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A model to predict phase equilibrium of CH_4 and CO_2 clathrate hydrate in aqueous electrolyte solutions

ZHENHAO DUAN* AND RUI SUN

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

ABSTRACT

A thermodynamic model to predict phase equilibrium of methane and carbon dioxide hydrate in aqueous electrolyte solutions is presented. Using the Pitzer model to account for the variation of water activity due to electrolytes and dissolved gas in aqueous solutions, we extended the model based on ab initio molecular potential developed recently by us for the CH_4-H_2O and CO_2-H_2O binary systems to the CH_4 (or CO_2)-H_2O-salts system. Comparison of the model with extensive experimental data indicates that this model can accurately predict the phase equilibrium of CH_4 hydrate and CO_2 hydrate in various electrolyte solutions (such as aqueous NaCl, KCl, $CaCl_2$, NaCl + KCl, NaCl + $CaCl_2$ solutions, and seawater) from zero to high ionic strength (about 6 *m*) and from low to high pressures.

Keywords: Methane hydrate, carbon dioxide hydrate, thermodynamic stability, electrolyte solution, phase equilibrium, formation conditions

INTRODUCTION

Gas hydrates are non-stoichiometric crystalline compounds that consist of a hydrogen-bonded network of host water molecules and enclathrated guest molecules. They are generally stable at low temperatures and high pressures. When electrolytes are present in the liquid water, the hydrate formation is inhibited. It is of great importance to predict the phase equilibrium of gas hydrate in aqueous electrolyte solutions for many engineering, environmental, and geochemical problems, such as inhibiting the formation of hydrate in natural gas pipelines (Sloan 1998), exploring and exploiting methane hydrate reservoirs in marine sediments, sequestrating CO_2 on the ocean floor, analyzing the salinity of fluid inclusions (Collins 1979; Diamond 1994), and desalinating seawater (Barduhn et al. 1962; Smirnov 1990).

In the last half century, various thermodynamic models for the calculation of phase equilibrium properties of the gas hydrate system were developed, such as the models proposed by Parrish and Prausnitz (1972), Ng and Robinson (1976), John et al. (1985), and Lee and Holder (2002). Most of these models are based on the statistical mechanical model proposed by van der Waals and Platteeuw (1959) and calculate Langmuir constants from the Kihara potential model with parameters determined from phase equilibrium data of gas hydrates. Recently, we proposed a new method to compute the Langmuir constant from angle-dependent ab initio intermolecular potentials (Sun and Duan 2005). This method can accurately predict both phase equilibria and cage occupancy of methane hydrate and carbon dioxide hydrate in gas-water binary systems.

Electrolytes cannot enter the lattice of hydrates, but they act by lowering the activity of water in the coexisting liquid phase, causing hydrates to form at lower temperatures and higher pressures compared to their formation in pure water. Using the Pitzer-Mayorga activity coefficient model (Pitzer and Mayorga 1973) to account for the activity depression of water in aqueous electrolyte solutions, Englezos and Bishnoi (1988) presented a method to predict gas hydrate formation in aqueous solutions of electrolytes. Because the Pitzer-Mayorga model doesn't consider the neutral species dissolved in aqueous solution, Englezos and Bishnoi (1988) neglected the effect of the dissolved gas component on water activity in aqueous solution. Although it can produce good results for systems with substances sparingly soluble in water (e.g., light hydrocarbons, nitrogen), it leads to systematic errors for soluble gases (such as CO_2), because the effect of soluble gas on water activity is significant. Englezos (1992) tried to predict the formation condition of CO_2 hydrate in aqueous NaCl solution from the Aasberg-Petersen's model (Aasberg-Petersen et al. 1991). However, the average absolute deviation of this model for CO_2 stability in 10 wt% NaCl solution is more than 11%. Tse and Bishnoi (1994) examined three models [including Chen and Evans (1986), Zuo and Guo (1991), and Aasberg-Petersen et al. (1991)] that can treat the aqueous electrolyte phase, and found that the model of Zuo and Guo (1991) gave the best results for predicting incipient equilibrium condition of CO_2 hydrate in aqueous single salt solutions. Tohidi et al. (1995) predicted the inhibition effect of electrolyte on phase equilibrium of gas hydrates based on their thermodynamic model for aqueous electrolyte solution. Dickens and Quinby-Hunt (1997) predicted methane hydrate stability in seawater from the Pitzer-Mayorga model and achieved good agreement with experiments. Dubessy et al. (1992) and Bakker et al. (1996) predicted the CO_2 hydrate stability field in CO_2-H_2O-salts system from the Pitzer-Mayorga model, using an approximate method to include CO_2 solubility and to calculate the activity of water in CO_2-H_2O-salts system.

In general, the previous models can predict phase equilibria

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* E-mail: duanzhenhao@yahoo.com

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of gas hydrates in aqueous electrolyte solutions with reasonable accuracy, but there is substantial room for improvements. The common flaw in the previous hydrate models is that they calculated the Langmuir constants from the Kihara potential with parameters derived from experimental data of gas hydrates. Although these models can well reproduce the experimental data that were used in parameterization, they generally have poor capability to extrapolate beyond data range. Another disadvantage of most previous models is that the water-electrolyte interaction parameters used by them were evaluated at 25 °C or higher temperature. It is well known that the gas hydrate stability in aqueous electrolyte solution generally occurs at temperatures below 25 °C (from –25~25 °C). The parameters at 25 °C cannot accurately predict the activity coefficients of water-salts system at temperatures below 25 °C due to the temperature-dependence of the activity coefficient.

Pitzer and Silvester (1976) improved the Pitzer-Mayorga model and developed a rigorous method to deal with the aqueous electrolyte systems containing dissolved neutral components like gases. We have developed a new model to predict thermodynamic stability of methane hydrate and carbon dioxide hydrate in pure water from ab initio molecular potentials (Sun and Duan 2005). This model can work well in a wide *P*-*T* range with high accuracy because the parameters used are evaluated from quantum mechanical calculations rather than from phase equilibrium data of gas hydrates. The purpose of this study is to combine our recent model (Sun and Duan 2005) and the Pitzer model to predict phase equilibrium of methane hydrate and carbon dioxide hydrate in aqueous electrolyte solutions without fitting to any additional experimental data. This model has been programmed and can be downloaded from www.geochem-model.org/programs.htm.

THERMODYNAMIC MODEL OF GAS HYDRATES

There are three structural forms of clathrate hydrate known as structure I, structure II, and structure H. Methane hydrate and carbon dioxide hydrate are structure I hydrates (Sloan 1998). A detailed discussion on the structure of CH_4 and CO_2 hydrates can be found in our recent paper (Sun and Duan 2005).

Gas hydrate thermodynamics makes it possible to predict the pressure-temperature conditions at which hydrates form or dissociate. At three-phase (hydrate, hydrate-forming gas, and aqueous phases) equilibrium, the following equation must be satisfied

$$\Delta\mu_w^H = \Delta\mu_w^L \tag{1}$$

where $\Delta\mu_w^H$ represents the chemical potential difference of water between the hypothetical empty and occupied hydrate lattices, $\Delta\mu_w^L$ denotes the chemical potential difference of water between the empty hydrate lattice and the aqueous solution.

$\Delta\mu_w^H$ is calculated from the statistical mechanics model proposed by van der Waals and Platteeuw (1959)

$$\Delta\mu_w^H(T,P) = -\mathrm{R}T\sum_{i=1}^{2}\nu_i \ln(1-\sum_{j=1}^{N_C}\theta_{ij}) \tag{2}$$

$$\theta_{ij} = C_{ij}f_j / (1+\sum_{j=1}^{N_C}C_{ij}f_j) \tag{3}$$

where R is gas constant, ν_i is the number of *i*-type cages (also called "cavities") per water molecule, θ_{ij} is the fractional occupancy of *i*-type cavities with *j*-type guest molecules, C_{ij} is the temperature-dependent Langmuir constant of gas component *j* in *i*-type cavity, and f_j is the fugacity of gas component *j* in hydrate phase, which equals to the fugacity of gas *j* in gas phase.

Most of the previous hydrate models calculated the Langmuir constant from the Kihara potential model with parameters determined from phase equilibrium data of gas hydrates. We recently presented a new method to calculate C_{ij} from angle-dependent ab initio intermolecular potentials (Sun and Duan 2005). This gas-water binary model is extended to include electrolytes in this work. An accurate equation of state developed by Duan et al. (1992a) was used to calculate the fugacity of CH_4 and CO_2.

$\Delta\mu_w^L$ is calculated from the expression proposed by Holder et al. (1980)

$$\frac{\Delta\mu_w^L(T,P)}{\mathrm{R}T} = \frac{\Delta\mu_w^0(T_0,0)}{\mathrm{R}T_0} - \int_{T_0}^{T}(\frac{\Delta h_w^L}{\mathrm{R}T^2})dT + \int_0^P(\frac{\Delta V_w^L}{\mathrm{R}T})\mathrm{d}P - \ln a_w \tag{4}$$

where a_w is the activity of water in aqueous electrolyte solution. The focus of this study is to calculate a_w more rigorously than previous models. The meaning and the values of the remaining parameters in Equation 4 can be found in our previous study (Sun and Duan 2005).

This study calculated a_w from the Pitzer model. Equation 5 shows the relationship between a_w and the osmotic coefficient, ϕ

$$\ln a_w = -\frac{MW}{1000}\left(\sum_i m_i\right)\phi \tag{5}$$

where *MW* is the molecular weight of water, m_i is the molality of the solute species. The sum over *i* represents the sum over all solutes: cations, anions, and neutrals. The equation for ϕ proposed by Pitzer and Silvester (1976) was rearranged by Harvie et al. (1984) and Felmy and Weare (1986) as

$$\begin{aligned}\left(\sum_i m_i\right)(\phi-1) = 2\Bigg\{&-\frac{A^\phi I^{1.5}}{1+1.2I^{0.5}} + \sum_c\sum_a m_c m_a\left(B_{ca}^\phi + ZC_{ca}\right)\\ &+\sum\sum_{c<c'} m_c m_{c'}\left(\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a}\right) + \sum\sum_{a<a'} m_a m_{a'}\left(\Phi_{aa'}^\phi + \sum_c m_a \psi_{aa'c}\right)\\ &+\sum_n\sum_c m_n m_c \lambda_{nc} + \sum_n\sum_a m_n m_a \lambda_{na} + \sum_n\sum_c\sum_a m_n m_c m_a \zeta_{nca}\Bigg\}\end{aligned} \tag{6}$$

where *I* is the ionic strength, the subscripts *c*, *a*, and *n* represent cation, anion, and neutrals, respectively. The summation index, *c*, denotes the sum over all cations in the system. The double summation index, $c < c'$, denotes the sum over all distinguishable pairs of dissimilar cations. Analogous definitions apply to the summation indices for anions. A^ϕ is one third of the Debye-Hückel limiting slope and equals to 0.39 at 25 °C. *B*, Φ values, and λ values represent measurable combinations of the second virial coefficients. *C*, ψ values, and ζ are measurable combinations of the third virial coefficients.

As in the treatment of Pitzer (1973), the virial coefficients, B_{ca} and Φ_{ijk}, are the functions of ionic strength while the third virial coefficients, C_{ca} and ψ_{ijk}, are assumed to be independent of the ionic strength. The equations to describe the ionic strength dependence of B_{ca} and Φ_{ijk} are listed in Appendix A. Pitzer and Mayorga (1973, 1974), Pitzer and Kim (1974), and Pitzer (1975) evaluated most of the electrolyte parameters (i.e., water-electrolyte interaction parameters, including B, C, Φ values, and ψ values) at 25 °C. The hydrate models developed by Englezos and Bishnoi (1988) and Dubessy et al. (1992) predicted hydrate equilibrium in aqueous electrolyte solutions from the Pitzer-Mayorga model with the electrolyte parameters determined at 25 °C. The water-salt interaction parameters in the activity coefficients model of Chen and Evans (1986), Zuo and Guo (1991), and Aasberg-Petersen et al. (1991) were also determined at 25 °C or higher temperatures. However, the temperature-dependence of the activity coefficients of water-salts system cannot be neglected. The electrolyte parameters determined at 25 °C cannot predict the osmotic coefficient and activity coefficients of water-salts system at temperatures other than 25 °C. Pabalan and Pitzer (1987), Moller (1988), and Greenberg and Moller (1989) published the electrolyte parameters for the Na-K-Ca-Mg-Cl-SO_4-H_2O system from 0 or 25 °C to high temperatures. Spencer et al. (1990) evaluated the electrolyte parameters for Na-K-Ca-Mg-Cl-SO_4-H_2O system at low temperatures (from –55 to 25 °C). Since gas hydrate equilibrium in aqueous electrolyte solutions occurs at low temperatures (–25~25 °C), we chose the set of parameters determined by Spencer et al. (1990) (Table 1).

The effect of pressure on activity coefficients at a specific temperature should be included in the theoretical calculation. However, Monnin (1990) found that the effect of pressure on the activity of water is small and can be ignored. We also confirmed this result from temperature- and pressure-dependent parameters for aqueous NaCl solution published by Pitzer et al. (1984). Thus, this model will neglect the effect of pressure on water activity.

The second and third virial coefficients, λ_{ni} and ζ_{nij}, represent the interactions between ions and neutral species. $\lambda_{CH_4\text{–i}}$, $\lambda_{\mathrm{CO_2}\text{–i}}$, $\zeta_{CH_4\text{–}ij}$, and $\zeta_{\mathrm{CO_2}\text{–}ij}$ have been determined by the gas solubility model of Duan and coworkers (Duan et al. 1992b; Duan and Sun 2003). Duan et al. (1992b) set $\lambda_{CH_4\text{–Cl}}$ to zero and evaluated $\lambda_{CH_4\text{–Na}}$ and $\zeta_{CH_4\text{–Na–Cl}}$ from CH_4 solubility in aqueous NaCl solution. $\lambda_{CH_4\text{–K}}$ was approximated to be equal to $\lambda_{CH_4\text{–Na}}$; $\lambda_{CH_4\text{–Ca}}$ was as twice as large as $\lambda_{CH_4\text{–Na}}$. Analogous treatment was applied to $\lambda_{\mathrm{CO_2}\text{–i}}$ by Duan and Sun (2003). All $\zeta_{CH_4\text{–}ij}$ and $\zeta_{\mathrm{CO_2}\text{–}ij}$ were assumed to be equal to $\zeta_{CH_4\text{–Na–Cl}}$ and $\zeta_{\mathrm{CO_2}\text{–Na–Cl}}$, respectively. $\lambda_{CH_4\text{–Na}}$, $\lambda_{\mathrm{CO_2}\text{–Na}}$, and $\zeta_{\mathrm{CO_2}\text{–Na–Cl}}$ were treated as the functions of temperature and pressure while $\zeta_{CH_4\text{–Na–Cl}}$ was assumed to be constant (–6.2394380 × 10^{-3}). The following are the equations for $\lambda_{CH_4\text{–Na}}$, $\lambda_{\mathrm{CO_2}\text{–Na}}$, and $\zeta_{\mathrm{CO_2}\text{–Na–Cl}}$.

$$\lambda_{CH_4-\mathrm{Na}} = 0.099223079 + 2.5790681\times10^{-5}T + 0.018345140P/T - 8.0719672\times10^{-6}P^2/T \tag{7}$$

$$\lambda_{\mathrm{CO_2\text{-}Na}} = -0.41137059 + 6.0763201\times10^{-4}T + 97.534771/T - 0.023762247P/T + 0.017065624P/(630-T) + 1.4133583\times10^{-5}T\ln(P) \tag{8}$$

$$\zeta_{\mathrm{CO_2\text{-}Na\text{-}Cl}} = 3.3638972\times10^{-4} - 1.9829898\times10^{-5}T \tag{9}$$

In general, Equations 2, 4, 5, and 6 form the basic equations of this model to predict gas hydrate stability in aqueous electrolyte solutions. All the parameters presented in these equations have been evaluated by previous researchers. No adjustable parameter is needed to fit to the phase equilibrium data of gas hydrates formed in aqueous electrolyte solution.

RESULTS AND DISCUSSION

At a given temperature, the dissociation pressure of methane hydrate or carbon dioxide hydrate is calculated by solving Equations 1, 2, and 4 by iteration. The prediction of this model for CH_4 hydrate equilibrium in aqueous electrolyte solution is presented in the first subsection. The prediction of this model for CO_2-hydrate equilibrium in aqueous electrolyte solution is presented in the second subsection.

Methane hydrate equilibrium

Several researchers reported the hydrate-liquid-gas (HLV) equilibrium of methane hydrate in aqueous electrolyte solution. Kobayashi et al. (1951) was the first to measure the dissociation pressure of methane hydrate in aqueous NaCl solution. However, the data of Kobayashi et al. (1951) are widely scattered, and of poor quality. de Roo et al. (1983) published CH_4 hydrate equilibrium data in aqueous NaCl solution up to 5.5 m and 110 bar. Recently, Jager and Sloan (2001) reported CH_4 hydrate equilibrium data in aqueous NaCl solution up to 700 bar. Kharrat and Dalmazzone (2003) and Dalmazzone et al. (2004)

TABLE 1. The temperature dependence of the Debye-Huckel parameter, A^{ϕ}, and the single and mixed electrolyte parameters of Pitzer model*, † determined by Spencer et al. (1990)

Parameter	c_1	c_2	c_3	c_4	c_5	c_6
A^{ϕ}	86.6836498	8.48795942d-2	–1.32731477d+3	–17.6460172	–8.88785150d-5	4.88096393d-8
$\beta^{(0)}_{\mathrm{Na,Cl}}$	7.87239712	–8.3864096d-3	–4.96920671d+2	–0.82097256	1.4413774d-5	–8.7820301d-9
$\beta^{(1)}_{\mathrm{Na,Cl}}$	8.66915291d+2	0.606166931	–1.70460145d+4	–1.67171296d+2	–4.8048921d-4	1.88503857d-7
$C^{\phi}_{\mathrm{Na,Cl}}$	1.70761824	2.32970177d-3	–1.35583596	–0.387767714	–2.46665619d-6	1.21543380d-9
$\beta^{(0)}_{\mathrm{K,Cl}}$	26.5718766	9.92715099d-3	–7.5570722d+2	–4.6730077	–3.6232333d-6	–6.2842718d-11
$\beta^{(1)}_{\mathrm{K,Cl}}$	1.69742977d+3	1.22270943	–3.28684422d+4	–3.28813848D+2	–9.9904449d-4	4.04786721d-7
$C^{\phi}_{\mathrm{K,Cl}}$	–3.27571680	–1.27222054d-3	90.7747666	0.580513562	4.71374283d-7	1.1162507d-11
$\beta^{(0)}_{\mathrm{Ca,Cl}}$	–56.2764702	–3.00771997d-2	1.11730349d+3	10.6664743	1.05630400d-5	3.3331626d-9
$\beta^{(1)}_{\mathrm{Ca,Cl}}$	3.4787	–1.5417D-2	0.	0.	3.1791d-5	0.
$C^{\phi}_{\mathrm{Ca,Cl}}$	26.4231655	2.46922993d-2	–4.18098427d+2	–5.35350322	–2.48298510d-5	1.22421864d-8
$\theta_{\mathrm{Na,K}}$	–18.2266741	–3.6903847d-3	6.12415011d+2	3.02994981	0.	0.
$\psi_{\mathrm{Na,K,Cl}}$	6.48108127	1.46803468d-3	–2.04354019d+2	–1.09448043	0.	0.
$\theta_{\mathrm{Na,Ca}}$	0.05	0.	0.	0.	0.	0.
$\psi_{\mathrm{Na,Ca,Cl}}$	–7.63980	–1.2990d-2	0.	1.8475	1.1060d-5	0.

* The equation to describe the temperature dependence of the parameters in Pitzer's model has the following form:

$$Par(T) = c_1 + c_2T + c_3/T + c_4\ln T + c_5T^2 + c_6T^3 \cdot$$

† The meanings of the parameters $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}, θ, and ψ were given Appendix A.

measured CH_4 hydrate equilibrium in aqueous $CaCl_2$ solutions. Dholabhai et al. (1991) and Dickens and Quinby-Hunt (1994, 1997) measured CH_4 hydrate equilibrium in mixed electrolytes solutions and in seawater.

Figure 1 shows the prediction of this model for CH_4 hydrate dissociation pressure in aqueous NaCl solution with electrolyte parameters from Spencer et al. (1990). The prediction of this model agrees well with all experimental data sets. The absolute average deviation is about 4.5%. The good consistency of this model with the experimental data of Jager and Sloan (2001) indicates that this model can work well, not only at low and moderate pressures, but also at high pressures.

Figure 2 compares the prediction of this model with the experimental data of methane hydrate in aqueous $CaCl_2$ solution. It can be seen that this model can accurately predict CH_4 hydrate stability in the CH_4-H_2O-$CaCl_2$ system up to high ionic strength (9 *m*).

Figure 3 compares the prediction of this model with experimental data for CH_4 hydrate in mixed NaCl and KCl solution. It is obvious that the prediction of this model for this system is highly accurate. The average deviation from the experimental data is about 2%. This model can also predict the equilibrium pressure of CH_4 hydrate in mixed NaCl + $CaCl_2$ solution and in seawater. The average deviation for the two systems is less than 2%.

In general, this model can predict phase equilibrium of methane hydrate in various aqueous electrolyte solutions from low to high ionic strength with high accuracy. Table 2 and Table 3 give the temperature-pressure conditions for the stability of methane hydrate in aqueous NaCl solution and in seawater, respectively.

Carbon dioxide hydrate equilibrium

The HLV equilibria of carbon dioxide hydrate have been measured extensively. Larson (1955), Vlahakis et al. (1972), Bozzo et al. (1975), Dholabhai et al. (1993), Englezos and Hall (1994), and Tohidi et al. (1997) reported experimental studies of CO_2 hydrate equilibrium in aqueous NaCl solutions. However,

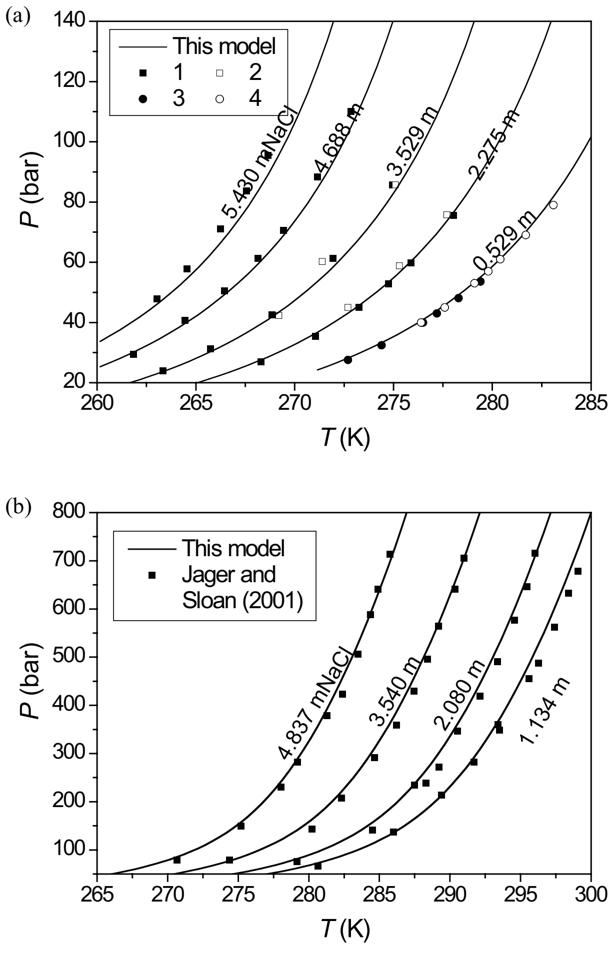

FIGURE 1. Prediction of the thermodynamic stability of CH_4 hydrate in CH_4-H_2O-NaCl system. (**a**) At pressures below 100 bar. The sources of the experimental data are: 1 = de Roo et al. (1983); 2 = Kharrat and Dalmazzone (2003); 3 = Dholabhai et al. (1991); 4 = Maekawa (2001). (**b**) At pressures greater than 100 bar.

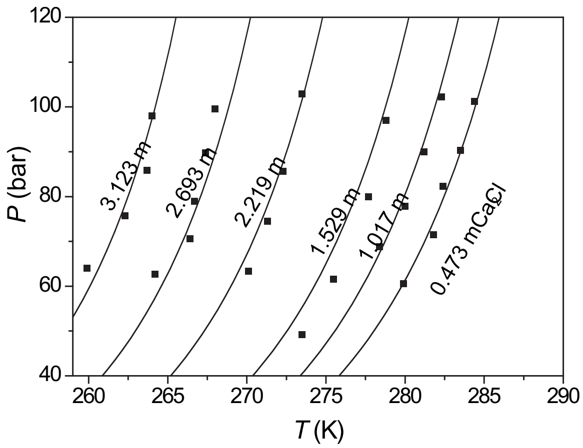

FIGURE 2. Prediction of the phase boundaries of CH_4 hydrate in the CH_4-H_2O-$CaCl_2$ system. The experimental data are from Kharrat and Dalmazzone (2003).

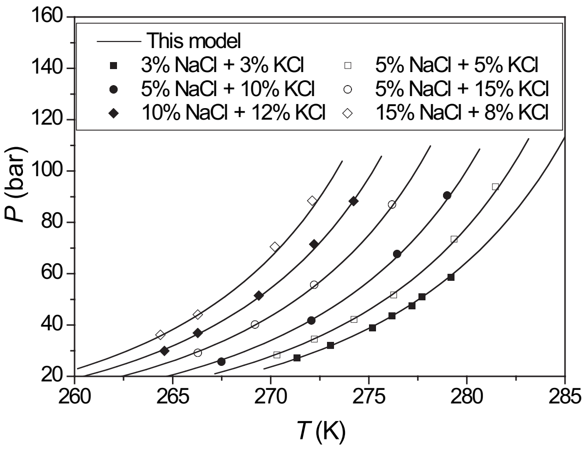

FIGURE 3. Prediction of the phase boundaries of CH_4 hydrate in aqueous NaCl-KCl solution. The experimental data are from Dholabhai et al. (1991).

TABLE 2. Temperature-pressure conditions for CH_4 hydrate stability in aqueous NaCl solution

1 *m* NaCl		2 *m* NaCl		3 *m* NaCl		4 *m* NaCl		5 *m* NaCl	
T (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)
270.15	24.46	266.15	20.95	262.15	18.28	258.15	16.33	253.15	13.75
271.15	26.94	267.15	23.09	263.15	20.18	259.15	18.15	254.15	15.23
272.15	29.69	268.15	25.47	264.15	22.29	260.15	20.07	255.15	16.86
273.15	32.74	269.15	28.10	265.15	24.62	261.15	22.20	256.15	18.67
274.15	36.12	270.15	31.02	266.15	27.20	262.15	24.57	257.15	20.69
275.15	39.88	271.15	34.26	267.15	30.08	263.15	27.20	258.15	22.92
276.15	44.08	272.15	37.87	268.15	33.27	264.15	30.13	259.15	25.58
277.15	48.76	273.15	41.89	269.15	36.84	265.15	33.40	260.15	28.39
278.15	54.01	274.15	46.39	270.15	40.82	266.15	37.06	261.15	31.52
279.15	59.91	275.15	51.44	271.15	45.28	267.15	41.15	262.15	35.03
280.15	66.57	276.15	57.12	272.15	50.30	268.15	45.76	263.15	38.97
281.15	74.12	277.15	63.54	273.15	55.95	269.15	50.95	264.15	43.40
282.15	82.73	278.15	70.83	274.15	62.36	270.15	56.84	265.15	48.41
283.15	92.59	279.15	79.14	275.15	69.65	271.15	63.53	266.15	54.10
284.15	103.95	280.15	88.68	276.15	78.00	272.15	71.19	267.15	60.58
285.15	117.12	281.15	99.69	277.15	87.61	273.15	80.00	268.15	68.01
286.15	132.47	282.15	112.48	278.15	98.75	274.15	90.23	269.15	76.58
287.15	150.42	283.15	127.44	279.15	111.77	275.15	102.18	270.15	86.56
288.15	171.43	284.15	145.00	280.15	127.07	276.15	116.25	271.15	98.28
289.15	195.98	285.15	165.66	281.15	145.13	277.15	132.94	272.15	112.14
290.15	224.52	286.15	189.92	282.15	166.49	278.15	152.79	273.15	128.68
291.15	257.44	287.15	218.26	283.15	191.71	279.15	176.40	274.15	148.51
292.15	295.04	288.15	251.10	284.15	221.27	280.15	204.35	275.15	172.26
293.15	337.55	289.15	288.77	285.15	255.61	281.15	237.14	276.15	200.58
294.15	385.06	290.15	331.48	286.15	295.03	282.15	275.12	277.15	233.99
295.15	437.71	291.15	379.35	287.15	339.71	283.15	318.52	278.15	272.87
296.15	495.52	292.15	432.48	288.15	389.75	284.15	367.47	279.15	317.40
297.15	558.61	293.15	490.93	289.15	445.22	285.15	421.98	280.15	367.67
298.15	627.09	294.15	554.75	290.15	506.17	286.15	482.12	281.15	423.70
299.15	701.13	295.15	624.11	291.15	572.69	287.15	547.97	282.15	485.54
300.15	780.88	296.15	699.13	292.15	644.94	288.15	619.64	283.15	553.23
301.15	866.64	297.15	780.03	293.15	723.07	289.15	697.31	284.15	626.94
302.15	958.71	298.15	867.12	294.15	807.37	290.15	781.24	285.15	706.85
303.15	1057.53	299.15	960.69	295.15	898.12	291.15	871.77	286.15	793.24
304.15	1163.50	300.15	1061.25	296.15	995.74	292.15	969.27	287.15	886.52
305.15	1277.24	301.15	1169.24	297.15	1100.78	293.15	1074.30	288.15	987.10
306.15	1399.43	302.15	1285.31	298.15	1213.80	294.15	1187.53	289.15	1095.67
307.15	1531.01	303.15	1410.32	299.15	1335.61	295.15	1309.80	290.15	1212.92
308.15	1672.84	304.15	1545.20	300.15	1467.21	296.15	1442.08	291.15	1339.83
309.15	1826.28	305.15	1691.08	301.15	1609.74	297.15	1585.67	292.15	1477.69
310.15	1992.64	306.15	1849.40	302.15	1764.70	298.15	1742.27	293.15	1627.92
311.15	2173.77	307.15	2022.04	303.15	1933.85	299.15	1914.09	294.15	1792.70
				304.15	2119.67	300.15	2103.70	295.15	1974.90
								296.15	2177.95

there is some inconsistency between these data sets. Most data published by Englezos and Hall (1994) are inconsistent with the data reported by Dholabhai et al. (1993). The deviation of the equilibrium pressure is from 5 to 25%. The equilibrium pressures in 10 wt% NaCl solution published by Tohidi et al. (1997) agree well with those of Dholabhai et al. (1993), but the data for 20 wt% NaCl solution deviate from those of Dholabhai et al. (1993) by about 10%. Dholabhai et al. (1993), Englezos and Hall (1994), and Tohidi et al. (1997) also measured the formation/dissociation pressure of CO_2 hydrate in aqueous solutions containing electrolyte besides NaCl, such as KCl, $CaCl_2$, and NaCl + KCl. We note that no data are reported for CO_2 hydrate-liquid water-liquid carbon dioxide (HLL) equilibria.

Figure 4 compares the equilibrium pressure of CO_2 hydrate in aqueous NaCl solution predicted by this model with the experimental data. It is obvious that the predictions agree well with the experimental data when the weight percent of NaCl in solution is less than 10 wt%. The model also gives reasonable predictions in 15 wt% NaCl solutions, since the calculated values are located between the measurements of Dholabhai et al. (1993) and those of Englezos and Hall (1994). However, the predictions in 20 wt% NaCl solution are somewhat less accurate as compared to the measurements of Dholabhai et al. (1993) and Tohidi et al. (1997).

Figure 5 shows the prediction of this model for the equilibrium pressure of CO_2 hydrate in aqueous $CaCl_2$ solutions. For the aqueous solutions with low and moderate concentration of $CaCl_2$ concentration, the predictions are consistent with the experimental data. For 15 and 20% $CaCl_2$ solutions, the deviation between the experimental data of Dholabhai et al. (1993) and those of Zhang and Frantz (1989) is large. The prediction of this model for the dissociation temperature of CO_2 hydrate is higher than that reported by Dholabhai et al. (1993) but is lower than that reported by Zhang and Frantz (1989).

Figure 6 shows that this model can predict the stability of CO_2 hydrate in seawater (Salinity = 35 wt‰) with high accuracy. Table 4 and Table 5 give the temperature-pressure conditions for the stability of carbon dioxide hydrate in aqueous NaCl solution

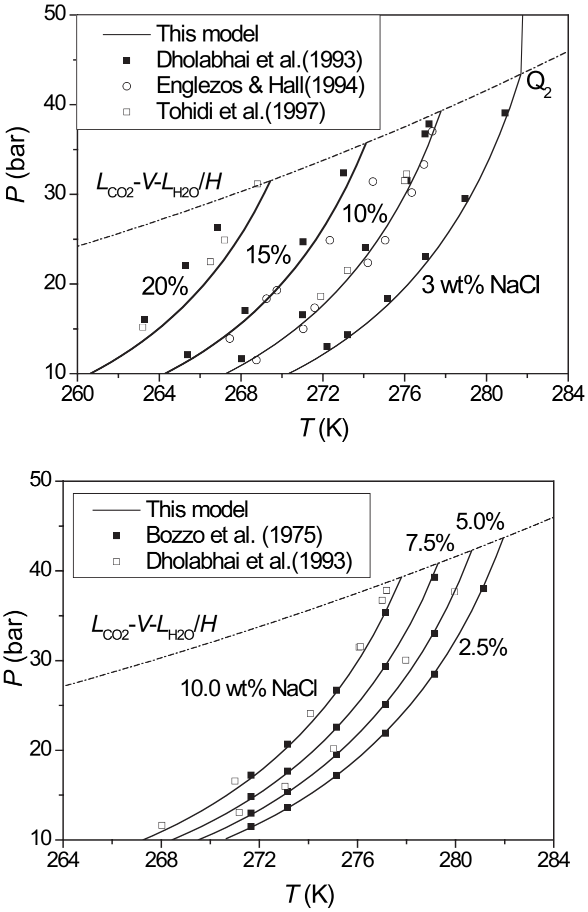

FIGURE 4. Prediction of the phase boundaries of CO_2 hydrate in CO_2-H_2O-NaCl system. The solid line represents the prediction of this study and the dashed line represents L_{CO_2}-V-L_{H_2O}/H equilibrium.

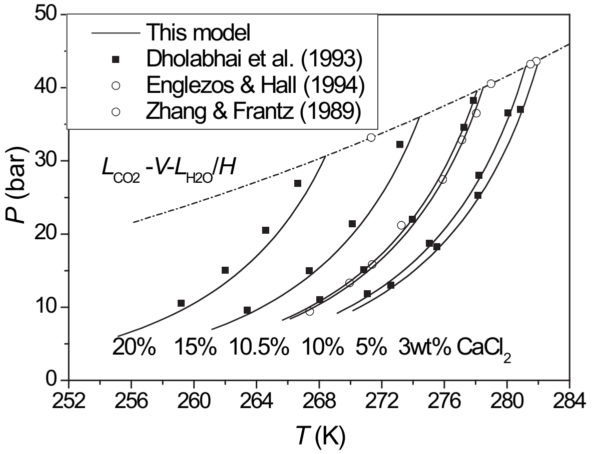

FIGURE 5. Prediction of the phase boundaries of CO_2 hydrate in CO_2-H_2O-$CaCl_2$ system. The concentrations of $CaCl_2$ of the data of Zhang and Frantz (1989) are 3.2, 5.3, 10, and 21 wt%.

and in seawater, respectively.

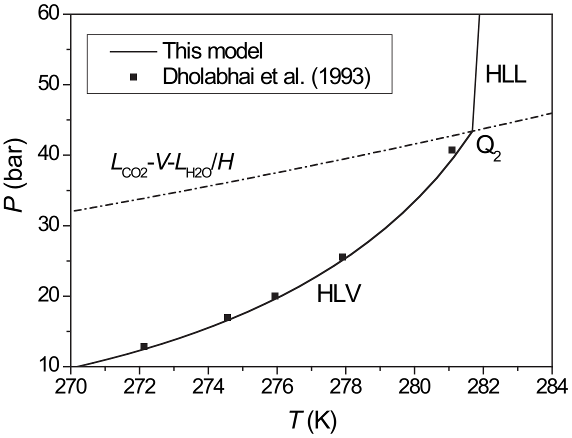

FIGURE 6. Prediction of the stability CO_2 hydrate in seawater (Salinity = 35 wt‰).

TABLE 3. Temperature-pressure conditions for CH_4 hydrate stability in seawater (Salinity = 35 wt‰)

T (K)	P (bar)
271.15	24.47
272.15	26.94
273.15	29.68
274.15	32.70
275.15	36.07
276.15	39.80
277.15	43.96
278.15	48.60
279.15	53.80
280.15	59.64
281.15	66.22
282.15	73.67
283.15	82.15
284.15	91.84
285.15	102.99
286.15	115.89
287.15	130.89
288.15	148.39
289.15	168.84
290.15	192.71
291.15	220.44
292.15	252.43
293.15	288.99
294.15	330.36
295.15	376.69
296.15	428.05
297.15	484.53
298.15	546.21
299.15	613.20
300.15	685.66
301.15	763.73
302.15	847.72
303.15	937.82
304.15	1034.50

Note: The chemical composition of seawater is from Holland (1978).

There exists a quadruple invariant point (Q_2 point as shown in Fig. 6) in the phase diagram of CO_2 hydrate where CO_2 hydrate phase coexists with liquid CO_2, vapor CO_2, and aqueous solution phase. For CO_2-H_2O binary system, the temperature of Q_2 is invariant at about 283.15 K. When electrolytes are present in the aqueous phase, the temperature of Q_2 decreases. Therefore, to determine the salinity of fluid inclusions, an accurate prediction of the dissociation temperature of CO_2 hydrate at Q_2 point is required (Collins 1979; Diamond 1994).

Figure 7 compares the prediction of this model for the dissociation temperature of CO_2 hydrate at Q_2 point in NaCl, KCl, and NaCl + KCl (of equal molality ratio) solutions with

TABLE 4. Temperature-pressure conditions for CO_2 hydrate stability in aqueous NaCl solution

Type of Equilibria*	1 *m* NaCl		2 *m* NaCl		3 *m* NaCl		4 *m* NaCl		5 *m* NaCl	
	T (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)	*T* (K)	*P* (bar)
Q_1	268.30	9.07	264.82	7.92	261.01	6.81	256.72	5.71	251.82	4.64
HLV	269.15	9.99	265.15	8.23	262.15	7.76	257.15	6.00	252.15	4.83
	270.15	11.20	266.15	9.22	263.15	8.72	258.15	6.74	253.15	5.43
	271.15	12.57	267.15	10.35	264.15	9.79	259.15	7.58	254.15	6.11
	272.15	14.13	268.15	11.63	265.15	11.01	260.15	8.52	255.15	6.88
	273.15	15.91	269.15	13.08	266.15	12.40	261.15	9.59	256.15	7.74
	274.15	17.95	270.15	14.73	267.15	13.98	262.15	10.80	257.15	8.72
	275.15	20.30	271.15	16.62	268.15	15.80	263.15	12.18	258.15	9.84
	276.15	23.03	272.15	18.81	269.15	17.88	264.15	13.76	259.15	11.11
	277.15	26.25	273.15	21.34	270.15	20.31	265.15	15.57	260.15	12.56
	278.15	30.07	274.15	24.30	271.15	23.15	266.15	17.67	261.15	14.22
	279.15	34.73	275.15	27.82	272.15	26.52	267.15	20.11	262.15	16.14
	280.15	40.60	276.15	32.08	273.15	30.59	268.15	22.98	263.15	18.38
			277.15	37.37	274.15	35.65	269.15	26.40	264.15	21.00
							270.15	30.55	265.15	24.11
									266.15	27.87
Q_2	280.35	41.98	277.40	38.92	274.17	35.76	270.55	32.49	266.42	29.03
HLL	281.15	97.37	278.15	84.67	275.15	101.10	271.15	50.15	267.15	51.04
	282.15	213.53	279.15	201.14	276.15	223.74	272.15	165.93	268.15	170.76
	283.15	348.09	280.15	336.78	277.15	366.15	273.15	303.54	269.15	313.80
	284.15	500.65	281.15	491.06	278.15	528.41	274.15	462.09	270.15	479.63
	285.15	672.06	282.15	665.03	279.15	711.99	275.15	642.76	271.15	669.80
	286.15	864.47	283.15	861.02	280.15	919.67	276.15	847.86	272.15	886.04
	287.15	1081.3	284.15	1082.6	281.15	1155.2	277.15	1079.9	273.15	1127.6

* Q_1 means the quadruple invariant point where CO_2 hydrate phase, ice phase, liquid water phase, and vapor CO_2 phase coexistence; Q_2 means the quadruple invariant point where CO_2 hydrate phase, liquid water phase, vapor CO_2 phase, and liquid CO_2 phase coexistence; HLV represents CO_2 hydrate-liquid water-vapor CO_2 phase equilibrium; HLL represents CO_2 hydrate-liquid water-liquid CO_2 phase equilibrium.

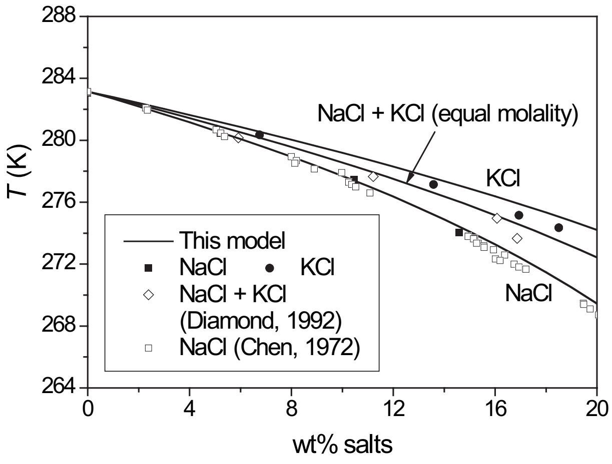

FIGURE 7. Prediction of the dissociation temperature of CO_2 hydrate at Q_2 point in NaCl, KCl, and NaCl + KCl (of equal molality ratio) solutions.

TABLE 5. Temperature-pressure conditions for CO_2 hydrate stability in seawater (Salinity = 35 wt‰)

T (K)	*P* (bar)
269.74	9.581
270.15	10.02
271.15	11.23
272.15	12.60
273.15	14.16
274.15	15.93
275.15	17.96
276.15	20.30
277.15	23.02
278.15	26.20
279.15	29.99
280.15	34.58
281.15	40.33
281.58	43.31
282.15	76.50
283.15	187.4
284.15	317.1
285.15	464.5
286.15	630.2
287.15	815.9
288.15	1024.

Note: The chemical composition of seawater is from Holland (1978).

the experimental data of Chen (1972) and Diamond (1992). For the Q_2 point of CO_2 hydrate in aqueous NaCl solution, the prediction of this model agrees well with the experimental data of Chen (1972) and Diamond (1992) at salinity less than 15 wt%. At higher salinity, this model overestimates slightly the temperature of Q_2. For CO_2-H_2O-KCl system, the temperature of Q_2 is also slightly overestimated; however, the deviation is less than 0.6 K.

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APPENDIX A. THE IONIC STRENGTH DEPENDENCE OF PITZER-SILVESTER MODEL

Equation A1 is the equation rearranged by Felmy and Weare (1986) for the osmotic coefficient, ϕ,

$$\left(\sum_i m_i\right)(\phi-1)=2\left\{-\frac{A^{\phi}I^{1.5}}{1+1.2I^{0.5}}+\sum_c\sum_a m_c m_a\left(B^{\phi}_{ca}+ZC_{ca}\right)\right.$$
$$+\sum\sum_{c<c'} m_c m_{c'}\left(\Phi^{\phi}_{cc'}+\sum_a m_a\psi_{cc'a}\right)+\sum\sum_{a<a'} m_a m_{a'}\left(\Phi^{\phi}_{aa'}+\sum_c m_a\psi_{aa'c}\right)$$
$$\left.+\sum_n\sum_c m_n m_c\lambda_{nc}+\sum_n\sum_a m_n m_a\lambda_{na}+\sum_n\sum_c\sum_a m_n m_c m_a\zeta_{nca}\right\} \quad \text{(A1)}$$

The meanings of the parameters presented in Equation A1 have been explained in the text. Here we list the equations to describe the ionic strength dependence of the second virial coefficients, B_{ca} and Φ_{ijk}.

The ionic strength, I, was defined as

$$I=\frac{1}{2}\sum_i m_i z_i^2 \quad \text{(A2)}$$

where z_i is the charge of ion i.

Function Z in Equation A1 was defined as

$$Z=\sum_i m_i\left|z_i\right| \quad \text{(A3)}$$

The ionic strength dependence of the second virial coefficient, B^{ϕ}_{MX} was given by Pitzer (1973) as

$$B^{\phi}_{MX}=\beta^{(0)}_{MX}+\beta^{(1)}_{MX}e^{-\alpha_{MX}\sqrt{I}}+\beta^{(2)}_{MX}e^{-12\sqrt{I}} \quad \text{(A4)}$$

when either cation M or anion X is univalent, $\alpha_{MX}=2.0$. For 2-2 or higher valence pairs, $\alpha_{MX}=1.4$. In most cases $\beta^{(2)}$ equals zero for univalent type pairs. For 2-2 electrolytes a non-zero $\beta^{(2)}$ is more common.

The single electrolyte third virial coefficient, C_{MX}, was defined as

$$C_{MX}=C^{\phi}_{MX}/2\sqrt{\left|z_M z_X\right|} \quad \text{(A5)}$$

The second virial coefficient, Φ, which accounts for the interactions between ions of like sign, is given the following form

$$\Phi^{\phi}_{ij}=\Theta_{ij}+{}^{E}\Theta_{ij}(I)+I\,{}^{E}\Theta'_{ij}(I) \quad \text{(A6)}$$

where Θ_{ij} is a single parameter for each pair of anions or each pair of cations. The functions, ${}^{E}\Theta_{ij}(I)$ and ${}^{E}\Theta'_{ij}(I)$ account for the electrostatic unsymmetrical mixing effects and depend on ionic strength and the electrolyte pair type. Integrals defining these terms are given by Pitzer (1975) and are summarized in the Appendix of the paper of Pitzer (1987).

$\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^{ϕ}_{MX} for each cation-anion pair are determined from the experimental data of aqueous solution of single electrolyte MX. Θ_{ij} for each cation-cation and anion-anion pair, and ψ_{ijk} for each cation-cation-anion and anion-anion-cation triplet can be derived from the experimental data of common-ion mixed electrolytes solutions.