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Exploring the effect of important parameters on decomposition of gas hydrate structure I: A molecular dynamics simulation study

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ABSTRACT

The aim of this study was to investigate the stability of methane hydrate in the NPT ensemble using MD simulation. Methane hydrate at 6 different cage occupancies ranging from 75 to 100% was placed arbitrarily in a cubic cell. Methane hydrate decomposition was explored at the equilibrium pressure for varied temperatures (T = 290, 300, and 310 K). The effect of cage occupancy of the hydrate structure – ranging from fully hydrate to empty small cage structures – on the hydrate stability and decomposition rate was examined. Simulation results showed that at constant temperatures, the decomposing process was accelerated at lower cage occupancy. Decomposition process increased the total energy of the system and enhanced the diffusion coefficient. When hydrate structure decomposed, the coulombic energy term was increase about 18% while LJ potential energy decreased about 33%. In stable hydrate crystal, diffusion coefficient of water oxygen in hydrate had an order of magnitude of 10^{-15} m^2/s while in decomposed hydrate structure, the diffusion coefficient order of magnitude was changed to 10^{-9} m^2/s. This changed the RDF curve of the system from solid to liquid-like structure by reducing the number of peaks versus distance. In addition, the value of coordination number of water-water molecules at a distance of 1 nm in the system during the decomposing process enhanced about 20% which confirmed changing the structure from solid state to liquid. Also, after dissociation of hydrate structure, the number of hydrogen bonding were decreased. Finally, results suggested that each of these parameters could be successfully applied to predict the decomposition of gas hydrate structure from ice-like stable phase to liquid-like structure.

1. Introduction

Clathrate hydrates are ice-like inclusion compounds formed at low temperature and high pressure. The host lattice of these clathrate hydrates is composed of water molecules that encage small guest atoms or molecules in cavities. Each cavity is large enough to accommodate at least one guest (Makogon, 1997; Takeuchi et al., 2013; Rodger, 1991; Sloan, 2003). The empty lattice is thermodynamically unstable, and its existence is dependent upon hydrogen bond stabilization derived from the enclathration of the trapped solutes. Three famous known structures of gas hydrates formed by various gas molecules are: structure I (sI), structure II (sII) and structure H (sH) hydrate. Structure I hydrate consists of two types of cavities: a small cage consisting of 12 pentagonal rings of water (5^{12}), and a larger cage consisting of 12 pentagonal and two hexagonal rings ($5^{12}6^2$). This structure can be formed by methane, xenon, carbon dioxide, ethylene oxide, and similar molecules (Sloan, 2003; Roosta et al., 2013; Yuhara et al., 2015). Structure II hydrate also consists of two types of cavities, a small cage (5^{12}) and a larger cage made of 12 pentagonal and four hexagonal rings of water ($5^{12}6^4$). This hydrate structure can be formed by propane, iso butane and transportation gases like O_2 and N_2 (Makogon, 1997). Structure H hydrates consist of three types of cages; a 5^{12} cage, a larger $5^{12}6^8$ cage and an intermediate cage consisting of 3 squares, 6 pentagonal and 3 hexagonal rings of water ($4^35^66^3$). It appears that structure I and II hydrates are more likely to form in nature than in other structures. Structure H is mostly found in artificial systems. For example, structure II is often developed in oil and gas pipelines and structure H is favored when a heavy hydrocarbon such as methyl cyclohexane or neohexane is present with methane and water in the pipeline (Takeuchi et al., 2013; Sloan, 1998).

Gas hydrate formation poses a serious challenge to oil and gas industry. Gas hydrate can be hazardous and cause economic loss in oil and gas transmission lines, tie-backs, and off-shore process equipment (Sloan, 1998; Qin et al., 2015). The stability of clathrate hydrates is significantly dependent on the temperature and gas pressure of the guest species to be encapsulated. Among various types of hydrate,

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methane hydrate has been the subject of growing attention due to the abundance of methane in terrestrial hydrates. To assess the risk of hydrate formation in a pipeline or other installation in connection with hydrocarbon extraction, numerous experimental (Roosta et al., 2015, 2016; Hao et al., 2008) and computational (Platteeuw and Van der Waals., 1958; Sloan and Koh., 2008; Walsh et al., 2011; Barnes and Sum., 2013) studies have been undertaken with regard to methane hydrate formation and dissociation. The structural, dynamical, and thermal properties of this hydrate have been characterized (Bagherzadeh et al., 2012; Jensen et al., 2010; English and Phelan, 2009; Barnes et al., 2014; Alavi et al., 2010; Jacobson and Molinero, 2010), but laboratory measurements have been unable to identify the molecular mechanism of hydrate deformation, due to the instability associated with the precise targeting of the time and spatial domain of a collapse event, which may occur in nanoseconds on the nanometer-length scale (Koh et al., 1996, 2000). Applying molecular simulations can help overcome these problems (Bagherzadeh et al., 2012; Jensen et al., 2010; English and Phelan., 2009; Anderson et al., 2004; Baghel et al., 2013; Kvamme et al., 1997). Among various types of molecular simulation, classical molecular dynamics simulation (MDS) can be useful for this purpose. By applying MD simulation, it is possible to follow the nano-scale trajectories of molecules for the formation and decomposition of hydrates (Sloan and Koh, 2008; Walsh et al., 2011; Barnes et al., 2014; Alavi et al., 2010; Jacobson and Molinero, 2010).

So far, many parameters have been proposed to discover the behavior of gas hydrates in the simulation environment, but accurate classifications of these parameters have not been conducted.

In 2002, Chialvo et al. studied the structural and a thermo-physical property of structure I clathrate hydrates and drew the radial distribution functions of host and guest molecules. Also, they applied various water force fields such as SPC, SPC/E and TIP5P to perform isothermal-isobaric molecular dynamics simulations. Their results showed that the strength of the host-guest interactions affected the realistic molecular descriptions of the host intermolecular potentials. Also, they changed host occupancy (θ) from 1 to zero without observing any visible change in the height of the first peak of radial distribution function curve for guest molecules at the cage occupancy of $1 \leq \theta \leq 0.5$ while this value changed from 3 to 8 for $0.5 \leq \theta \leq 0.125$ which in the end corresponded to dilute aqueous solution (Chialvo et al., 2002).

In 2005, Abascal and Vega discussed the ability of several water models to predict the properties of ice. Their simulation stressed the results for densities and coexistence curves between different ice forms. According to their results, TIP4P/Ice could successfully reproduce the solid phase of water and three-point force fields such as SPC and SPC/E were unable to determine the melting point and melting enthalpy of ice (Abascal and Vega, 2005).

In another study, Miyoshi et al. investigated thermodynamic stability of type-I and type-II clathrate hydrates using various chemical species of the guest substances such as methane. They calculated Lennard-Jones parameters for methane component as guest molecule by assuming zero charge of species in Coulombic term. According to their findings assuming methane as a sphere with zero point charge was a reliable assumption (Miyoshi et al., 2007).

In 2009, English and Phelan studied the thermally-driven methane hydrate dissociation at different hydrate cage occupancies from complete to 85% occupancy at a temperature range of 280–340 K, concluding that in all cases, the diffusion of methane molecule into the surrounding liquid water was an important step limiting the overall rate of breakup. They concluded that partially-occupied hydrates had an effective impact on the hydrate thermal dissociation (English and Phelan, 2009).

In 2009, Myshakin et al. have studied MD simulations of the dissociation of methane hydrate at different cage occupancies as 85%, 95%, and 100% in the temperature range from 265 to 300 K. The decomposition of the hydrate was characterized by a breakdown of the hydrogen bond network of the hydrate lattice and the diffusion of methane molecules from partially open cages into the liquid phase. They concluded that the break-up rate displays Arrhenius temperature dependence and is relatively sensitive to methane composition (Myshakin et al., 2009).

In 2010, Luis et al. investigated the structural properties of fully methane hydrate using rigid water models such as SPC/E, TIP4P and TIP5P. Their study focused on the capabilities of these water models in the near region of phase transition line. A comparison of their results with experimental data suggested that all water models were able to predict the dissociation of the clathrates. Also, they concluded that the coordination number was a useful criterion to demonstrate the dissociation of clathrates (Luis et al., 2010).

In 2013, Conde and Vega simulated three-phase coexistence line in methane hydrate at a pressure of 100 bars by applying five different potential functions such as SPC, SPC/E, TIP4P, TIP4P/2005 and TIP4P/ice. Their results showed that the three-phase coexistence line for fully hydrate by applying SPC and SPC/E potential functions appeared at much lower temperatures in comparison to the application of TIP4P-like model. This observation was in agreement with the experimental results. They concluded that SPC and SPC/E models were not appropriate to predict melting point of ice (Conde and Vega, 2013).

These studies have provided valuable vision into the stability of hydrates and their dissociation behavior in molecular level. However, a review of literature suggests the paucity of studies on the decomposition process at cage occupancy lower than 100% in clathrate hydrate structure which is not based on the number of gas molecules released from hydrate interface to bulk. In addition, in previous studies, methane hydrate decomposition was reported at a constant temperature. There are few studies that focus on the effect of temperature on dissociation state at wide range of cage occupancy and temperatures. One of main challenges facing methane hydrate dissociation is investigating the stability of structure I methane hydrate when the cage is not fully occupied by methane molecules at different temperatures. It is necessary to explore the simultaneous effects of cage occupancy and temperature on the dissociation process.

The aim of this study is to classify important hydrate structure parameters and investigate their effects on the decomposition process of methane hydrate at a wide range of cage occupancies and temperatures. To this end, MD simulation was applied. Also, the effect of cage occupancy and temperature on the decomposing process was investigated in various cage occupancies in the range of 75–100% at three temperatures (290, 300 and 310 K). Moreover, total energy, radial distribution function, diffusion coefficient of molecules as well as coordination number and hydrogen bonding were calculated in terms of simulation time.

2. Simulation details

2.1. System preparation

To construct the hydrate structure, the initial positions of oxygen atoms of water molecules were determined using crystallography data obtained from the literature (Takeuchi et al., 2013; McMullan and Jeffrey, 1965). A box with 3.6 nm × 3.6 nm × 3.6 nm dimensions in x, y and z axes was constructed that included 1242 water molecules in 27 unit cells of hydrate. Then, one methane molecule was placed in the middle of each small and large cage to produce structure I methane hydrate with 100% cage occupancy, as shown in Fig. 1. For other cage occupancies, methane molecules in small cage were removed randomly. Cage occupancy was estimated by θ = N/216 where N is the number of methane in the box and 216 is the number of methane in 27 fully-occupied unit cells and it contains at most 8 methane atoms per unit cell. The cage occupancy was a measure of gas content in the hydrate phase. It should be noted that cage occupancy ratios changed from $G{\cdot}5(3/4)\ H_2O$ to $G{\cdot}7(2/3)\ H_2O$ in this work. In other words, simple hydrates tend to have more water molecules than the ideal composition