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Calculation of three-phase methane–ethane binary clathrate hydrate phase equilibrium from Monte Carlo molecular simulations

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ABSTRACT

Methane and ethane are the simplest hydrocarbon molecules that can form clathrate hydrates. Previous studies have reported methods for calculating the three-phase equilibrium using Monte Carlo simulation methods in systems with a single component in the gas phase. Here we extend those methods to a binary gas mixture of methane and ethane. Methane–ethane system is an interesting one in that the pure components form sI clathrate hydrate whereas a binary mixture of the two can form the sII clathrate. The phase equilibria computed from Monte Carlo simulations show a good agreement with experimental data and are also able to predict the sI–sII structural transition in the clathrate hydrate. This is attributed to the quality of the TIP4P/Ice and TRaPPE models used in the simulations.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds in which guest molecules occupy the cavities formed by the water molecules connected to each other in a tetrahedral fashion via hydrogen bonds. Integrating the Gibbs–Duhem equation for mixtures (see Eq. (10)), it can be shown that the occupancy of these cavities by the guest molecules stabilizes the hydrate phase by lowering the chemical potential of water in the hydrate phase, thereby making it stable over the aqueous phase [1–3]. Depending upon the nature of the guest molecules, hydrates occur in different crystal structures of which sI, sII and sH are the most common. There is a tremendous interest towards understanding of clathrate hydrates because of their applications in different scientific and technical areas including energy [1,4–6], gas storage and transportation [7,8], desalination of water [9–11], etc. The role played by hydrates in blocking transmission pipelines in oil/gas industries [12] and dissociation of methane hydrates leading to rise in global warming [13] also contributes to the importance of study of clathrate hydrates.

Methane and ethane are some of the simplest molecules that form clathrate hydrates. When the gas phase consists of either pure methane or pure ethane, the corresponding clathrate hydrate has sI structure. A unit cell of the sI structure contains 46 water molecules with two types of cavities: two small (5^{12}) cavities and six large ($5^{12}6^{2}$) cavities. Till 1990s, it was believed that the binary methane–ethane mixture also formed sI clathrate hydrate. However, the predictions from vdWP theory for methane–ethane binary hydrates were not good under certain thermodynamic conditions [14]. The theoretical study by Hendriks et al. [15] suggested that the mismatch between the theoretical predictions and the experimental data was due to structural transitions that lead to formation of methane–ethane binary hydrate in sII structure. Recent experimental studies [16–19] have confirmed that the methane–ethane binary hydrates undergo structural transitions and exist in sII structure, under certain thermodynamic conditions. Unlike the sI structure, a unit cell of sII clathrate contains 136 water molecules with two types of cavities: sixteen small (5^{12}) cavities and six large ($5^{12}6^{4}$) cavities. With the help of this new experimental evidence, the theoretical prediction [20,21] for methane–ethane binary hydrates phase equilibrium has shown improvements.

There have been considerable experimental [16–19,22] and theoretical [15,20,21,23] studies of methane–ethane binary clathrate hydrate system. The determination of sI–sII structural transition points via experiments is difficult and requires techniques such as Raman and NMR spectroscopic measurements [16–19]. In theoretical studies, van der Walls and Platteuw (vdWP) theory has been successfully used to predict the hydrate phase equilibria. But, vdWP theory needs experimental phase equilibrium data to regress the unknown parameters in the theory and also it has its own drawbacks [24,2,25–29]. Hendriks et al. [15] were able to use the vdWP theory to predict the structural transitions after regression with the methane–ethane binary hydrate phase equilibrium data. However,

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Table 1
Forcefield parameters used in molecular simulations for water, methane and ethane.

Molecule	Group	ϵ/k_B (K)	σ (Å)	$q(e)$
Water (H_2O)				
$\angle$H—O—H = 104.52°	O	106.1	3.1668	0.0
d_{OH} = 0.9572 Å	H			0.5897
d_{OM} = 0.1577 Å	M			−1.1794
Methane (CH_4)	CH_4	148.0	3.73	0.0
Ethane (C_2H_6)	CH_3	98.0	3.75	0.0

they were not in good quantitative agreement with the experimental data. To get correct structural transitions using vdWP theory additional information in the form of the location of the lower structural transition was needed. With this additional information, vdWP theory was able to successfully predict the upper transition point [20,21].

Molecular simulations have been successful in the qualitative and quantitative prediction of hydrate phase equilibria [30–32,25]. Methane hydrate phase equilibrium calculated using molecular simulations with TIP4P/Ice molecular model for water has shown close agreement with the experimental methane hydrate phase equilibrium. This motivated us to compute the methane–ethane binary hydrate phase equilibrium using currently existing forcefields and molecular models, and compare with experimental data on (i) the three phase equilibrium line for ethane hydrates, (ii) the three-phase equilibrium line for methane–ethane mixture hydrates and (iii) structural transitions between sI and sII clathrate hydrate.

2. Molecular model

Methane and ethane molecules are modeled using TRaPPE forcefield [33]. According to TRaPPE, methane is modeled as a rigid single site molecule and ethane is modeled as a rigid two site dumbbell with each site representing CH_3 group. The distance between the CH_3 groups is 1.54 A. Each site of the hydrocarbon molecules interacts with the rest of the system via van der Waals forces only that are modeled using Lennard–Jones potential. The forcefield has been parameterized (see Table 1) to match the VLE of methane and ethane [33]. Water molecule is modeled using four site TIP4P/Ice model [34]. The four sites correspond to one oxygen (O) atom, two hydrogen (H) atoms and one additional (designated as M) site near the oxygen lying on the HOH bisector. The O—H bond distance is 0.9572 A and the HOH angle is 104.52°. Each hydrogen (H) atom contains partial positive charge on them which is countered by the negative charge on the site M. This site is located at a distance of 0.1577 A from the oxygen atom. The net charge on water molecule is zero. The oxygen site interacts with the rest of the system via van der Waals forces modeled using the Lennard–Jones potential. The TIP4P/Ice model has been parameterized (see Table 1) to reproduce the solid–liquid phase diagram of water containing various phases of ice [34]. The van der Waals interactions between unlike sites are modeled using Lorentz–Berthelot rules.

3. Methodology and simulation details

The equivalence of temperature, pressure and fugacities of all components in all phases is the ternary hydrate phase equilibrium criteria. Similar to previous studies [31,35,25,24], we assume that the mole fractions of the hydrocarbons in the aqueous phase and water in the vapor phase are negligible. Accordingly, the three phase equilibrium criteria get modified as follows.

$$T^l = T^H = T^v \tag{1}$$

$$P^l = P^H = P^v \tag{2}$$

$$f_w^l = \hat{f}_w^H \tag{3}$$

$$\hat{f}_m^v = \hat{f}_m^H \tag{4}$$

$$\hat{f}_e^v = \hat{f}_e^H \tag{5}$$

where T, P and f represent the temperature, pressure and fugacity respectively. The superscripts l, v and H represent the liquid, vapor and hydrate phases respectively and the subscripts w, m and e represent water, methane and ethane respectively. The three-phase equilibrium is obtained by applying the above criteria to the equations of state for liquid, vapor and hydrate phases. The equations of state are determined from data obtained through Monte Carlo molecular simulations of each phase. The procedure [25] for determining the equations of state and calculating the phase equilibria is explained in the following subsections.

3.1. Liquid phase

As mentioned earlier, the liquid phase is assumed to be pure water since the solubility of methane and ethane is very low. The equation of state of the liquid phase is obtained by integrating the Gibbs–Duhem equation and is given as

$$\ln\left(\frac{f_w^l}{f_{w,0}^l}\right) = -\int_{T_0}^{T}\left(\frac{H_R^l}{RT^2}\right)_P dT + \int_{P_0}^{P}\left(\frac{V^l}{RT}\right)_{T_0} dP \tag{6}$$

where H_R is the residual molar enthalpy, and V is the molar volume. The subscript 0 indicates the reference state. The reference state for the liquid phase used in this study has been set to P_0 = 20 bar and T_0 = 280 K. The values of H_R^l and V^l are obtained from Monte Carlo simulations in the isothermal–isobaric ensemble. The simulations contained 400 water molecules with 100,000 equilibrium cycles and 100,000 production cycles. They were performed in the pressure range from 5 bar to 1100 bar and the temperature range from 270 K to 305 K. The electrostatic interactions were computed using Ewald summation techniques. The values of H_R^l and V^l were fitted to function of T and P. The form of fit is similar to the one suggested in Pimpalgaonkar et al. [25] and are given as follows:

$$V^l = a_1 + a_2T + a_3P + a_4PT$$

$$H_R^l = a_1P + \frac{a_3}{2}P^2 + a_5 + a_6T$$

Substitution of the above equation into Eq. (6) gives the following expression for fugacity.

$$\begin{aligned} ln\left(\frac{f_w^l}{f_{w,0}^l}\right) &= \left(\frac{a_1}{R}\right)\left(\frac{P}{T}-\frac{P_0}{T_0}\right) + \left(\frac{a_2}{R}\right)(P-P_0) \\ &\quad + \left(\frac{a_3}{2R}\right)\left(\frac{P^2}{T}-\frac{P_0^2}{T_0}\right) + \left(\frac{a_4}{2R}\right)(P^2-P_0^2) \\ &\quad + \left(\frac{a_5}{R}\right)\left(\frac{1}{T}-\frac{1}{T_0}\right) - \left(\frac{a_6}{R}\right)\ln\left(\frac{T}{T_0}\right) \end{aligned} \tag{7}$$

The values of the coefficients are regressed from the simulation data and given in Table 2. A comparison of the simulation data and the predictions of V^l and H_R^l from regression are given in Fig. 1. The fugacity of water at the reference state was calculated by the method of Hamiltonian integration [36] and determined to be $f_{w,0}^l = 24.35$ Pa.