Measurements and Predictions of Hydrate-Containing Phase Equilibria for CO_2, Methane and Ethane in the Presence of NaCl

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ABSTRACT

Phase equilibria involving gas hydrates are of importance in natural gas recovery and carbon dioxide sequestration. Due to high equilibrium pressures two- and three-phase equilibria for gas hydrates containing systems have been computed using equations of state and van der Waals and Platteeuw model for fugacity of guest components in gas hydrates. So far the inhibition effect has been accounted for by excess Gibbs function models, which are less appropriate than an equation of state for high-pressure applications. In the present study ethane and carbon dioxide solubilities in hydrate-liquid water equilibria containing sodium chloride were measured. Carbon dioxide concentrations in the aqueous phase were determined by expanding dissolved gas from the external sampling loop. Ethane solubilities in the aqueous phase were measured by an indirect method due to very small solubility. The presence of the salt were found to show the inhibition effect that increases equilibrium pressure in three-phase equilibria and the salting-in effect that increases gas solubilities in two-phase equilibria. Phase equilibria of measured and literature data for the systems were predicted using the electrolyte lattice fluid equation of state, in which long-range electrostatic interactions were modeled using the mean spherical approximation. The present model was found to predict various phase equilibria including inhibition and salting-in effects.

Keywords: gas hydrate, hydrocarbon, electrolyte, phase equilibria, equation of state

1. INTRODUCTION

Gas hydrates are water crystal structures stabilized by guest molecules such as carbon dioxide, methane and ethane. Phase equilibria involving gas hydrates are of importance in natural gas recovery and carbon dioxide sequestration. Studies on gas hydrates were comprehensively reviewed in Sloan's book (Sloan, 1999). Various three-phase equilibria involving gas hydrates and the inhibition effects of alcohols and electrolytes on the formation of gas hydrates have been extensively studied. However, studies on two-phase equilibria and inhibition effects involving gas hydrates are relatively rare. The two-phase equilibria of hydrate and water-rich liquid phase were experimentally studied for carbon dioxide, methane and ethane (Yang et al., 2000, 2001; Servio and Englezos, 2002; Kim et al., 2003; Someya et al., 2005). For carbon dioxide systems liquid samples were expanded to determine the amount of dissolved gas in water in equilibrium with gas hydrates (Yang et al., 2000; Servio and Englezos, 2002; Someya et al., 2005). The expansion method is not accurate enough for small solubility measurements for methane and ethane systems. Kim et al. (2003) used an indirect method in which equilibrium temperatures were measured for predetermined liquid phase compositions. Effects of inhibitors have not been reported on hydrate containing two-phase equilibria.

High pressure two- and three-phase equilibria for systems containing gas hydrates have been computed using equations of state and van der Waals and Platteeuw model for the fugacity of guest components in gas hydrates. So far the inhibition effect has mostly been modelled for three-phase equilibria using an excess Gibbs function model, which are less appropriate than an equation of state for high-pressure applications. For various phase equilibrium calculations in the absence of inhibitors present authors applied lattice fluid equation (Yang et al., 2000, 2001; Kim et al., 2003), which was extended to electrolyte containing systems recently.

In the present study experimental hydrate-containing two-phase equilibria for carbon dioxide or ethane in the presence of sodium chloride are reported. The previous computation methods (Yang et al., 2000, 2001; Kim et al., 2003) are extended to two- and three-phase equilibria containing sodium chloride using the electrolyte lattice fluid equation of state.

2. THERMODYNAMIC MODELS

The equality condition of chemical potential for different phases is the basic relations for phase equilibrium calculations. A Helmholtz free energy model applicable to fluid phases conveniently yields expressions for volumetric equation of state (EOS) and chemical potential. Thus for given temperature, pressure and phase compositions, the EOS is solved for phase volume, which in turn is used for the calculation of the chemical potential in fluid phases. Chemical potential is expressed using the reference state of pure ideal gas at 1 bar. The phase equilibrium condition for fluid phases α and β is then the equality of the chemical potential departure from the ideal gas value, μ_i^0 at 1 bar and system temperature.

$$\mu_i^\alpha - \mu_i^0 = \mu_i^\beta - \mu_i^0 \tag{1}$$

This relation is extended to multi-phase equilibria by adding the equality relation for the corresponding phase. For hydrate-containing phase equilibria, we need the chemical potential of water in hydrate phases that has been modelled by van der Waals and Platteeuw (1959).

$$\mu_W^H = \mu_W^{EH} - RT\sum_m \nu_m \ln[1+\sum_j C_{j,m} f_j^\Pi] \tag{2}$$

where m denotes the cavity type which guest molecules can occupy, μ_W^{EH} is the chemical potential of the hypothetical empty hydrates, ν_m is the number of cavities of type m per water molecule in the hydrate lattice, $C_{j,m}$ is the Langmuir constant of guest component j for the mth type of cavities, and f_j^Π is the fugacity of a component j in the equilibrium fluid phase Π that may be liquid or vapor. Fugacity is related with chemical potential by

$$f_j^\Pi = P^0 \exp[(\mu_j^\Pi - \mu_j^0)/RT] \tag{3}$$

The Langmuir constant depends on temperature according to the relation,

$$C_{j,m}(T) = \frac{4\pi}{kT}\int_0^{R_i} \exp\left(-\frac{W(r)}{kT}\right) r^2 dr \tag{4}$$

where k is Boltzmann's constant and $W(r)$ is a spherically symmetric cell potential function. The chemical potential of the empty hydrate is also represented by a departure function from ideal gas at 1bar,

$$\mu_W^{EH} = \mu_W^0 + RT\ln\left(P_W^{satEH}\phi_W^{satEH}\right) + V_W^{satEH}[P - P_W^{satEH}] \tag{5}$$

The fugacity coefficient of water, ϕ_W^{satEH}, in the empty hydrate phase is assumed to be unity.

In the absence of electrolytes two- and three-phase equilibria for hydrate-containing systems were computed using a non-random lattice fluid based equation of state, in which the Helmholtz free energy is represented by a sum of athermal, residual, and association contributions. The model has been applied to hydrate-containing two- and three-phase equilibria (Yang et al., 2000, 2001; Kim et al., 2003). Working equations and the calculated results are collected in the cited references. With the addition of the long-range interaction term due to the mean spherical approximation (Ball et al., 1985), the equation of state is extended to systems with electrolytes in the present study, details of which is described in a separate paper in preparation. Working equation for the long-range contribution is given below.

The long-range contribution is from the mean spherical approximation (Ball et al., 1985). The MSA model describes the long-rang interactions between ions in electrolyte solutions and is based on the primitive model in which ions are considered as the hard spheres in a dielectric medium. The Helmholtz energy for long-range contribution is written as

$$\beta A_{lr} = \frac{\Gamma^3 V}{3\pi} - \frac{\alpha^2}{4\pi} \sum\nolimits_{ions} \left(\frac{N_k z_k^2 \Gamma}{1 + \Gamma \sigma_k} \right) \tag{7}$$

where N_k is the mole number of ion species k, z_k is the charge of ion species k and σ_i is the hydrated ionic diameter that is adjustable for each salts. Volume, V, is written in the lattice frame by

$$V = V_H N_r \tag{8}$$

where V_H is the volume of a lattice cell. The shielding parameter Γ is obtained from

$$4\Gamma^2 = \alpha^2 \sum\nolimits_{ions} \frac{N_k}{V} \left(\frac{z_k}{1 + \Gamma \sigma_k} \right)^2 \tag{9}$$

$$\alpha^2 = e^2 \beta / \varepsilon_0 D \tag{10}$$

$$D = 1 + (D_S - 1) \frac{1 - \xi_3}{1 + \xi_3 / 2} \tag{11}$$

$$\xi_3 = (\pi / 6V) \sum\nolimits_{ions} N_k \sigma_k^3 \tag{12}$$

e is the charge of an electron. ε_o is the dielectric permitivity of vacuum, and D and D_s are dielectric constants of solution and pure solvent, respectively. The Helmholtz free energy as a function of temperature, volume and mole numbers readily yield expressions for thermodynamic properties. Pressure and chemical potentials are obtained from the partial derivatives of Helmholtz free energy with respect to volume and solute mole numbers, respectively.

$$\beta P_{lr} = -\frac{\Gamma^3}{3\pi} - \frac{\alpha^2 N_a}{4\pi D} \left(\frac{\partial D}{\partial V} \right)_{T,N} \sum\nolimits_{ions} \left(\frac{N_k z_k^2 \Gamma}{1 + \Gamma \sigma_k} \right) \tag{13}$$

where

$$\left(\frac{\partial D}{\partial V} \right)_{T,N} = \frac{3}{2V} (D_S - 1) \frac{\xi_3}{(1 + \xi_3 / 2)^2} \tag{14}$$

and

$$\beta \mu_{i,lr} = -\frac{\alpha^2}{4\pi} \frac{z_I^2 \Gamma}{(1 + \Gamma \sigma_i)} + \frac{\alpha^2}{4\pi D} \left(\frac{\partial D}{\partial N_i} \right)_{T,V,N_j} \sum\nolimits_{ions} \left(\frac{N_k z_k^2 \Gamma}{1 + \Gamma \sigma_k} \right) \tag{15}$$

where

$$\left(\frac{\partial D}{\partial N_i} \right)_{T,V,N} = -\frac{N \pi \sigma_i^3}{4V} (D_S - 1) \Big/ \left(1 + \xi^3 / 2\right)^2 \tag{16}$$

The mean spherical approximation is in the McMillan-Meyer framework and solvent is approximated as dielectric continuum. Therefore, partial derivatives with respect to solvent mole numbers vanish.

3. PARAMETERS

For physical interactions represented by athermal and residual contributions segment number, r_i, and interaction energy parameters, ε_i, are needed and obtained by fitting saturated liquid density and vapour pressure for non-electrolytes. They are correlated as functions of temperature.

$$\varepsilon_i / k = \varepsilon_a + \varepsilon_b (T - T_0) + \varepsilon_c \left[T \ln(T_0 / T) + T - T_0 \right] \tag{17}$$

$$r_i = r_a + r_b (T - T_0) + r_c \left[T \ln(T_0 / T) + (T - T_0) \right] \tag{18}$$

where T_0 is 298.15 K. The correlation parameters are presented in Table 1. These parameters are obtained from (Kim et al., 2003) for water, methane and ethane with the change of T_0 from 273.15K to 298.15K. CO_2 parameters are from You et al. [1994] by converting to present temperature correlations given by eqns (17) and (18). For interactions between segments of different species a binary interaction parameter is required.

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}(1 - k_{ij}) \tag{19}$$

The binary interaction parameter is assumed to be temperature dependent and represented by,

$$k_{ij} = A + B/T + C/T^2 . \tag{20}$$

C value in eqn (20) for interactions between water and CO_2 is fitted to the vapour-liquid equilibrium data of Knapp et al. (1982) salt up to 360K and the hydrate containing equilibrium data of Kim et al. (2003) and the present experimental data in Table 2. For other interactions C is set to zero. These parameters are listed in Table 3.

Association contribution is characterized by the numbers of donors and/or acceptors and association free energy for each type of hydrogen bonds. For water with two donors and two acceptors per molecule the previously fitted hydrogen-bonding energy and entropy were –19.95 kJ/mol and –25.0 J/mol-K for each bond in a temperature range of 240~295 K (Kim et al, 2003).

Electrolyte contributions are from physical interactions, associations and long-range contributions. Ion segment numbers, r_i, are obtained from crystal radii by the method described (*). Segment interaction energies, ε_i, and hydrated ionic diameters, σ_i, are assumed to be identical for cations and anions of an electrolyte. Only cations are assumed to participate in association to form hydration shell. For sodium ion the number of donors is assumed to be 4. Solution densities (*), osmotic coefficients and mean activity coefficients at 298. 15 K (Robinson and Stokes, 1955) were fitted to obtain 3.02×10^{-10} m for σ_i, ε_i, and 24.86 kJ/mol for the hydration free energy. For interactions between water and ion k_{ij} is set to zero. ε_i and r_i are given in Table 1.

The vapour pressure of empty hydrates in (5) is from Kim et al. (2003) that are fitted to equilibrium pressures of multi-guest and simple hydrates. The regressed vapour pressures are represented as

$$\ln[P_W^{satEH}/MPa] = 15.107 - 6072.25/T \quad \text{for structure I} \tag{20}$$

and

$$\ln[P_W^{satEH}/MPa] = 15.212 - 6121.34/T \quad \text{for structure II} \tag{21}$$

The molar volumes of empty hydrate are from the correlations of Avlonitis (1994). Structural information of hydrates such as ν_m in eqn (2) is from Sloan (1997).

Kihara potential with spherical core (McKoy and Sinanoglu, 1963) was used as the potential function for Langmuir constant evaluation. For a hydrate cell the potential is represented by

$$W(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^{6}}{R^{5}r}\left(\delta^{4} + \frac{a}{R}\delta^{5}\right)\right] \tag{22}$$

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right] \tag{23}$$

The Kihara potential parameters ε, a, and σ are unique to each guest molecule, but they remain unchanged in the different cavity types. In this work, they are obtained from the three-phase equilibrium pressure of methane, ethane and carbon dioxide. With spherical core radii(a) fixed at Sloan (1998) values, remaining two parameters were fitted to available data at four different temperatures from the literature and correlated. A set of values least sensitive to temperature variation was chosen and slightly adjusted to give better mixed-guest equilibria. The potential parameters are from Kim et al. and areshown in Table 4.

4. EXPERIMENTS

The solubilities of carbon dioxide and ethane in sodium chloride solutions for hydrate (H)-liquid water (Lw) equilibria were measured. Carbon dioxide concentrations in the aqueous phase that are in equilibrium with hydrates were determined by expanding dissolved gas in the sampled liquid phase. The detailed experimental procedures were described in Yang et al. (2000, 2001). Ethane solubilities in the aqueous phase were measured by an indirect method due to very small solubility and the experimental procedures were given in Kim et al. (2003). In this method the amounts of gas and sodium chloride solution were pre-determined and the system was bought to equilibrium for the composition at constant pressures by slowly varing the temperature. The equilibrium temperature was determined by visual observations when negligible amounts of gas hydrates were present in the system. To apply the indirect method the initial compositions need to be found by trial to be in the two-phase region close to solubility limits. The accuracy in measured mole fraction of carbon dioxide and ethane were estimated to be less than 7.7 and 5.3 %, respectively. Solubility data are collected in Table 2.

5 RESULTS AND DISCUSSIONS

Electrolytes are known to inhibit hydrate formation. Literature data for Lw-H-V 3-phase equilibriua containing sodium chloride are listed and compared with predicted results by the present electrolyte lattice fluid EOS in Table 5. It is noted that parameters involving electrolytes are determined in non-hydrate forming conditions. They are also shown in Figs. 1 and 2. The increase of the three-phase equilibrium pressure in the presence of sodium chloride is fairly accurately predicted for carbon dioxide and methane by the present model below 10 wt% salt concentrations. For methane in higher salt concentrations some systematic deviations are observed. In general the calculated results are less accurate above 10 wt%.

Solubilities of carbon dioxide and ethane in Lw-H two-phase equilibria increase with the increase of sodium chloride concentration as shown in Table 2. The table also shows that present experimental solubility data and salting-in effects are fairly accurately calculated using the present equation of state. The average absolute deviation (AAD%) for carbon dioxide and ethane were 7.0 and 0.3 %, respectively, when the present experimental data are compared with predicted values by electrolyte lattice fluid EOS. Effects of electrolytes in two-phase equilibria with hydrates are further examined below.

The solubility data of carbon dioxide in the presence of gas hydrate are shown in Fig. 3. The figure shows that solubilites increase with the addition of sodium chloride indicating salting-in effect. This behaviour is contrary to general salting-out effect of electrolytes in the absence of hydrates. The figure also shows that solubilities increase with the increase of temperature. This tendency is in agreements with Yang et al. (2001), Servio and Englezos (2002) and Someya et al. (2005) for salt-free systems. The pressure effect shown in the figure is neither strong nor conclusive considering the scatter of the data points. For salt-free carbon dioxide and water mixtures with hydrate Yang et al. observed slightly decreasing solubilities with pressure. However, Someya et al. noted that solubilities increase with pressure using their data for salt-free systems that are in general agreements with Yang et al. data but less scattered. Servio and Englezos pointed out that the pressure effect is not strong.

Solubilities of ethane in the presence of hydrates are shown in Figure 4. In the indirect method used for the solubility measurements liquid phase compositions are fixed. Lines drawn in the figure are predicted isobars, which should increase with increase of temperature as data points show and in accordance with the general observation discussed above. Then gas solubilities in liquid phase should increase with the addition of sodium chloride and should decrease with pressure. The only problem is in the pressure effect that is contrary to the observation of Someya et al. electrolytewas found to increase with increasing temperature for hydrate-containing phase equilibria as reported by Servio and Englezos (2002) and Someya et al. (2005).

6. CONCLUSIONS

The H-Lw equilibria containing sodium chloride for carbon dioxide and ethane + water system were experimentally studied. The accuracy in measured mole fraction of carbon dioxide and ethane were estimated to be less than 7.7 and 5.3 %, respectively.

H-Lw and H-Lw-V containing sodium chloride were predicted and compared with experimental data from literatures and present works. The electrolyte lattice fluid equation of state was used for prediction. The present model was found to predict hydrate phase equilibria with sodium chloride including inhibition and salting-in effects.

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Table 1. Physical parameters for electrolyte NLF-HB EOS

species	ε_a [K]	ε_b	ε_c	r_a	$r_b\times10^3$	r_c
H_2O	142.172	0.216	-1.305	1.817	-1.067	-0.033
CO_2	88.810	0.006	-0.052	3.670	2.436	-0.068
CH_4	53.542	0.016	-0.103	3.911	0.942	0.004
C_2H_6	76.378	0	-0.110	5.221	-0.009	0.001
Na	9.492	0	0	0.488	0	0
Cl	9.492	0	0	3.375	0	0

Table 2. Experimental solubilities for H-Lw equilibria for carbon dioxide and ethane containing sodium chloride

gases	salt molality	P/MPa	T / K	Solute mole fraction	
				measured	calculated
CO_2	0.5 M	9.20	279.3	0.0263	0.0243
		9.31	279.3	0.0264	0.0241
		10.27	279.3	0.0259	0.0240
		10.51	279.2	0.0260	0.0239
		12.40	279.4	0.0267	0.0238
		9.36	280.3	0.0272	0.0264
		11.90	280.3	0.0269	0.0257
		14.24	280.3	0.0270	0.0254
		14.52	280.3	0.0270	0.0252
C_2H_6	1 M	10.00	275.5	0.000496	0.000497
		15.00	276.0	0.000496	0.000496
		20.00	276.7	0.000496	0.000499

Table 3. Binary interaction energy parameters for eqn (19) between water and guest molecules

	CO_2+H_2O	CH_4+H_2O	C_2H_6+H_2O	CO_2+Cl	CH_4+Cl	C_2H_6+Cl
A	-3.509	0.7610	0.6147	5.10	0	0.75
B	2134.7	-177.23	-120.25	0	0	0
C	-3163277	0	0	0	0	0

Table 4. Optimized Kihara potential parameters for structure I and II hydrate formers

species	ε / k [K]	σ [Å]	a [a)] [Å]
CO_2	143.07	2.9298	0.6805
CH_4	141.52	2.9488	0.3834
C_2H_6	145.52	3.2849	0.5651

a) radius of the spherical core (*a*) was from Sloan (1998)

Table 5. Comparisons of experimental and calculated equilibrium pressures for 3-phase equilibria containing sodium chloride

guests	no. of points	AAD %	T range/K	P range/MPa	salt concentration	Reference
CO_2	31	6.7	271.6 – 280.4	1.32 – 4.23	4.79 – 6.13 wt %	Vlahakis et al. (1972)
	6	1.6	272.2 – 280.9	1.30 – 3.91	3 wt %	Dholabhai et al. (1993)
	5	5.1	271.2 – 279.2	1.31 – 3.77	5 wt %	Dholabhai et al. (1993)
	6	10.7	271.0 – 277.2	1.66 – 3.78	10 wt %	Dholabhai et al. (1993)
CH_4	11	3.6	280.7 – 299.1	6.60 – 67.8	2.001 mol %	Jager and Sloan (2001)
	11	8.2	279.2 – 296.0	7.51 – 71. 6	3.611 mol %	Jager and Sloan (2001)

	10	17.1	274.4 – 291.0	7.92 – 70. 6	5.994 mol %	Jager and Sloan (2001)
	10	33.0	270.7 – 285.8	7.85 – 71.3	8.014 mol %	Jager and Sloan (2001)
	8	22.9	270.0 – 284.3	2.59 – 13.4	10 wt %	Kobayashi et al. (1951)
	6	0.8	274.4 – 277.2	3.24 – 4.30	3 wt %	Dholabhai et al. (1991)

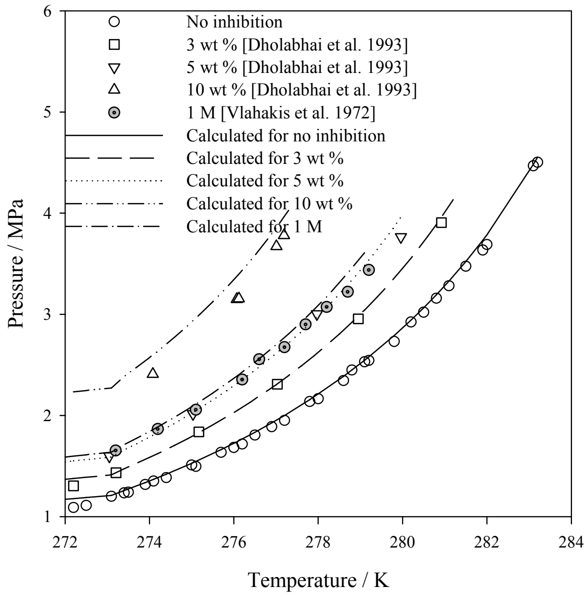

Fig. 1. Comparisons of predicted dissociation pressures with experimental data for carbon dioxide hydrate in equilibrium with aqueous sodium chloride solution.

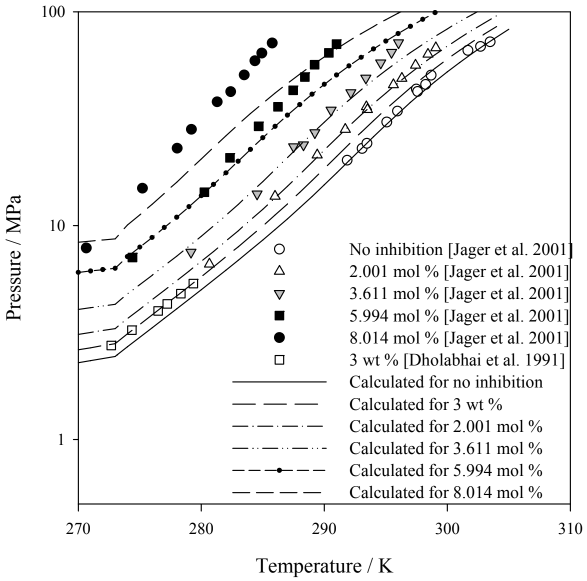

Fig. 2. Comparisons of predicted dissociation pressures with experimental data for methane hydrate in equilibrium with aqueous sodium chloride solution.

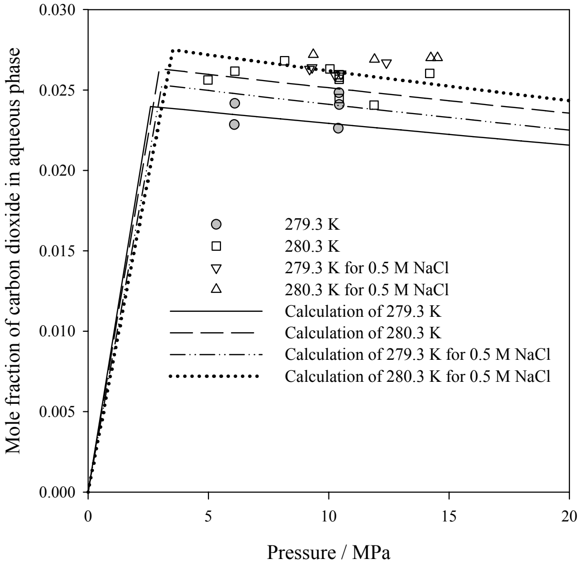

Fig. 3. Comparisons of predicted solubilities with experimental data for carbon dioxide in aqueous sodium chloride solutions in equilibrium with gas hydrate.

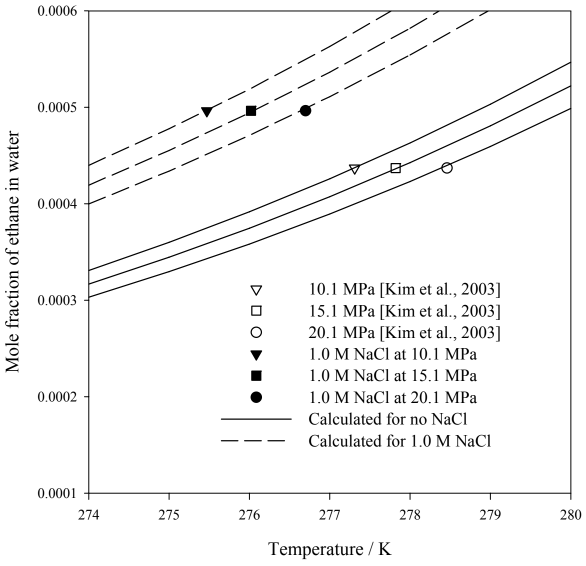

Fig. 4. Comparisons of predicted solubilities with experimental data for ethane in aqueous sodium chloride solutions in equilibrium with gas hydrate.