	294.35	1^+	1	0.84	0.84
Muller [49]	Water	289.35–290.35	1^+	2	1.32	1.97
Adeney and Becker [50]	Water	276.7–308.3	1^+	7	2.32	5.19
Wiebe et al. [38]	Water	298.15	25.33–1013.25	7	6.82	13.2
Wiebe et al. [6]	Water	298.15–373.15	25.33–1013.25	32	5.84	13.2
Saddington and Krase [19]	Water	338.15–513.15	101.3–304	15	6.23	14.13
VansSlyke et al. [51]	0–0.16 m NaCl	298.15–311.15	1^+	14	1.01	2.12
Hawkins and Shilling [34]	Water	311.15	1^+	1	2.05	2.05
Morrison and Billett [31]	Water	285.65–345.65	1^+	12	1.76	4.66
Eichelberger [52]	Water	338	70.88–203.25	6	4.69	6.02
Mishnina et al. [11]	0–6.3 m NaCl	283.15–343.15	1^+	156	1.89	8.92
Farhi et al. [29]	Water	276.25–310.2	1^+	6	0.62	1.01
Klots and Benson [30]	Water	275.01–300.16	1^+	33	0.47	1.22
Douglas [53]	Water	276.25–302.65	1^+	5	1.01	1.38
Douglas [45]	Seawater	275.25–303.14	1^+	21	3.79	5.01
O'Sullivan and Smith [39]	0–1 m NaCl	324.65–375.65	101.3–607.9	18	4.78	10.09
Murray et al. [37]	Water	273.73–303.86	1^+	10	0.77	1.54
	Seawater	273.73–303.86	1^+	51	2.10	5.24
O'Sullivan and Smith [8]	0–4.6 m NaCl	324.65–398.15	101.3–616.1	50	3.79	10.49
Power and Stegall [54]	Water	310.15	1^+	1	0.04	0.04
Wilcock and Battino [55]	Water	298.15	1^+	2	0.94	0.94
Cosgrove and Walkley [56]	Water	278.15–313.15	1^+	8	0.84	2.17
Alvarez et al. [22]	Water	336.3–589.3	5.34–256	25	3.69	8.44
Kennan and Pollack [23]	Water	298.15	45.17–117.37	7	1.08	1.46
Alvarez and Fernandez-Prini [7]	Water	582.8	172.2–545.4	6	4.03	9.25
Chapoy et al. [2]	Water	274.19–363.02	9.71–70.43	52	2.55	4.51

AAD: average absolute deviations calculated from this model; MAD: maximal absolute deviations calculated from this model; "1^+" denotes that partial pressure of nitrogen is 1 atm.

[a] *N*: number of data points.

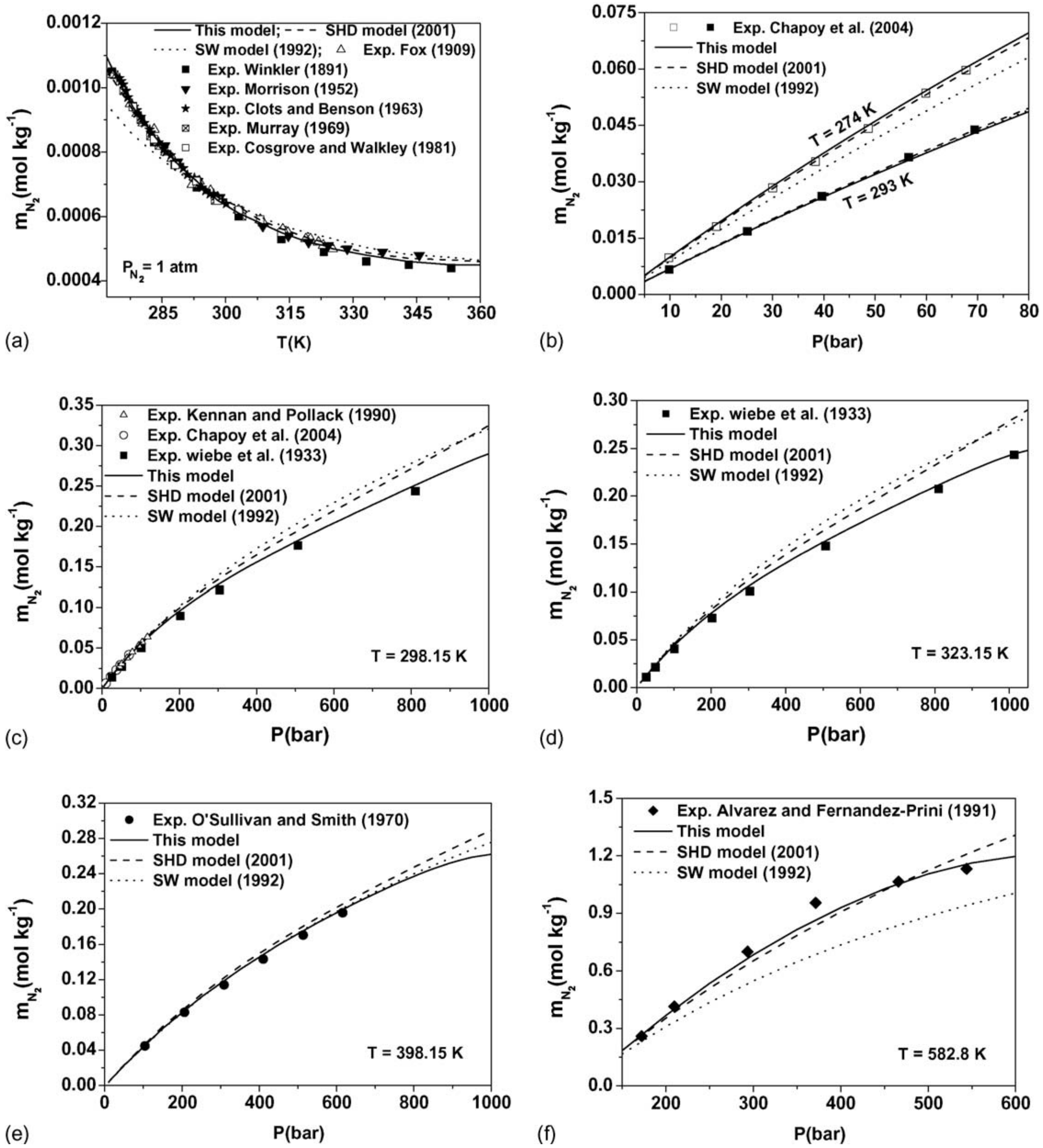

Fig. 2. N_2 solubility in pure water (model predictions vs. experimental data).

solubility model of this study:

$$\begin{aligned}\frac{\overline{V}_{N_2(l)}}{RT} &= \frac{\partial}{\partial P}\left(\frac{\mu^{l(0)}}{RT}\right)_{T,m} + \left(\frac{\partial \ln \gamma_{N_2}}{\partial P}\right)_{T,m} \\ &= \frac{\partial}{\partial P}\left(\frac{\mu^{l(0)}}{RT}\right)_{T,m} + \sum_{c} 2m_c \left(\frac{\partial \lambda_{N_2-c}}{\partial P}\right)_{T,m} \\ &\quad + \sum_{a} 2m_a \left(\frac{\partial \lambda_{N_2-a}}{\partial P}\right)_{T,m} \\ &\quad + \sum_{c}\sum_{a} m_c m_a \left(\frac{\partial \lambda_{N_2-c-a}}{\partial P}\right)_{T,m} \end{aligned} \tag{9}$$

$$k_H(T) = \frac{y_{N_2}\varphi_{N_2} P}{x_{N_2}} \exp\left(\frac{-\overline{V}_{N_2(l)}(P - P^{s}_{H_2O})}{RT}\right) \tag{10}$$

$$\left(\frac{\partial \, \mathrm{Par}(T, P)}{\partial P}\right)_{T,m} = c_6 + c_7 T + \frac{c_8}{T} + \frac{2c_9 P}{T} \tag{11}$$

The predicted partial volume of N_2 in aqueous NaCl solutions (Table 9) and Henry's constant of N_2 in water (Table 10) are compared with those calculated from the reliable models or experimental data [24,42], which exhibit a good agreement. These, from another point, prove the reliability of this model.

5. Applications of this model

5.1. Calculating N_2 solubility in seawater

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

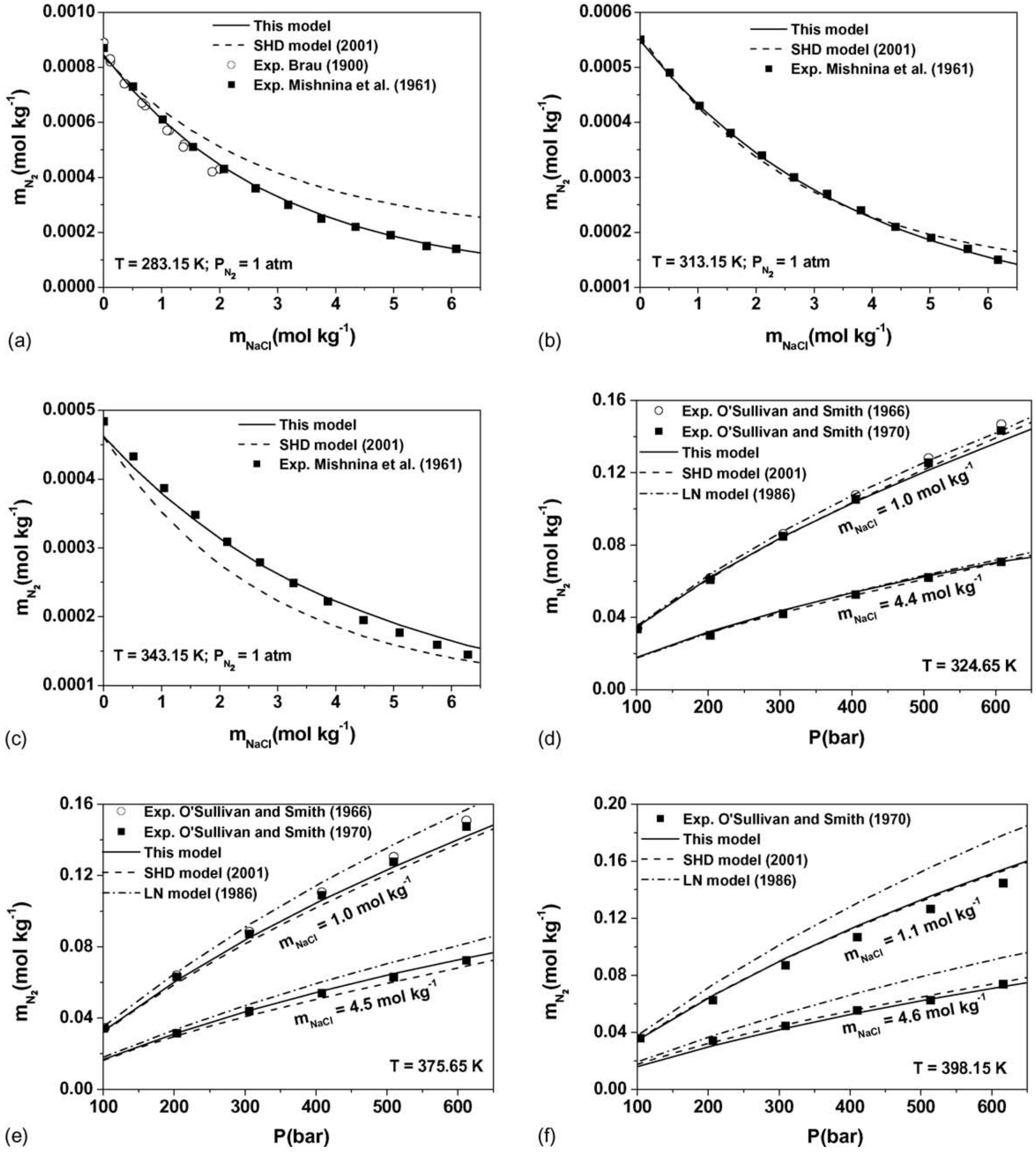

Fig. 3. N_2 solubility in aqueous NaCl solutions (model predictions vs. experimental data).

other than NaCl, it is impossible to fit directly to experimental measurements. We therefore take a predictive approach to this problem. According to Duan et al. [43] and Duan and Mao [44], 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 and contribute little to the activities. Using the similar approach, we approximate all N_2–monovalent-cation and N_2–bivalent-cation interaction parameters as $\lambda_{N_2-Na^+}$ and $2\lambda_{N_2-Na^+}$, respectively. The same treatment applies to the ternary parameters. With this simplification, Eq. (7) becomes

$$\ln m_{N_2} = \ln(y_{N_2}\varphi_{N_2}P) - \frac{\mu_{N_2}^{l(0)}}{RT} - 2\lambda_{N_2-Na^+}(m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} + 2m_{Mg^{2+}}) - \xi_{N_2-Na^+-Cl^-}(m_{Na^+} + m_{K^+} + 2m_{Ca^{2+}} + 2m_{Mg^{2+}})(m_{Cl^-} + 2m_{SO_4^{2-}}) - 4\lambda_{N_2-SO_4^{2-}}m_{SO_4^{2-}} \qquad (12)$$

where $\lambda_{N_2-SO_4^{2-}} = 0.0371$. In order to test this approximation, we compare the calculated results from Eq. (12) with experimental data of N_2 solubility in seawater [37,45] (Table 8 and

Table 9
The partial volume of N_2 ($\overline{V}_{N_2(l)}$) in aqueous NaCl solutions

T (K)	P (atm)	M_{NaCl} (mol dm^{-1})	$\overline{V}_{N_2(l)}$[a] (cm^3 mol^{-1})	$\overline{V}_{N_2(l)}$[b] (cm^3 mol^{-1})
375.65	200	0	37.7	39.99
		1	40.3	39.60
		4	41.2	38.27
	400	0	37.7	37.81
		1	37.9	37.91
		4	39.6	38.26
	600	0	37.7	35.63
		1	35.5	36.23
		4	38.0	38.22
398.15	200	0	43.1	40.90
		1	50.5	40.44
		4	62.7	38.92
	400	0	38.9	38.72
		1	41.9	38.77
		4	46.7	38.95
	600	0	34.6	36.54
		1	33.2	37.10
		4	30.8	38.94

[a] O'Sullivan and Smith [8].
[b] This study.

Fig. 4). It can be seen that the agreement between this approach and the experimental measurements is good. Since the model is highly accurate for aqueous NaCl solution up to 4.5 m in ionic strength, Eq. (12) should be reliable up to the same ionic strength for brines containing other salts than NaCl.

5.2. *Calculating liquid phase density of N_2–H_2O–NaCl system at equilibrium*

Liquid phase density of the N_2–H_2O–NaCl system at equilibrium can also be calculated from this model. In order to calculate the density, an accurate density model for H_2O–NaCl system is required. There are two good density models for the H_2O–NaCl system covering a large T–P–m range. One was developed by Spivey et al. [46] with a valid T–P–m region (273–548 K, 1–2000 bar and 0–6 mol kg^{-1}) and the other one was presented by Rogers and Pitzer [47] 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 N_2–H_2O–NaCl system at phase equilibrium:

$$m_{sol} = 1000 + m_{NaCl}M_{NaCl} + m_{N_2}M_{N_2} \qquad (13)$$

$$V_{sol} = \frac{1000 + m_{NaCl}M_{NaCl}}{\rho_{H_2O\text{–}NaCl}} + m_{N_2}\overline{V}_{N_2(l)} \qquad (14)$$

$$\rho_{sol} = \frac{m_{sol}}{V_{sol}} \qquad (15)$$

Table 10
Henry's constants (k_H) of N_2 in water

T (K)	k_{H1} (bar)	k_{H2} (bar)	k_{H3} (bar)
273	52651	54005	
278	59415	60440	59380
283	66399	66891	66389
288	73095	73265	73139
293	79612	79472	79829
298	85681	85426	86012
303	91776	91051	91838
308	97284	96281	97291
313	102335	101059	102277
318	106888	105342	106719
323	110914	109096	110485
350	123082	119769	
400	110216	104953	
450	76027	72685	
500	43411	44113	
550	21127	24374	

k_{H1}: calculated from this model; k_{H2}: from Fernandez-Prini et al. [42]; k_{H3}: from Rettich et al. [24].

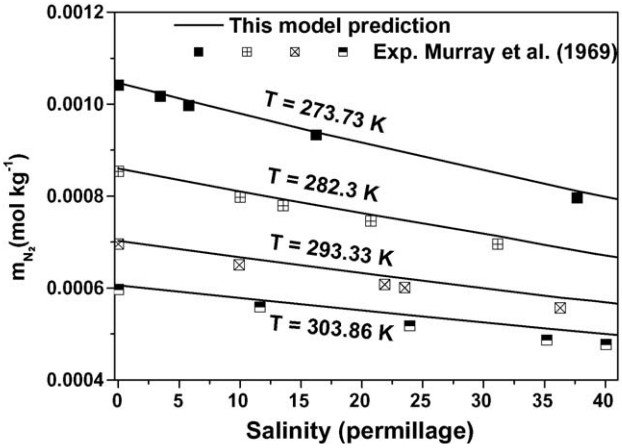

Fig. 4. The prediction of N_2 solubility in seawater.

Table 11
Liquid phase density of N_2–H_2O–NaCl system calculated from this model

T (K)	P (bar)	m_{NaCl} (mol kg^{-1})	$m_{\mathrm{N_2}}$ (mol kg^{-1})	$\rho_{\mathrm{H_2O–NaCl}}$ (g cm^{-3})	$\rho_{\mathrm{N_2–H_2O–NaCl}}$ (g cm^{-3})
273.15	1	0	0.000625	0.99702	0.99701
	10	1	0.004805	1.03660	1.03654
	50	2	0.017323	1.07413	1.07392
	75	3	0.019439	1.10846	1.10821
	100	4	0.019660	1.14058	1.14032
	125	5	0.018898	1.17070	1.17045
	150	6	0.017678	1.19899	1.19874
323.15	50	0	0.023282	0.99016	0.98990
	100	1	0.034922	1.02998	1.02958
	200	2	0.050436	1.06856	1.06796
	300	3	0.056259	1.10447	1.10378
	400	4	0.057228	1.13809	1.13735
	500	5	0.055711	1.16965	1.16886
	600	6	0.052881	1.19931	1.19848
373.15	50	0	0.021213	0.96064	0.96040
	100	1	0.032917	1.00041	1.00003
	200	2	0.049483	1.03900	1.03842
	300	3	0.056892	1.07490	1.07421
	400	4	0.059294	1.10847	1.10771
	500	5	0.058911	1.13993	1.13912
	600	6	0.056934	1.16945	1.16858
423.15	50	0	0.025285	0.91957	0.91929
	100	1	0.038183	0.96155	0.96110
	200	2	0.054843	1.00202	1.00138
	300	3	0.059239	1.03933	1.03861
	400	4	0.057681	1.07396	1.07322
	500	5	0.053353	1.10617	1.10544
	600	6	0.047875	1.13617	1.13544
473.15	50	0	0.030818	0.86729	0.86697
	100	1	0.047836	0.91395	0.91341
	200	2	0.064029	0.95828	0.95753
	300	3	0.061550	0.99844	0.99769
	400	4	0.052792	1.03520	1.03451
	500	5	0.042770	1.06896	1.06837
	600	6	0.033463	1.10002	1.09951

Note: m_{N2} is the calculated solubility data from this model; $\rho_{\mathrm{H_2O–NaCl}}$ from Spivey et al. (273–528 K and 1–2000 bar) [46].

where the partial molar volume of N_2, $\overline{V}_{\mathrm{N_2(l)}}$, can be obtained from Eqs. (9) and (11), the molar mass of NaCl $M_{\mathrm{NaCl}} = 58.4428\ \mathrm{g\,mol^{-1}}$ and the molar mass of N_2 $M_{\mathrm{N_2}} = 28.0134\ \mathrm{g\,mol^{-1}}$. $\rho_{\mathrm{H_2O–NaCl}}$ is the liquid phase density of the H_2O–NaCl system, either calculated from the Spivey model or from Roger–Pitzer model. The calculated liquid phase density of N_2–H_2O–NaCl system at phase equilibrium based on the Spivey model is compiled in Table 11.

5.3. Calculating homogenization pressure of fluid inclusions with N_2–H_2O–NaCl

Fluid inclusions provide the most direct information on the formation conditions (such as temperature, pressure and composition) of geological bodies. With the model of this study, we can calculate the homogenization pressure of inclusions containing N_2–H_2O–NaCl if the homogenization temperature and compositions of the fluid inclusions are known from microthermometric and spectroscopic techniques. At a given temperature, the uncertainty of pressure increases with molality of N_2 and

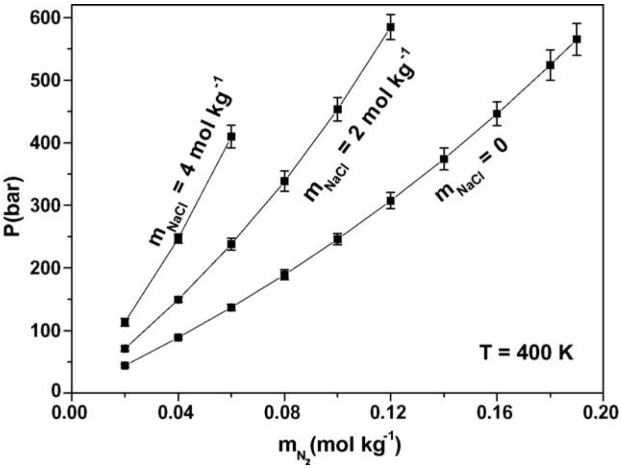

Fig. 5. The uncertainty of pressure vs. molality of N_2 at a given temperature.

NaCl (Fig. 5) and the average uncertainty of pressure in the studied region is about 4.15%.

6. Conclusions

Based on a simple semi-empirical equation and a highly accurate EOS [9] for gas phase, and the electrolyte solution theory of [10] for liquid phase, an accurate model is presented to calculate N_2 solubility in pure water (273–590 K and 1–600 bar) and in aqueous NaCl solutions (273–400 K, 1–600 bar and 0–6 mol kg^{-1}). From this model, liquid phase density of N_2–H_2O–NaCl system at phase equilibrium can also be accurately calculated with experimental accuracy. With a simple approach, this model is extrapolated to predict the N_2 solubility in other aqueous solutions containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and $SO_4{}^{2-}$ like seawater within experimental uncertainty. In addition, this model can be used to calculate the homogenization pressure of fluid inclusions (N_2–H_2O–NaCl). A FORTRAN code is developed for this model and can be downloaded from the website: www.geochem-model.org/programs.htm.

List of symbols

m_i	molality (mol kg^{-1}) of component i in liquid phase
P	total pressure, that is $P_{N_2} + P_{H_2O}$ in bar
Par	parameter
R	universal gas constant (83.14472 bar cm^3 mol^{-1} K^{-1})
T	absolute temperature (K)
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
$\lambda_{N_2\text{–ion}}$	interaction parameter
$\xi_{N_2\text{–cation–anion}}$	interaction parameter

Subscripts

a	anion
c	cation
sol	solution

Superscripts

l	liquid
v	vapor
(0)	standard state

Acknowledgements

We thank the two anonymous reviewers and Dr. Peter Cummings for their constructive suggestions. This work is supported by Zhenhao Duan's "key Project" funds (40537032) and his outstanding young scientist funds (#40225008) awarded by National Natural Science Foundation of China.

Appendix. The equation of state for supercritical N_2

$$Z = \frac{P_m V_m}{RT_m} = 1 + \frac{a_1 + (a_2/T_m^2) + (a_3/T_m^3)}{V_m} + \frac{a_4 + (a_5/T_m^2) + (a_6/T_m^3)}{V_m^2} + \frac{a_7 + (a_8/T_m^2) + (a_9/T_m^3)}{V_m^4} + \frac{a_{10} + (a_{11}/T_m^2) + (a_{12}/T_m^3)}{V_m^5} + \frac{a_{13}}{T_m^3 V_m^2}\left(1 + \frac{a_{14}}{V_m^2}\right)\exp\left(-\frac{a_{14}}{V_m^2}\right) \quad (A1)$$

$$P_m = \frac{3.0626\sigma^3 P}{\varepsilon} \quad (A2)$$

$$T_m = \frac{154T}{\varepsilon} \quad (A3)$$

$$V = 1000V_m\left(\frac{\sigma}{3.691}\right)^3 \quad (A4)$$

where P_m is in bar, T_m in K, V_m in dm^3, and V is in cm^3; $R = 0.08314467$ bar dm^3 K^{-1} mol^{-1}, $\sigma = 3.63$ A and $\varepsilon = 101.0$ K. The parameters a_1–a_{14} are as follows: $a_1 = 3.75504388\text{E}{-02}$, $a_2 = -1.08730273\text{E}{+04}$, $a_3 = 1.10964861\text{E}{+06}$, $a_4 = 5.41589372\text{E}{-04}$, $a_5 = 1.12094559\text{E}{+02}$, $a_6 = -5.92191393\text{E}{+03}$, $a_7 = 4.37200027\text{E}{-06}$, $a_8 = 4.95790731\text{E}{-01}$, $a_9 = -1.64902948\text{E}{+02}$, $a_{10} = -7.07442825\text{E}{-08}$, $a_{11} = 9.65727297\text{E}{-03}$, $a_{12} = 4.87945175\text{E}{-01}$, $a_{13} = 1.62257402\text{E}{+04}$ and $a_{14} = 8.99000000\text{E}{-03}$. The fugacity coefficient of N_2 can be derived from Eq. (A1):

$$\ln\varphi(T, P) = Z - 1 - \ln Z + \frac{a_1 + (a_2/T_m^2) + (a_3/T_m^3)}{V_m} + \frac{a_4 + (a_5/T_m^2) + (a_6/T_m^3)}{2V_m^2} + \frac{a_7 + (a_8/T_m^2) + (a_9/T_m^3)}{4V_m^4} + \frac{a_{10} + (a_{11}/T_m^2) + (a_{12}/T_m^3)}{5V_m^5} + \frac{a_{13}}{2T_m^3 a_{14}} \times \left[2 - \left(2 + \frac{a_{14}}{V_m^2}\right) \times \exp\left(-\frac{a_{14}}{V_m^2}\right)\right] \quad (A5)$$

References

[1] R. Sun, W. Hu, Z. Duan, J. Sol. Chem. 30 (6) (2001) 561–573.

[2] A. Chapoy, A.H. Mohammadi, B. Tohidi, D. Richon, J. Chem. Eng. Data 49 (2004) 1110–1115.

[3] I. Soreide, C.H. Whitson, Fluid Phase equilib. 77 (1992) 217–240.

[4] Y.-K. Li, L.X. Nghiem, Can. J. Chem. Eng. 64 (1986) 486–496.

[5] R. Battino, T.R. Rettich, T. Tominaga, J. Phys. Chem. Ref. Data 13 (2) (1984) 563–600.

[6] R. Wiebe, V.L. Gaddy, C.J. Heins, J. Am. Chem. Soc. 55 (1933) 947–953.
[7] J. Alvarez, R. Fernandez-Prini, Fluid Phase Equilib. 66 (1991) 309–326.
[8] T.D. O'Sullivan, N.O. Smith, J. Phys. Chem. 74 (7) (1970) 1460–1466.
[9] Z. Duan, N. Moller, J.H. Weare, Geochim. Cosmochim. Acta 1996 (7) (1996) 1209–1216.
[10] K.S. Pitzer, J. Phys. Chem. 77 (1973) 268–277.
[11] T.A. Mishnina, O.I. Avdeeva, T.K. Bozhovakaya, Materialy Vses. Nauchn. Issled. Geol. Inst. 46 (1961) 93–110.
[12] K. Denbigh, The Principles of Chemical Equilibrium, vol. 3d, Cambridge University Press, Cambridge, 1971.
[13] Y. Shibue, Fluid Phase equilib. 213 (2003) 39–51.
[14] W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data 22 (3) (1993) 783–787.
[15] A.H. Mohammadi, A. Chapoy, B. Tohidi, D. Richon, J. Chem. Eng. Data 50 (2005) 541–545.
[16] M. Rigby, J.M. Prausnitz, J. Phys. Chem. 72 (1) (1968) 330–334.
[17] A.Y. Namiot, M.M. Bondareva, Solubility of Gases in Water, Gostekhizdat, Moscow, 1959.
[18] K. Althaus, Fortschritt-Berichte VDI 3 (1999) 350.
[19] A.W. Saddington, N.W. Krase, J. Am. Chem. Soc. 56 (1934) 353–361.
[20] K.S. Pitzer, J.C. Peiper, R.H. Busey, J. Phys. Chem. Ref. Data 13 (1984) 1–102.
[21] R. Battino, Solubility Data Series, vol. 10, Pergamon Press, Oxford, England, 1982.
[22] J. Alvarez, R. Crovetto, R. Fernandez-Prini, Berichte der Bunsen-Gesellschaft-Phys. Chem. 92 (1988) 935–940.
[23] R.P. Kennan, G.L. Pollack, J. Chem. Phys. 93 (4) (1990) 2724–2735.
[24] T.R. Rettich, R. Battino, E. Wilhelm, J. Sol. Chem. 13 (5) (1984) 335–348.
[25] S. Emerson, C. Stump, D. Wilbur, P. Quay, Mar. Chem. 64 (1999) 337–347.
[26] R.C. Hamme, S.R. Emerson, Deep-Sea Res. I 51 (2004) 1517–1528.
[27] J.B. Goodman, N.W. Krase, Ind. Eng. Chem. 23 (1931) 401–404.
[28] H.A. Pray, C.E. Schweickert, B.H. Minnich, Ind. Eng. Chem. 44 (1952) 1146–1151.
[29] L.E. Farhi, T. Homma, A.W.T. Edwards, J. Appl. Physiol. 18 (1) (1963) 97–106.
[30] C.E. Klots, B.B. Benson, J. Mar. Res. 21 (1) (1963) 48–57.
[31] T.J. Morrison, F. Billett, J. Chem. Soc. (1952) 3819–3822.
[32] C. Bohr, Z. Phys. Chem. 71 (1) (1910) 47–50.
[33] C.J.J. Fox, Trans. Faraday Soc. 5 (1909) 68–87.
[34] J.A. Hawkins, C.W. Shilling, J. Biol. Chem. 113 (1936) 273–279.
[35] G. Hufner, Z. Phys. Chem. 57 (5) (1907) 611–624.
[36] H.L. Clever, R. Battino, J.H. Saylor, D.M. Gross, J. Phys. Chem. 61 (1957) 1078–1082.
[37] C.N. Murray, J.P. Riley, T.R.S. Wilson, Deep-Sea Res. 16 (3) (1969) 297–310.
[38] R. Wiebe, V.L. Gaddy, C. Heins, Ind. Eng. Chem. 24 (1932) 927.
[39] T.D. O'Sullivan, N.O. Smith, Geochim. Cosmochim. Acta 30 (6) (1966) 617–619.
[40] N.O. Smith, S. Kelemen, B. Nagy, Geochim. Cosmochim. Acta 26 (9) (1962) 921–926.
[41] L. Braun, Z. Phys. Chem. 33 (6) (1900) 721–741.
[42] R. Fernandez-Prini, J.L. Alvarez, A.H. Harvey, J. Phys. Chem. Ref. Data 32 (2) (2003) 903–916.
[43] Z. Duan, N. Moller, J.H. Weare, Geochim. Cosmochim. Acta 56 (1992) 1451–1460.
[44] Z. Duan, S. Mao, Geochim. Cosmochim. Acta 70 (13) (2006) 3369–3386.
[45] E. Douglas, J. Phys. Chem. 69 (1965) 2608–2610.
[46] J.P. Spivey, W.D. Mccain, R. North, J. Can. Pet. Technol. 43 (7) (2004) 52–60.
[47] P.S.Z. Rogers, K.S. Pitzer, J. Phys. Chem. Ref. Data 11 (1) (1982) 15–77.
[48] L.W. Winkler, Berichte der Deutschen Chemischen Gesellschaft 24 (1891) 3602–3610.
[49] C. Muller, Z. Phys. Chem. 81 (4) (1912) 483–503.
[50] W.E. Adeney, H.G. Becker, Philos. Mag. 38 (225) (1919) 317–337.
[51] D.D. VansSlyke, R.T. Dillon, R. Margaria, J. Biol. Chem. 105 (1934) 571–596.
[52] W.C. Eichelberger, Ind. Eng. Chem. 47 (1955) 2223–2228.
[53] E. Douglas, J. Phys. Chem. 68 (1964) 169–174.
[54] G.G. Power, H. Stegall, J. Appl. Physiol. 29 (1970) 145–149.
[55] R.J. Wilcock, R. Battino, Nature 252 (1974) 614–615.
[56] B.A. Cosgrove, J. Walkley, J. Chromatogr. A 216 (1981) 161–167.