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Prediction of CH_4 and CO_2 hydrate phase equilibrium and cage occupancy from ab initio intermolecular potentials

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Abstract—Presented is an improved model for the prediction of phase equilibria and cage occupancy of CH_4 and CO_2 hydrate in aqueous systems. Different from most hydrate models that employ Kihara potential or Lennard-Jones potential with parameters derived from experimental phase equilibrium data of hydrates, we use atomic site-site potentials to account for the angle-dependent molecular interactions with parameters directly from ab initio calculation results. Because of this treatment, our model can predict the phase equilibria of CH_4 hydrate and CO_2 hydrate in binary systems over a wide temperature-pressure range (from 243–318 K, and from 10–3000 bar for CH_4 hydrate; from 253–293 K, and from 5–2000 bar for CO_2 hydrate) with accuracy close to experiment. The average deviation of this model from experimental data is less than 3% in pressures for a given temperature. This accuracy is similar to previous models for pressures below 500 bar, but is more accurate than previous models at higher pressures. This model is also capable of predicting the cage occupancy and hydration number for CH_4 hydrate and CO_2 hydrate without fitting any experimental data. The success of this study validates the predictability of ab initio intermolecular potentials for thermodynamic properties. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

Gas hydrates, a solid network of water molecules with cavities that encapsulate guests, have been found in oil and natural gas pipelines (Hammerschmidt, 1934), ocean sediment, permafrost regions (Sloan, 1998), and in comets and certain outer planets (Lunine and Stevenson, 1987). The total amount of natural gas stored in gas hydrate (mainly methane hydrate) reservoirs is estimated to be enormous and is considered as a future energy resource. Gas hydrates in the earth also provide two additional considerations; they are possible indicators of (1) current and ancient climate change, and (2) geological hazards (Sloan, 1998). In recent years the idea of sequestrating global warming gases, mainly carbon dioxide, on the ocean floor in the form of CO_2 hydrate as methods to hold the CO_2 concentration below a given level has been proposed. Alternatively, Ohgaki et al. (1994) proposed the idea of CO_2 storage in linkage with methane exploitation.

The thermodynamics of gas hydrate are important in many applications, such as inhibiting the formation of hydrate in oil and gas pipelines, exploring and exploiting hydrate reservoirs, sequestrating CO_2 on the ocean floor, and analyzing the salinity of fluid inclusions (Collins, 1979; Diamond, 1994; Bakker, 1997). Due to the limitation of experimental data, studies on the development of thermodynamic model for the predicting of the phase behavior of hydrates are of great importance. A variety of thermodynamic models for the calculation of phase equilibrium properties of the hydrate system have been discussed and reviewed in the literature (e.g., Holder et al., 1988; Englezos, 1993; Sloan, 1998). The basic model for the phase equilibrium of gas hydrate was derived from statistical thermodynamics by van der Waals and Platteeuw (1959), and was generalized by Parrish and Prausnitz (1972) for the predicting of dissociation pressures of gas hydrates. Later, Holder at al. (1980) further simplified the Parrish-Prausnitz model so that the reference hydrate was eliminated from the model by introducing universal reference properties for each type of structure. This led to an established methodology for nearly all of the later thermodynamic models of gas hydrates. The difference among these models lies in the choice of different molecular potentials.

Most published models predict gas hydrate phase equilibrium from Kihara potential with parameters regressed from the experimental equilibrium and cage occupancy data of 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. Many models (e.g., Parrish-Prausnitz model and CSMHYD program of Sloan [1998]) can predict phase equilibria of gas hydrates only at pressures below 400 to 500 bar. The structure changes in mixture hydrates (as the transition from structure I to structure II in the methane-ethane hydrate [Subramanian et al., 2000]) cannot be predicted unless new potential parameters are used (Ballard and Sloan, 2000; Clarke and Bishnoi, 2003). Furthermore, the Kihara potential surface derived from experimental data of hydrates are inconsistent with that derived from second virial coefficient and viscosity data by Tee et al. (1966). The latter was used by John et al. (1985) and Lee and Holder (2002) to predict phase equilibrium of gas hydrate. However, this treatment overestimates the cage occupancy of nonspherical guests, especially the occupancy fraction in a small cage.

The inadequacy of previous hydrate models implies that Kihara potential model cannot accurately describe the interaction between water and guest molecules. Accurate intermolecular potentials between a gas molecule and water are essential for the prediction of hydrate phase equilibrium. It is difficult to determine molecular interactions directly from macroscopic

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properties. Ab initio quantum chemical methods seem to provide an independent means to directly obtain accurate intermolecular potentials for guest-molecule water interactions. In the last two decades great progress on ab initio quantum calculation has been made, and the intermolecular potential energy surfaces for the interaction between gas and water molecules have been studied extensively. These studies showed that the intermolecular potential is strongly angle dependent. Cao et al. (2001a, 2001b) and Klauda and Sandler (2002, 2003) succeeded in predicting phase equilibria of methane hydrate from the ab initio potentials determined by themselves. However, the cage occupancies of CH_4 hydrate predicted by them are inconsistent with experimental data.

The objective of this paper is to predict phase equilibria and cage occupancy of CH_4 hydrate and CO_2 hydrate accurately from angle-dependent ab initio intermolecular potentials. An atomic site-site potential model was used to fit the ab initio calculations for the convenience of calculating the Langmuir constants. Our approach is different from previous studies in two aspects: (1) unlike spherical potentials, the atomic site-site potential takes account of the angle dependence of molecular interactions, and (2) unlike previous studies (e.g., EPM2 potential model for CO_2 developed by Harris and Yung [1995]), the parameters of the atomic site-site potential are evaluated from ab initio calculation results instead of from macroscopic experimental data. The Langmuir constants are computed from the ab initio potential for the application in van der Waals-Platteeuw model to predict the cage occupancy and equilibrium pressures of CH_4 and CO_2 hydrate. Similar work was published by Anderson et al. (2004) after the manuscript of this paper was submitted.

2. THERMODYNAMIC MODEL OF HYDRATE

Gas hydrates are nonstoichiometric crystalline compounds that consist of a hydrogen-bonded network of host water molecules and enclathrated guest molecules. In general, gas hydrates have three structural forms: structure I(sI), structure II(sII), and structure H(sH). Within the pressure range of this study ($P < 3000$ bar), methane hydrate and carbon dioxide hydrate are generally considered as sI hydrates (Sloan, 1998; Loveday et al., 2001b). The structure of sI hydrate has been studied extensively, such as the work of von Stackelberg and Muller (1951, 1954) and McMullan and Jeffrey (1965). Structure I (sI) is a body-centered cubic structure. The cubic cell contains 46 H_2O molecules, including two small cages, 12-hedra (5^{12}), and 6 large cages, 14-hedra ($5^{12}6^2$); where the notation 5^{12} is used to indicate that the polyhedron contains 12 five-member ring faces, $5^{12}6^2$ is used to indicate that the polyhedron contains 12 five-member ring faces and two six-member ring faces (Sloan, 1998). The lattice parameter varies with temperature, pressure, and the type of guest molecule. In recent years, Gutt et al. (2000) measured the structure of deuterated methane hydrate; Ikeda et al. (2000) and Udachin et al. (2001) measured the structure of deuterated carbon dioxide hydrate. Several reports suggested possible phase transition of methane hydrate from structure I hydrate to other structures at high pressures. Chou et al. (2000) found that CH_4 forms structure II hydrate at pressure ~1000 bar; they later (Chou et al., 2001) suggested that the structure of CH_4 hydrate at 1250 bar is not structure II, but a new unknown structure. The studies of Hirai et al. (2000, 2001), Loveday et al. (2001a), and Shimizu et al. (2002) suggest that structure-I methane hydrate is thermodynamically stable up to ~9000 bar (Loveday et al., 2001b).

Gas hydrate thermodynamics make it possible to predict the pressure-temperature conditions at which hydrates form or decompose. If hydrate and water are at equilibrium, the chemical potentials of water in the hydrate and those in the coexisting water phase, π (liquid water or ice), are identical:

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^\pi = \Delta\mu_w^\pi \tag{1}$$

where μ_w^H is the chemical potential of water in hydrate, μ_w^π is the chemical potential of water in the coexisting water phase, and μ_w^β is the chemical potential of water in the hypothetical empty hydrate lattice at the same temperature and pressure.

From statistical mechanics, van der Waals and Platteeuw (1959) obtained the following expression for the difference of chemical potentials between the hypothetical empty and fully filled hydrate lattices:

$$\Delta\mu_w^H(T, P) = -RT\sum_{i=1}^{2} v_i \ln\,(1 - \sum_{j=1}^{N_c}\theta_{ij}) \tag{2}$$

where v_i is the number of i-type cages (also called "cavities") per water molecule, and θ_{ij} is the fractional occupancy of i-type cavities with j-type guest molecules. For sI hydrate, the number of small cavities, v_1, equals to 1/23, the number of large cages, v_2, equals to 3/23. The expression for θ_{ij} is

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

where f_j is the fugacity of gas component j in hydrate phase, which equals the fugacity of gas j in gas phase; C_{ij} is the temperature-dependent Langmuir constant of gas component j in i-type cavity, which accounts for the gas-water interaction in the cavity. The Langmuir constant is defined as

$$C_{ij} = \frac{1}{RT}\int\int \exp\left[-\frac{W(r,\Omega)}{kT}\right] dr\, d\Omega \tag{4}$$

where r is the position vector and Ω is the orientation vector of the guest molecule in the cavity, $W(r, \Omega)$ represents the interaction potential between the guest molecule and water molecules surrounding it. The integration space was confined to the inside of the cage.

The expression for the chemical potential difference between empty hydrate lattice and liquid water or ice is given by Holder et al. (1980) as

$$\frac{\Delta\mu_w^\pi(T,P)}{RT} = \frac{\Delta\mu_w^0(T_0,0)}{RT_0} - \int_0^T\left(\frac{\Delta h_w^\pi}{RT^2}\right)dT + \int_O^P\left(\frac{\Delta V_w^\pi}{RT}\right)dp - \ln\gamma_w x_w \tag{5}$$

where $\Delta\mu_w^0(T_0, 0)$ is the reference chemical potential difference at the reference temperature, T_0, usually taken to be 273.15 K, and zero pressure. ΔV_w^π is the difference of the molar volume between hydrate and liquid water or ice. The temperature dependence of the enthalpy term Δh_w^π is given by

$$\Delta h_w^\pi = \Delta h_w^0(T_0) + \int_o^T \Delta C_p^\pi \, dT \qquad (6)$$

where the heat capacity difference is approximated by

$$\Delta C_p^\pi = \Delta C_p^0(T_0) + b(T - T_0) \qquad (7)$$

For the water-gas binary system, the activity coefficient of water, γ_w, can be assumed to be equal to unit because the solubility of gas is generally small. The concentration of water (x_w) can be estimated by eliminating the solubility of gas (x_{gas}) in aqueous solution as $x_w = 1 - x_{\mathrm{gas}}$.

The thermodynamic reference properties $\Delta\mu_w^0$, Δh_w^0, ΔC_p^0 and b are experimentally determined functions. The fugacity and solubility of the gas component can be calculated from the accurate equation of the state or solubility model. ΔV_w^π was assumed to be constant by most of the hydrate models.

It can be seen from the above discussions that the key to this model is to calculate Langmuir constants from appropriate intermolecular potential, which will be discussed in the next section in detail.

3. CALCULATION OF LANGMUIR CONSTANT

As can be seen from Eqn. 4, an accurate intermolecular potential is the premise to calculate the Langmuir constant, which is the key to predicting both cage occupancy and phase equilibrium of gas hydrates accurately. Most of previous hydrate models compute Langmuir constants from the Kihara potential model. However, the parameters of Kihara potential are empirically regressed from experimental data of phase equilibrium and cage occupancy and have little physical meaning. It has been proven that the ab initio potential can represent the intermolecular potential between water and gas molecules adequately. Cao et al. (2001a, 2001b) and Klauda and Sandler (2002, 2003) computed Langmuir constants from the ab initio potentials determined by them. From the Langmuir constants, they further calculated phase equilibria and cage occupancy of methane hydrate. Although the phase equilibrium of methane hydrate was predicted accurately by them, the cage occupancy prediction is not consistent with experimental data.

3.1. Modeling Based on Empiric Potential Model

In the original van der Waals-Platteeuw model (van der Waals and Platteeuw, 1959), the Langmuir constant was computed from the Lennard-Jones 12-6 potential model with the Lennard-Jones-Devonshire spherical cell potential approximation (LJD approximation), which assumes the cages are a perfect sphere and neglects the interaction between the guest molecule and the water molecules beyond the first water shell. This treatment only works well for hydrates formed by monatomic gases. It cannot predict the dissociation pressure of hydrates formed by polyatomic and nonspherical molecules quantitatively. McKoy and Sinanoglu (1963) demonstrated that the application of the Kihara potential with a spherical core yields improved predictions of dissociation pressures of gas hydrate. The parameters of the Kihara potential used by McKoy and Sinanoglu (1963) were determined from second virial coefficient data. Parrish and Prausnitz (1972) fitted Kihara parameters for gas-water interactions to dissociation pressure data of hydrate systems to predict phase equilibria of gas hydrates quantitatively. This method was adopted and extensively improved by subsequent researches, such as the work of Ng and Robinson (1976), 1977, Anderson and Prausnitz (1986), Englezos and Bishnoi (1988), (Lundgard and Mollerup 1991, 1992), Barkan and Sheinin (1993), Avlonitis (1994), and Sloan (1998).

Although phase equilibria of single-component hydrates and poly-component hydrates can be represented quantitatively from Kihara parameters derived from experimental equilibrium data and cage occupancy of hydrates, the parameters of Kihara potential computed from this method are not consistent with that derived from second virial coefficient and/or viscosity data. Although the hydrate models mentioned above can reproduce experimental data well, they generally cannot make accurate predictions beyond the *T-P* range for fitting. The prediction at high pressures (more than 400–500 bars) becomes poor.

Diamond (1994) adopted the model of Ng and Robinson (1976) to predict the dissociation pressure of hydrates in the CH_4 (CO_2, N_2, H_2S)-H_2O-NaCl system and applied it to the analysis of fluid inclusions. However, the Ng-Robinson model fails in predicting the dissociation pressure of CH_4 hydrate above 150 bar, even though the Kihara parameters for CH_4-H_2O interaction are fitted empirically. Bakker et al. (1996) refitted the Kihara parameters for CO_2-H_2O interaction. However, they had to use two sets of Kihara parameters for CO_2-H_2O interaction to predict the phase equilibrium of CO_2 hydrate up to high pressures. They also underestimated the isothermal compressibility of the hydrate phase.

Considering the spherical asymmetry of cavities and the contribution of the second and third water shells to the interaction energy as pointed out by (John and Holder 1981, 1982), John et al. (1985) used the Kihara potential parameters fitted to the second virial coefficient data, rather than the parameters fitted to hydrate equilibrium data, to predict phase equilibria of gas hydrates. They also used a corresponding state modification to account for the asymmetry of nonspherical guest molecules. Although the corresponding state correction has a theoretical basis, it varied by as much as five orders of magnitude, casting doubt on its validity. Considering that the size of hydrate lattice depends on the guest(s) occupying the cavities, Lee and Holder (2002) used a variable reference chemical potential to predict hydrate equilibria while the corresponding state modification was abandoned. However, this treatment overestimates the cage occupancy of nonspherical guests, especially the occupancy fraction in small cages. Another disadvantage of the model of (John et al. (1985) and Lee and Holder (2002) is that the Kihara parameters for water are still regressed from the experimental equilibrium data of hydrates.

3.2. Modeling Based on Spherical Ab Initio Potential

The inadequacy of previous hydrate models suggests that the simple Kihara potential model cannot describe the interaction between water and guest molecules adequately. In recent years, some researchers tried to predict phase equilibrium of gas hydrate from ab initio intermolecular potential. Cao et al. (2001a, 2001b) determined the ab initio potential energy surface for CH_4-H_2O dimer and applied it to predict phase equilibria of methane hydrate. The model of Cao can predict the equilibrium pressure of CH_4 hydrate accurately up to high pressures, but it gives unreasonable cage occupancy. The cage occupancy of the small cavity estimated by Cao et al. (2001b) was larger than the cage occupancy of the large cavity, which contradicts all experimental observations. The failure in predicting cage occupancy implies that the averaged ab initio potential determined by Cao et al. (2001a) was not accurate enough. We found that there are two major problems in the treatment of Cao et al. (2001a, 2001b). Firstly, Cao et al. (2001a) only chose two types of orientations between CH_4 and H_2O during calculating ab initio potential, which may not be sufficient for obtaining an accurate potential energy surface. However, the recent work by Anderson et al. (2004) changed our view on this. Secondly, Cao et al. (2001a, 2001b) performed spherical average on the intermolecular potential with the Boltzmann averaging algorithm before computing Langmuir constants. This treatment causes the loss of the quality of ab initio potential since ab initio intermolecular potential is strongly angle dependent. Using the Peng-Robinson equation of state (Peng and Robinson, 1976) to compute the fugacity of methane is also an insufficiency of the Cao model, since the prediction of the Peng-Robinson equation of state on the volumetric properties at high pressures is poor (more than 5% for CH_4 at pressures greater than 500 bar). After the manuscript of this paper was submitted, Anderson et al. (2004) tried to improve the earlier work of Cao et al. (2001a, 2001b). They found that angle-averaged potential results in large errors in the prediction of the cage occupancies in the study of Cao et al. (2001b). They used a site-site potential model to fit the ab initio potentials for CH_4-H_2O and improved the prediction of cage occupancies of methane hydrate, consistent with our predictions.

Klauda and Sandler (2002, 2003) also predicted cage occupancy and equilibrium pressure of some gas hydrates (including CH_4, C_2H_6, C_3H_8, N_2, H_2, and CO_2 hydrate) from ab initio potentials. They divided the hydrate cage into four sections and directly calculated the intermolecular potentials between guest and four sections of hydrate lattice. Although it is a good consideration to include many-body effects, significant improvements have not been observed with state-of-the-art techniques (Finney, 2001; Duan et al., 2004). It seems that the method of Klauda and Sandler (2002) does not effectively consider many-body effects and does not obtain accurate ab initio potentials. There are three possible reasons for their inaccuracy. Firstly, their ab initio potentials were determined at MP2 (the second-order Møller-Plesset perturbation theory) level of theory. The Quantum Mechanics (QM) calculations of Szczesniak et al. (1993) and Sadlej et al. (1998) indicate that MP2 level is inadequate to evaluate the intermolecular potential. The well depth of the intermolecular potentials increases 5 to 10% from MP2 level to MP4 level. Secondly, Klauda and Sandler (2002) used a smaller basis set than the work of Szczesniak et al. (1993) and Cao et al. (2001a). The smaller basis set will lead to the underestimating of the intermolecular potential. Thirdly, Klauda and Sandler (2002) only calculate the interaction between guest and the first water shell, and the interaction between guest and outer water shells is not included. This approach ignored the effect of the second and third water shells on the first water shell, which should be important in many-body effects. As shown by Table 7, the cage occupancy fraction of CH_4 hydrate predicted from the ab initio potential of Klauda and Sandler (2002) is far below the experimental value, while the prediction of this study is within the experimental accuracy.

3.3. Modeling Based on Angle-Dependent Ab Initio Potential

In the last two decades, the ab initio potentials of CH_4-H_2O and CO_2-H_2O system have been studied by several research groups in addition to the work of Cao et al. (2001a) and Klauda and Sandler (2002). Bolis et al. (1983), Latajka and Scheiner (1987), Novoa et al. (1991), Szczesniak et al. (1993), and Rovira et al. (1995) performed ab initio calculations for the CH_4-H_2O complex. Mehler (1981), Hurst et al. (1986), Block et al. (1992), Makarewicz et al. (1993), Kieninger and Ventura (1997), and Sadlej et al. (1998) carried out ab initio calculations for the CO_2-H_2O dimer. There are some differences between the results of different groups. The ab initio calculations of Szczesniak et al. (1993) for CH_4-H_2O complex and Sadlej et al. (1998) for CO_2-H_2O complex were chosen after we examined these studies carefully. Firstly, Szczesniak et al. (1993) and Sadlej et al. (1998) employed a high level of QM theory and large basis sets. The ab initio potential energy surfaces were calculated at MP2 level and corrected at MP4 level. They also included the basis set superposition error (BSSE) correction of interaction energies that was neglected by many studies in the twentieth century. Thus, their results should be more accurate. Secondly, the studies of Szczesniak et al. (1993) and Sadlej et al. (1998) included more types of orientation between the guest and water than many of the studies. Although Cao et al. (2001a) performed the ab initio calculations for many CH_4-H_2O configurations at MP2 level with a large basis set, the type of orientation between CH_4 and H_2O included by them is less than that included by Szczesniak et al. (1993). We think that including enough orientations between guest and water is important for describing the angle dependence of the intermolecular potential energy surface. The QM level and basis set used by Klauda and Sandler (2002) are less than the ab initio calculations of Szczesniak et al. (1993) and Sadlej et al. (1998). Thus, the ab initio potentials determined by Cao et al. (2001a) and Klauda and Sandler (2002) were not used by this study. However, the recent work of Anderson et al. (2004) shows that the ab initio calculations of Cao et al. (2001a) are also applicable in the predictions. Therefore, the ab initio calculations by both Cao et al. (2001a) and Szczesniak et al. (1993) are sufficiently accurate.

To calculate the Langmuir constant directly from ab initio calculation results by the numeric integration of Eqn. 4, the ab initio calculation results need to fit to an empiric formula. We found that Coulombic charge-charge interaction plays an important role in the interaction potential between gas and water, so an electrostatic term should be included in the formula. In the first place, we tried to fit ab initio potential by using a spherical Lennard-Jones 12-6 or a Kihara potential model. However, this treatment cannot represent ab initio potential energy surface adequately. Thus, we selected an atomic site-site analytical potential model to fit the ab initio intermolecular potential energy surface. The interacting sites are located on every atom of CH_4, CO_2, and H_2O molecules. In the case of water, one additional charge site located at the bisector of the

Table 1. Atomic site-site Lennard-Jones potential parameters for the CH_4-H_2O system.

CH_4	H_2O	ε/k (K)	σ (Å)
C	O	61.40	3.627
C	H	22.4	2.2
C	M	0.	0.
H	O	40.79	2.777
H	H	15.1	1.5
H	M	0.	0.

H-O-H angle is included. The Lennard-Jones formula plus the Coulombic charge-charge formula were selected for the potential model to fit the ab initio potential. Its form is as follows:

$$E(r_{ij}) = \sum_i \sum_j \left\{ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \right\} \qquad (8)$$

where i, j summation runs over all C, H centers on the CH_4 molecule (or C, O centers on CO_2 molecule), and O, H, M centers on the H_2O molecule, respectively.

A nonlinear least-square fitting method was used to fit ab initio potential data. For the CH_4-H_2O system, all the data points presented in the paper of Szczesniak et al. (1993) were used in the fitting procedure. For the CO_2-H_2O system, all the data points with energy lower than 3 kcal/mol were used. The Boltzmann factor-weighted objective function was used to minimize the energy difference between the ab initio calculations and the prediction of Eqn. 8. The formula for the objective function is the same as that used by Klauda and Sandler (2002) and Anderson et al. (2004). The parameters in Eqn. 8 were evaluated from the ab initio potentials at MP2 level with MP4 level corrections. Throughout the fitting of the potential and the calculation of Langmuir constants, the experimental geometries of CO_2 and CH_4 were adopted: r(CO) = 1.16 Å, O-C-O angle = 180° for CO_2; r(CH) = 1.09 Å, H-C-H angle = 109.4722° for CH_4. For H_2O, the geometry assumed by TIP4P model (Jorgensen et al., 1983) was adopted: r(OH) = 0.9572 Å, H-O-H angle = 104.52°, the additional interacting site "M" was located on the bisector of the H-O-H angle 0.15 Å away from the oxygen atom toward hydrogen atoms. We found that accurate fit could be obtained using the electrostatic representation of TIP4P model. Thus, $q_O = 0.0$, $q_H = 0.52$, $q_M = -1.04$ for water. Other parameters, including ε, σ, and the partial charges on carbon and hydrogen atoms of CH_4 molecule (or the partial charges on carbon and oxygen atoms of CO_2 molecule), were fitted to ab initio potential data for the CH_4-H_2O system (or CO_2-H_2O system) using the nonlinear procedure. The parameters obtained are listed in Table 1, Table 2 and Table 3, respectively.

Table 2. Atomic site-site Lennard-Jones potential parameters for the CO_2-H_2O system.

CO_2	H_2O	ε/k (K)	σ (Å)
C	O	53.40	2.955
C	H	25.16	2.40
C	M	0.	0.
O	O	90.23	3.034
O	H	42.56	2.48
O	M	0.	0.

Table 3. Partial charges of CH_4, CO_2, and H_2O molecule.

Atom	a
C_{CH_4}	−0.48
H_{CH_4}	0.12
C_{CO_2}	0.652
O_{CO_2}	−0.326
O_{H_2O}	0.0
H_{H_2O}	0.52
M_{H_2O}	−1.04

Figures 1 and 2 are the ab initio potential energy surfaces of CH_4-H_2O and CO_2-H_2O obtained by fitting to the ab initio calculations of Szczesniak et al. (1993) and Sadlej et al. (1998). Figures 3 and 4 are the corresponding configurations to the

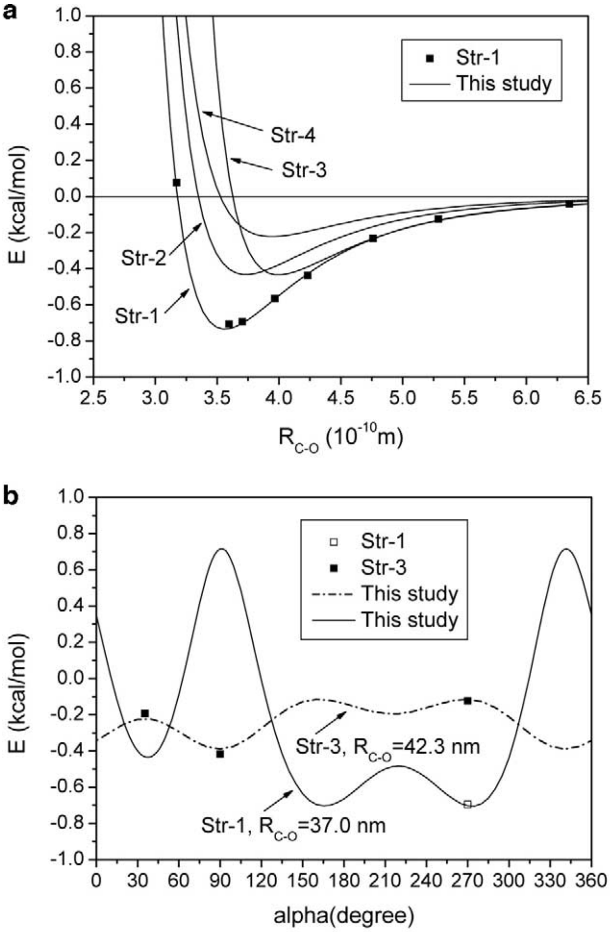

Fig. 1. The angle dependence of the potential energy surface of CH_4-H_2O: (a) the variation of the intermolecular potential with distance and (b) the variation of the intermolecular potential with angle alpha (angle alpha is defined as the angle between the bond C-H1 and z-axis in yz-plane). Solid squares and open squares represent the ab initio data obtained by Szczesniak et al. (1993) at MP2 level; solid lines and dotted line are the atomic site-site potential energy predicted for different orientations. Four orientations of CH_4-H_2O dimer presented in this figure are shown in Figure 3.

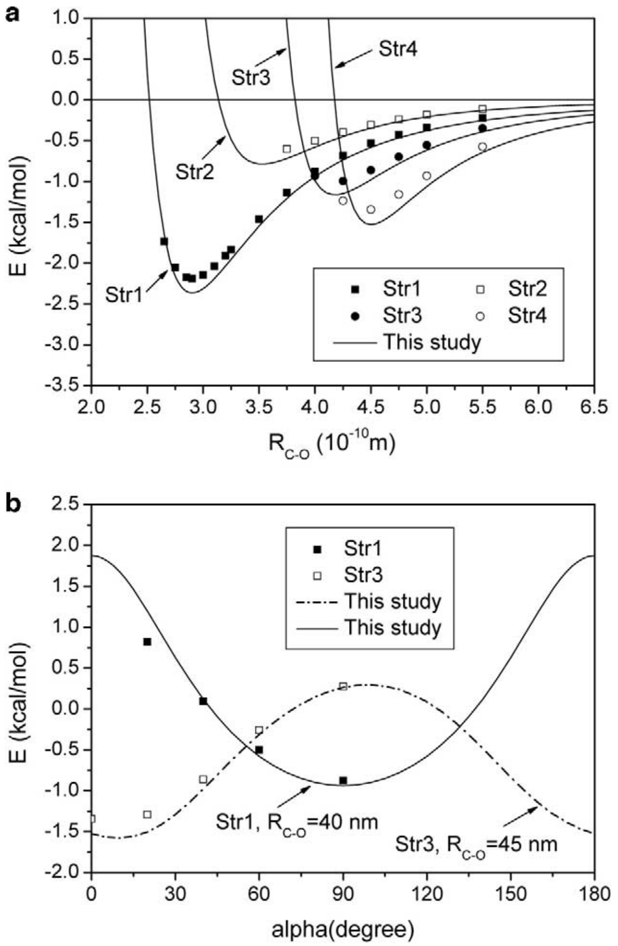

Fig. 2. The angle dependence of the potential energy surface of CO_2-H_2O: (a) the variation of intermolecular potential with distance and (b) the variation of intermolecular potential with angle alpha. (angle alpha is defined in Fig. 4). Solid squares, open squares, solid circles and open circles represent the ab initio data obtained by Sadlej et al. (1998) at MP2 level; solid lines and dotted line are the energy predicted by our atomic site-site potential for different orientations. Four orientations of CO_2-H_2O dimer presented in this figure are shown in Figure 4.

energy surfaces shown in Figures 1 and 2, respectively. From Figures 1 and 2 we can find that the atomic site-site potential used by this study (Eqn. 8) can represent the ab initio calculations of Szczesniak et al. (1993) and Sadlej et al. (1998) adequately, and that the potential energy surfaces are strongly angle dependent.

4. PARAMETERIZATION OF THE MODEL

After the parameters of the atomic site-site potential for CH_4-H_2O and CO_2-H_2O system was determined, Langmuir constant, C_{ij}, can be computed from Eqn. 4. The contributions of the spherical asymmetry of cavities and the interaction between guest and water molecules beyond the first water shell to the Langmuir constant were included by this study. Since $W(r, \Omega)$ depends both on the radial vector r and on the orientation vector Ω of the guest molecule in the cavity, we used 576 evenly divided orientations for the guest molecule to solve the integral of Eqn. 4. For each orientation, 576 positions on the sphere with radius r are used. W can be divided into two parts: the contribution to the interaction potential from the first shell of water molecules surrounding the gas molecule, W_1, and the contribution from the water molecules beyond the first shell, W_2. In this study, all the water molecules within 18 Å from the center of the cavity are included to compute W. Though the absolute value of W_2 is less than W_1, it can increase the value of Langmuir constant by as much as 300%. To save computing

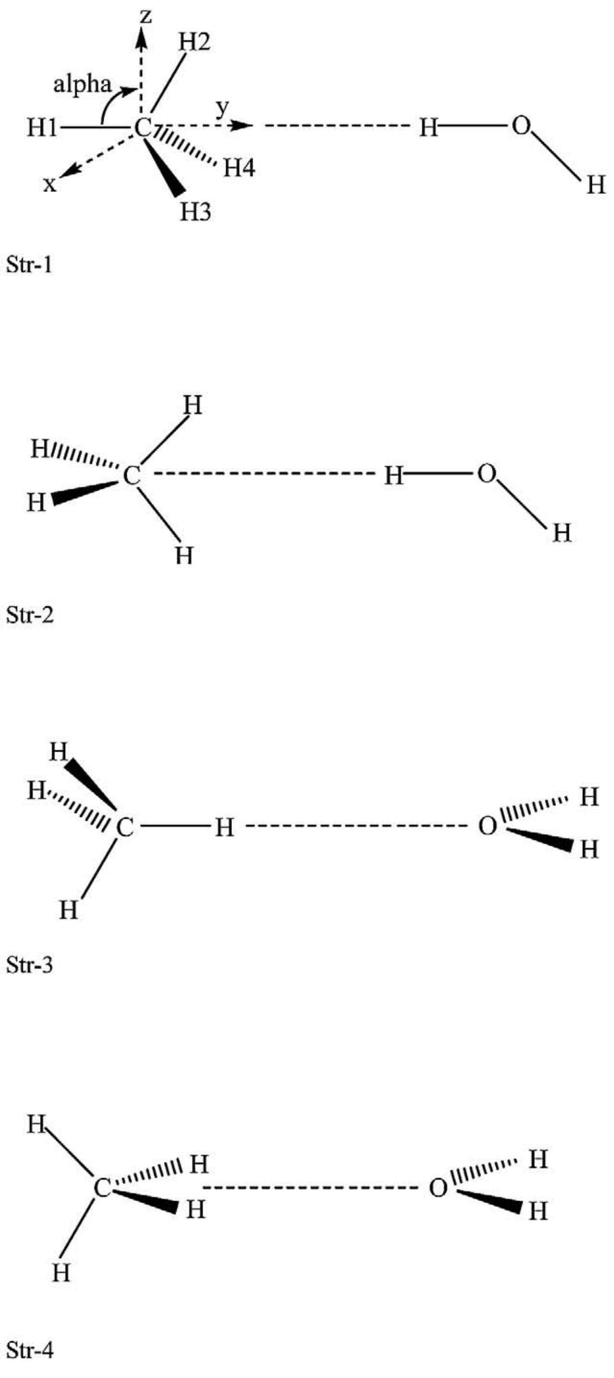

Fig. 3. Four orientations of CH_4-H_2O dimer. Str-1 is the most stable orientation determined by Szczesniak et al. (1993). Angle alpha is defined as the angle between the bond C-H1 and z-axis in yz-plane.

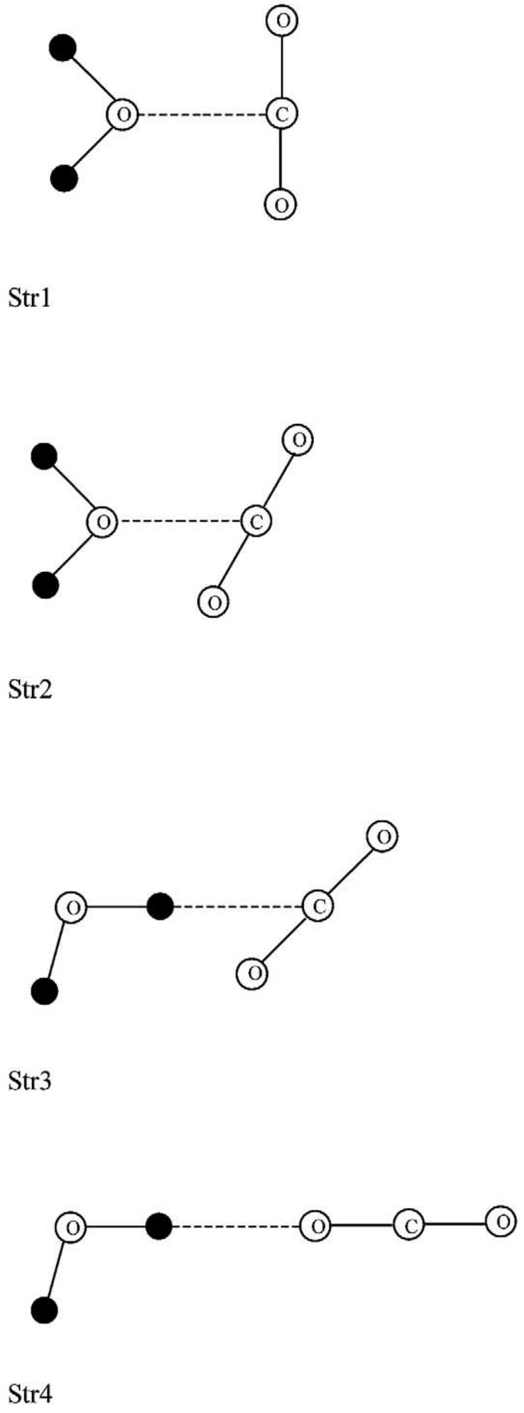

Fig. 4. Four orientations of CO_2-H_2O complex. Str1 is the most stable orientation determined by Sadlej et al. (1998). Angle alpha and beta describe the in-plane wagging of CO_2 and H_2O, respectively.

time, W_2 was calculated by assuming that the guest was located in the center of the cage, since the change of W_2 with r and Ω is very small. The change of Langmuir constants due to this assumption is ~1% (equivalent to ~1% variation of the equilibrium pressure of gas hydrate at a given temperature). The positions of water molecules in methane hydrate obtained by Gutt et al. (2000) and the positions of water molecules in carbon dioxide hydrate measured by Ikeda et al. (2000) were used. The lattice parameter of CH_4 and CO_2 hydrate was set 11.99 Å at 273.15 K and 10 bar according to the study of Gutt et al. (2000), Ikeda et al. (2000), and Udachin et al. (2001).

Many equations of state are available to compute the fugacity of pure CH_4 in vapor phase and the fugacity of pure CO_2 in vapor or liquid phase, such as the C-P equation of state (EOS) (Chueh and Prausnitz, 1967), S-RK EOS (Soave, 1972), P-R EOS (Peng and Robinson, 1976), and DMW-92 EOS (Duan et al., 1992a). At relative low pressures, all these equations of state are accurate for the prediction of volumetric properties of gaseous CO_2 or CH_4. However, at higher pressures (more than ~1000 bar), only DMW-92 EOS is adequately accurate. Bakker et al. (1996) found that DMW-92 EOS is the most accurate EOS for prediction of the fugacity coefficient of CO_2 along the CO_2 hydrate stability curve at high pressures ($P > 200$ bar). Figure 5 compares the molar volume of CH_4 along the CH_4 hydrate stability curve above 270 K predicted by the C-P EOS, S-RK EOS, P-R EOS, and DMW-92 EOS with that defined by Setzmann and Wagner (1991). The EOS of Setzmann and Wagner was chosen as a benchmark to check the performance of these EOS mentioned above, since it can represent the molar volume of methane with an uncertainty less than 0.1% in a wide T-P range. It is obvious that DMW-92 EOS is the most accurate for CH_4 at high pressures. The absolute average deviation is less than 1%. Since we try to predict the phase equilibria of CH_4 hydrate and CO_2 hydrate at high pressures as well as at low pressures, DMW-92 EOS is chosen to calculate the fugacity of pure CH_4 and CO_2.

The solubility of CH_4 in pure water is computed from a methane solubility model developed by Duan et al. (1992b), and the solubility of CO_2 in pure water is computed from a carbon dioxide solubility model published by Duan and Sun (2003). As shown by the authors, the two models are more accurate than other solubility models, especially at high pressures.

Most of the hydrate models assumed the difference of the molar volume between hydrate phase and liquid water or ice, ΔV_w^π, to be constant. This assumption is accurate at low pres-

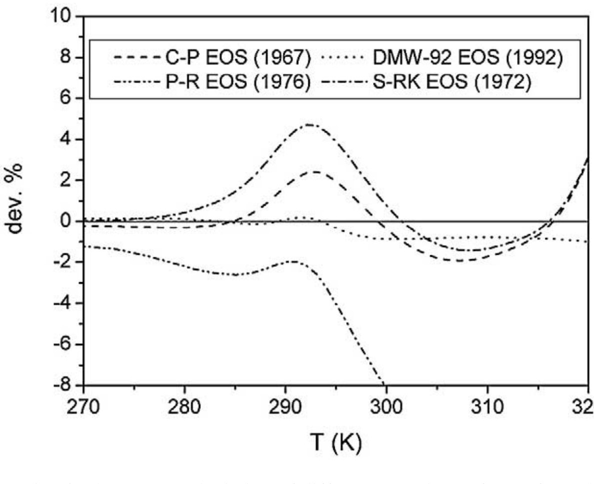

Fig. 5. The average deviation of different equations of state from the equation Setzmann and Wagner (1991), which is considered an accurate experiment in the temperature-pressure range of interests.

sures. However, the pressure dependency of ΔV_w^{π} cannot be neglected at high pressures. Bakker et al. (1996) assumed that the isothermal compressibility of the hydrate phase is equal to that of ice. Klauda and Sandler (2000) empirically fitted the molar volume of methane hydrate as a function of temperature and pressure. Klauda and Sandler (2000) also fitted the molar volume of ice and liquid water. The empiric formula for the molar volume of ice established by Klauda and Sandler (2000) was used by this study. However, the more accurate equation of state published by Sun et al. (2003) instead of the formula of Klauda and Sandler (2000) was used to estimate the molar volume of liquid water. We fit the molar volume of methane hydrate according to the thermal expansion of CH_4 hydrate and CO_2 hydrate measured by Gutt et al. (2000), Ikeda et al. (2000), Udachin et al. (2001), and the isothermal compressibility data of Hirai et al. (2000) for CH_4 hydrate. The molar volume of CO_2 hydrate was assumed equal to that of CH_4 hydrate at the same temperature and pressure. The following are the equations used by this study for the molar volume of ice and structure I hydrate:

$$V_w^{Ice}(T) = 1.912 \times 10^{-5} + 8.387 \times 10^{-10}T + 4.016 \times 10^{-12}T^2 \tag{9}$$

$$V_w^{\beta,1}(T,P) = (11.818 - 9.0871 \times 10^{-5}T + 3.9468 \times 10^{-6}T^2 - 4.7254 \times 10^{-9}T^3 - 8.4133 \times 10^{-4}P + 1.5207 \times 10^{-6}P^2 - 2.20 \times 10^{-9}P^3)^3 \frac{10^{-30}N_A}{N_w^{\beta}} \tag{10}$$

In Eqn. 10, N_A is Avogadro's number, N_w^{β} is the number of water molecules per hydrate cell. For sI hydrate, N_w^{β} equals 46. The unit of pressure in Eqn. 10 is MPa, and the unit of temperature in Eqn. 9 and Eqn. 10 is K. Eqn. 10 is more accurate than the formula of Klauda and Sandler (2000). The absolute average deviation of Eqn. 10 from the experimental data of Hirai et al. (2000) is 0.8%, while the absolute average deviation of the formula of Klauda and Sandler (2000) is 3%.

Many researchers evaluated the thermodynamic reference properties $\Delta\mu_w^0$ and Δh_w^0. However, the values given by different groups are not consistent with each other. Sloan (1998) reviewed previous studies on $\Delta\mu_w^0$ and Δh_w^0. In this study, $\Delta\mu_w^0$ and Δh_w^0 were determined from experimental equilibrium data of CH_4 hydrate and CO_2 hydrate following the method of Holder et al. (1984). The values obtained by us are listed in Table 4. The difference of the values of ΔC_p^0 and b given by different researchers is small. In this study, the values of ΔC_p^0 and b cited by Cao et al. (2001b) were used and are also listed in Table 4.

Table 4. Thermodynamic reference properties of sI hydrate.

T-range	$\Delta\mu_w^0$ (J/mol)	Δh_w^0 (J/mol)	ΔC_p^0 (J/(mol · K))	b (J/(mol · K^2))
$T < T(Q_1)$*	1202	1300	−38.12	0.141
$T > T(Q_1)$	1202	−4709.5[a]	0.565	0.002

* $T(Q_1)$ is the temperature at the invariant point Q_1 for the assemblage of hydrate-ice-liquid water-Gas. The $T(Q_1)$ for CH_4 hydrate predicted by this model = 272.9 K, and $T(Q_1)$ for CO_2 hydrate = 271.7 K.

[a] This parameter was not fit separately. It equals the difference of enthalpy between the empty hydrate and ice, 1300 J/mol, plus the latent heat of water, −6009.5 J/mol.

Table 5. Measurements of CH_4 hydrate phase equilibrium in CH_4-H_2O system.

Authors	T (K)	P (bar)	N[a]
Roberts et al. (1940)	259–286	16–108	5
Deaton & Frost (1946)	262–286	18–98	18
Kobayashi & Katz (1949)	295–302	340–775	4
Mcleod & Campbell (1961)	285–302	96–681	9
Marshall et al. (1964)	290–320	160–4000	20
Jhaveri & Robinson (1965)	273–294	26–286	8
Galloway et al. (1970)	283–289	71–131	4
Verma (1974)	275–291	30–186	7
Falabella (1975)	149–193	0.05–1.01	6
de Roo et al. (1983)	273–286	27–100	9
Thakore & Holder (1987)	275–281	28–61	6
Adisasmito et al. (1991)	273–286	27–106	11
Makogon & Sloan (1994)	190–262	0.8–18	6
Mei et al. (1996)	274–285	30–90	12
Nakano et al. (1999)	305–320.5	980–5000	16
Yang et al. (2001)	276–286	36–97	10
Jager & Sloan (2001)	291–303	201–723	12

[a] Number of measurements.

5. RESULTS AND DISCUSSION

The phase equilibria of CH_4 hydrate in the CH_4-H_2O system and CO_2 hydrate in the CO_2-H_2O system have been studied extensively by experiment. Sloan (1998) collected and reviewed the experimental phase equilibrium data published before 1998. Over the last few years, some new experimental data were reported. The sources of the experimental data of CH_4 hydrate and CO_2 hydrate are listed in Tables 5 and 6, respectively. For the phase equilibrium of CH_4 hydrate or CO_2 hydrate in binary systems, most of the experimental data are consistent with each other. The average deviation is less than 3%. However, the deviation of data at high pressures becomes larger (more than 5%), including some data of Jager and Sloan

Table 6. Measurements of CO_2 hydrate phase equilibrium in CO_2-H_2O system.

Authors	T (K)	P (bar)	N[a]
Deaton & Frost (1946)	273–283	13–43	19
Unruh & Katz (1949)	277–283	20–45	5
Larson (1955)	257–283	5–45	45
Miller & Smythe (1970)	151–192	0.005–0.22	8
Robinson & Mehta (1971)	274–283	13–45	7
Falabella (1975)	194–218	0.25–1.01	5
Ng & Robinson (1985)	279–284	27–144	9
Takenouchi & Kennedy (1965)	283–293	45–1900	15
Adisasmito et al. (1991)	274–283	14–44	9
Dholabhai et al. (1993)	273–279	13–25	4
Englezos & Hall (1994)	275–283	15–42	6
Breland & Englezos (1996)	275–280	16–30	3
Nakano et al. (1998)	289–294	1000–3300	13
Fan & Guo (1999)	273–283.6	13–129	13
Wendland et al. (1999)	271–283	10–45	9
Seo & Lee (2001)	274–283	15–45	5

[a] Number of measurements.

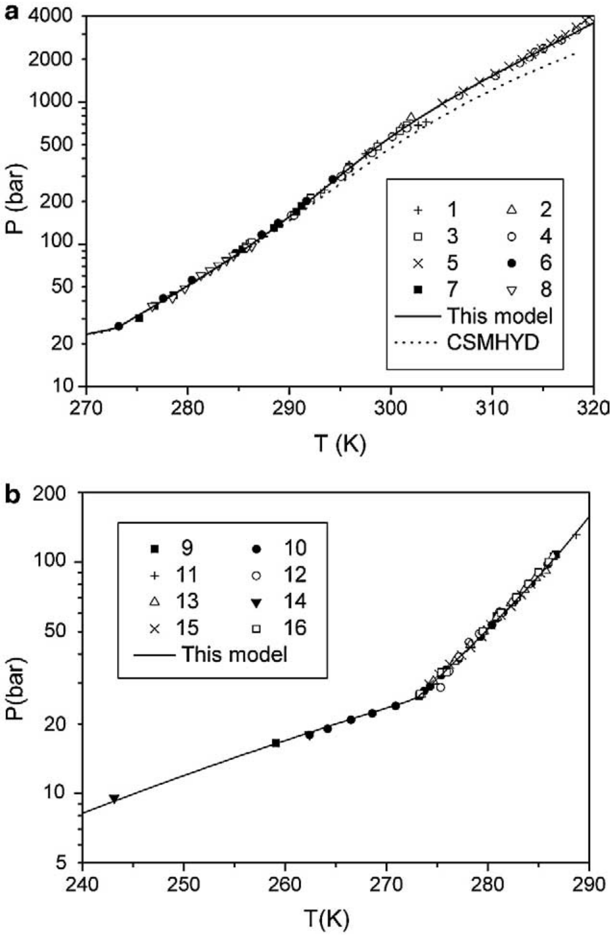

Fig. 6. Prediction of equilibrium pressure of CH_4 hydrate in the CH_4-H_2O system: (a) $T > 270$ K and (b) $T < 290$ K. The source of experimental data: 1: Jager and Sloan (2001), 2: Kobayashi and Katz (1949), 3: McLeod and Campbell (1961), 4: Marshall et al. (1964), 5: Nakano et al. (1999), 6: Jhaveri and Robinson (1965), 7: Verma (1974), 8: Yang et al. (2001), 9: Roberts et al. (1940), 10: Deaton and Frost (1946), 11: Galloway et al. (1970), 12: Thakore and Holder (1987), 13: Adisasmito et al. (1991), 14: Makogon and Sloan (1994), 15: Mei et al. (1996), and 16: de Roo et al. (1983).

(2001), Marshall et al. (1964), and Nakano et al. (1999) for CH_4 hydrate at pressures more than 600 bar, and a few data of Nakano et al. (1998) and Takenouchi and Kennedy (1965) for CO_2 hydrate at pressures more than 1000 bar.

After the parameters in Eqn. 2 and Eqn. 5 are determined, the equilibrium pressure of CH_4 hydrate or CO_2 hydrate at a given temperature can be calculated from solving Eqns. 1, 2, and 5 by iteration. Figure 6 compares the equilibrium pressure of CH_4 hydrate, at various temperatures predicted by this model, with experimental data. Figure 7 shows the prediction of CO_2 hydrate equilibrium by this study. It is obvious that this model can accurately predict the phase equilibria of CH_4 hydrate and CO_2 hydrate in a binary system in a wide *T-P* range. The absolute averaged deviation is less than 3%. The *T-P* range covered by this model is from 243 to 318 K and from 10 to 3000 bar for CH_4 hydrate, and from 253 to 293 K and from 5 to 2000 bar for CO_2 hydrate. The predictions of the CSMHYD program of Sloan (1998) are also shown in Figure 6 and Figure 7. Although the CSMHYD program fitted Kihara potential parameters to hydrate phase equilibrium and cage occupancy data of gas hydrates, it can only predict the equilibrium pressure of CH_4 hydrate and CO_2 hydrate at relatively low pressures. At pressures above 500 bar, the deviation from experiments is more than 10%.

Predicting cage occupancies and hydration number (the average number of water molecules per guest molecule in the hydrate) of the hydrate phase is important for evaluating the amount of gas stored in the hydrate phase. Cage occupancy can be calculated from Eqn. 3, and hydration number can be determined from cage occupancies according to its definition. Thus, the ability of this model to predict cage occupancies and hydration number is a rigid test for the reliability of the ab initio intermolecular potential because it does not fit any experimental data.

Quite a few experimental data sets are reported for the

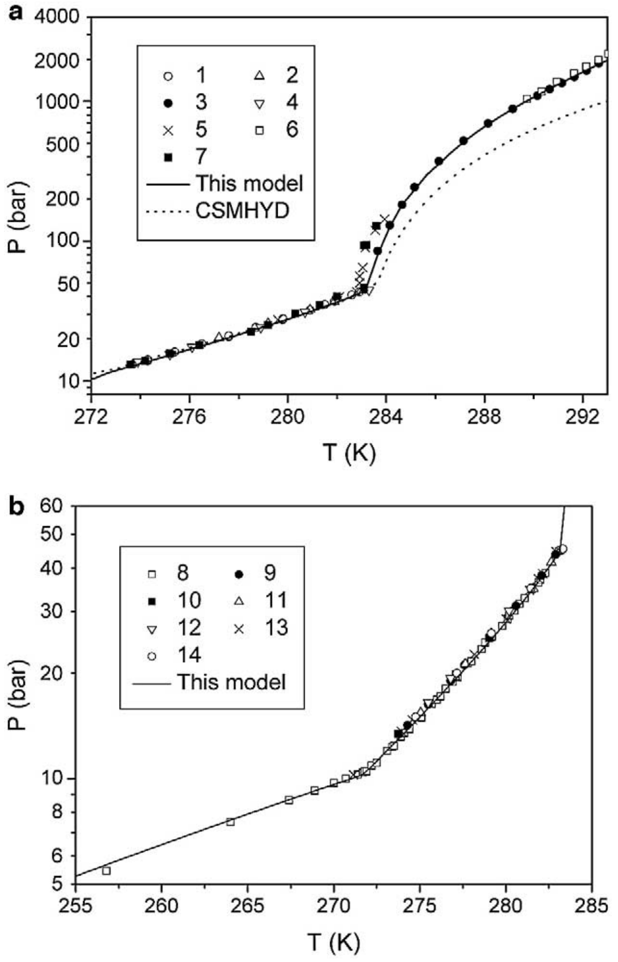

Fig. 7. Prediction of equilibrium pressure of CO_2 hydrate in the CO_2-H_2O system: (a) $T > 272$ K and (b) $T < 285$ K. The source of experimental data: 1: Deaton and Frost (1946), 2: Unruh and Katz (1949), 3: Takenouchi and Kennedy (1965), 4: Robinson and Mehta (1971), 5: Ng and Robinson (1985), 6: Nakano et al. (1998), 7: Fan and Guo (1999), 8: Larson (1955), 9: Adisasmito et al. (1991), 10: Dholabhai et al. (1993), 11: Englezos and Hall (1994), 12: Breland and Englezos (1996), 13: Wendland et al. (1999), and 14: Seo and Lee (2001).

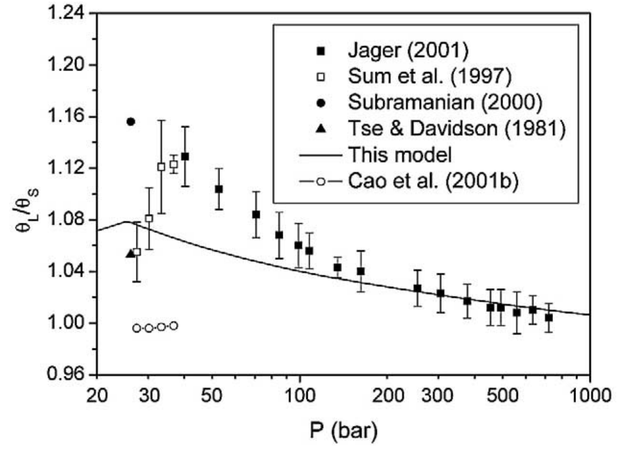

Fig. 8. Predicted and measured cage occupancy ratios for methane hydrate.

cage occupancy ratio (the fraction of the large cages occupied by the guest, θ_L, divided by the fraction of the small cages occupied, θ_S), θ_L/θ_S, and/or the hydration number for CH_4 hydrate. Figure 8 compares the cage occupancy ratios predicted by this model with the experimental data. From Figure 8 we can find that the uncertainty of the experimental data and the deviation between different data sets is relatively large. The value of θ_L/θ_S at 273.15 K and the equilibrium pressure reported by Tse and Davidson (1981) is 1.053, while the value given by Subramanian (2000) is 1.156. The value of θ_L/θ_S predicted by this model is 1.075, within the range of experimental values. The cage occupancy ratio measured by Jager (2001) decreases with increasing temperature and increasing pressure, while the data of Sum et al. (1997) shows a reverse trend. Considering the relatively large uncertainty in the data of Sum et al. (1997) and the small temperature range of 3 K as shown in Tables 7 and 8, we think that the trend of cage occupancy ratio varying with temperature shown by the data set of Sum et al. (1997) is unconvincing. Although there is large deviation among the experimental data sets for cage occupancy ratios, the prediction of this model generally agrees with these experimental data.

Table 7 compares the cage occupancy predicted by this model with the experimental data of Sum et al. (1997). The predictions of Cao et al. (2001b) and Klauda and Sandler (2002, 2003) are also listed in Table 7. It can be seen that the predictions of this model agree well with experimental data while the predictions of Cao et al. (2001b) and Klauda and Sandler (2002, 2003) are outside the experimental error bar. Cao et al. (2001b) underestimated the occupancy fraction of large cage and overestimated the occupancy fraction of small

Table 7. Comparison cage occupancy of CH_4 hydrate predicted by this model with the model of Cao et al. (2001b), Klauda and Sandler (2002, 2003), and the experimental data of Sum et al. (1997).

T (K)	Exp.	This model	Coa et al.	Klauda & Sandler
Occupancy fraction of methane in large cage, θ_L				
273.65	0.971 ± 0.002	0.966	0.957	0.942
274.65	0.972 ± 0.002	0.967	0.957	0.945
275.65	0.974 ± 0.002	0.969	0.961	0.947
276.65	0.973 ± 0.000	0.970	0.963	0.950
Occupancy fraction of methane in small cage, θ_S				
273.65	0.920 ± 0.021	0.899	0.961	0.738
274.65	0.899 ± 0.020	0.904	0.961	0.748
275.65	0.869 ± 0.028	0.908	0.964	0.758
276.65	0.866 ± 0.005	0.912	0.965	0.768

Table 8. Comparison of experimental and predicted hydration numbers n of CH_4 hydrate at equilibrium pressure.

T (K)	Experimental n	Prediction of this model
273.15	6.00[a]	6.066
273.15	6.30[b]	6.066
274.65	6.03±0.02[c]	6.043

[a] Data from Galloway et al. (1970).
[b] Data from de Roo et al. (1983).
[c] Data from Sum et al. (1997).

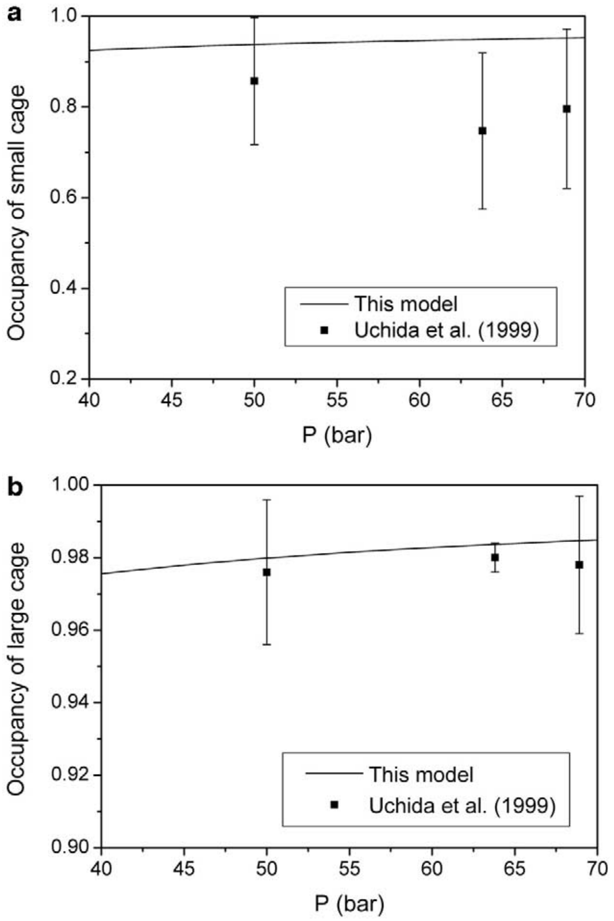

Fig. 9. Predicted and measured cage occupancy for methane hydrate at $T = 273.8$ K: (a) methane occupancy in small cage and (b) methane occupancy in large cage.

Table 9. Comparison of experimental and predicted hydration number n of CO_2 hydrate.

T (K)	P (bar)	Experimental n	Prediction of this model
268	9.9	7.0[a]	6.412
272	10.	6.6 ± 0.3[b]	6.505
273.15	12.	6.21[c]	6.441
273.15	12.	6.07[d]	6.441
273.65	12.	7.23[e]	6.548
276.	38.	6.20 ± 0.15[f]	6.099
278.	62.	6.4 ± 0.3[g]	6.093
283.	45.	5.6 ± 0.3[b]	6.151

[a] Ripmeester and Ratcliffe (1998).
[b] Anderson (2003).
[c] Yoon et al. (2003).
[d] Larson (1955).
[e] Kang et al. (2001).
[f] Udachin et al. (2001).
[g] Henning et al. (2000).

cage. Small cage occupancy predicted by them is even larger than the large cage occupancy, which indicates that the spherical ab initio potential obtained by Cao et al. (2001a, 2001b) is not accurate enough. Klauda and Sandler (2002, 2003) underestimated both the occupancy fraction of large cage and that of small cage by a large scale, which means that their multibody interaction approach can be in question, and the well depth of their ab initio potential is too shallow.

Uchida et al. (1999) reported the absolute cage occupancy data and hydration number for methane hydrates above the equilibrium pressure. Figure 9 compares the cage occupancy predicted by our study with the experimental data of Uchida et al. (1999). Table 8 compares the hydration number of CH_4 hydrate at equilibrium predicted by our study with the experimental data. It is obvious that our predictions are within or near to the experimental error of these data sets.

There is a large discrepancy in the cage occupancy and hydration number of CO_2 hydrate reported by different researchers as shown in Table 9. Ripmeester and Ratcliffe (1998) determined that the hydration number at 268 K is equal to 7.0. The hydration number at 273 K reported by Kang et al. (2001) is 7.23. However, the hydration number at 276 K and 38 bar measured by Udachin et al. (2001) is 6.20 ± 0.15. Uchida (1997) pointed out that the techniques for measuring the hydration number directly suffer from many problems concerning sample preparation and assumptions made in analysis. Based on the Clausius-Clapeyron equation, Larson (1955), Yoon et al. (2003), and Anderson (2003) derived the hydration number from the dissociation enthalpy of CO_2 hydrate. Table 9 compares the hydration number, predicted by this model, with experimental data. It can be seen that our predictions agree with the experimental data reported by Anderson (2003), Henning et al. (2000), Udachin et al. (2001) and Yoon et al. (2003).

6. CONCLUSION

By employing angle-dependent ab initio potentials of molecules, we improved the van der Waals-Platteeuw model to predict cage occupancy and phase equilibria of both CH_4 hydrate and CO_2 hydrate, with experimental accuracy. This approach is capable of extrapolating to high pressures, different from most hydrate models that employ Kihara potential with parameters derived from experimental equilibrium data of hydrates and that have little capability to extrapolate.

In this study, we use an atomic site-site Lennard-Jones formula plus an electrostatic term to fit the ab initio intermolecular potential energy surfaces of the CH_4-H_2O complex and the CO_2-H_2O complex to account for the angle-dependent molecular potential. This angle-dependent approach substantially improves the prediction of the hydrate properties. This study also includes the effect of water molecules beyond the first shell on Langmuir constants and used an accurate equation of state to calculate the fugacity of CH_4 and CO_2 at high pressures. The improved model can accurately predict the equilibrium pressure of CH_4 hydrate and CO_2 hydrate in binary systems over a wide T-P range. The absolute average deviation is less than 3%, which is within or close to the experimental uncertainty. The prediction of this model is more accurate than other hydrate models at high pressures (more than 500 bar). Furthermore, this model also can predict the cage occupancy and hydration number of CH_4 hydrate and CO_2 hydrate accurately without fitting any experimental data, which validates the method of computing thermodynamic properties from angle-dependent ab initio potential.

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