



Investigation on the kinetics of methane and carbon dioxide hydrates by using a modified kinetic model



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ABSTRACT

In this work, the experimental and modeling investigations are conducted on the formation kinetics of methane and carbon dioxide hydrates. First, the hydrate formation experiments are done under constant temperature and volume conditions. The experiments are also conducted at 400, 600 and 800 rpm stirrer speeds in the presence of pure water. Subsequently, a kinetic model based on the mass transfer restriction of the gas through the liquid film of the gas–liquid interface has been applied for describing the kinetics of hydrate formation. This kinetic model is expressed in terms of the mole fraction of hydrate former in the gas–liquid interface. Also, in order to determine interfacial mole fraction of hydrate former, the parachor model in terms of interfacial properties is applied. The results of this model have been applied for analyzing the effects of different parameters on kinetics of hydrate formation.

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1. Introduction

In recent years, clathrate hydrates or gas hydrates have been an intriguing area of research for industrial applications. These crystalline solid structures are inclusion compounds made up of water molecules and certain guest molecules with suitable sizes under favorable thermodynamic conditions (elevated pressures and/or low temperatures). The guest molecules are surrounded by water cavities formed due to hydrogen bonding between the molecules of water. The van der Waals forces between the guest molecules and the cavities of water lead to thermodynamically stable structure of gas hydrate. The crystallographic structure of gas hydrate mainly depends on the size of cavities and guest molecules. Structure I (sI), structure II (sII) and structure H (sH) are the three most common structures of gas hydrates (Torre' et al., 2012; Mohebbi et al., 2012).

Gas hydrate is capable of being used as an industrial way of water desalination, cool-energy storage, natural-gas storage, gas separation, etc (Okutani et al., 2008). It is known that the successful application of gas hydrate for industrial purposes mainly depends on the hydrate formation kinetics. On the other hand, gas hydrate formation is one of the most complex and stochastic processes; therefore, in order to study this process, using a kinetic model is of importance. According to the driving

forces applied for describing hydrate formation kinetics, such as temperature difference (Varaminian, 2000), concentration difference (Skovborg and Rasmussen, 1994) and fugacity difference (Englezos et al., 1987), etc, different kinetic models have been utilized for modeling the hydrate formation kinetics, for instance, semi-empirical model versus the rate of gas consumption (Vysniauskas and Bishnoi, 1983, 1985), the mass and heat transfer models of hydrate formation (Varaminian, 2002; Clarke and Bishnoi, 2005), the kinetic models versus hydrate growth (Ribeiro and Lage, 2008) and the kinetic models in terms of non equilibrium thermodynamics such as chemical affinity (Roosta et al., 2013; Seyfi Mazraeno et al., 2013; ZareNezhad and Varaminian, 2012; Mottahedin et al., 2011).

Various modeling and experimental efforts have already been done in order to investigate the kinetics of hydrate formation process. Monfort et al. (2000) conducted a complete experimental investigation on the formation kinetics of ethane and propane hydrates in an agitated and semi-batch cell. Furthermore, they suggested new correlations for evaluating the rate of hydrate crystal growth. Sun et al. (2003) investigated on the hydrate formation rate of R12 (CCl₂F₂) at the temperature of 277.1 K and the pressures of 0.24 MPa and 0.32 MPa in a circulating flow system. By using the material balance, they developed a mathematical model for gas consumption, average hydrate particle size and shading ratio. Jerbi et al. (2010) studied the kinetics of carbon dioxide hydrate formation and dissociation in semi-batch agitated cell. They concluded that the hydrate growth rate of CO₂ hydrate was approximately

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1.8×10^{-31} hydrate s^{-1} at the stirring velocity of 450 rpm. This investigation indicated that for their system, by using an isothermal circulation loop, the kinetics of hydrate formation varied from 1.8×10^{-31} to 1.8×10^{-3} hydrate s^{-1} . Tajima et al. (2010) conducted the experimental and modeling investigation on the HFC 134a hydrate formation kinetics in a static mixer. They found that the hydrate formation rate was equal to the mass transfer rate of hydrate shedding from the gas bubble. Furthermore, they determined the kinetic constant of hydrate formation. Bergeron et al. (2010) performed particle size distribution measurements for methane hydrate formation in formation in a semi-batch stirred cell. They also applied Bergeron and Servio (2008) model to estimate the reaction rate constant for methane hydrate formation. Al-Otaibi et al. (2010) obtained experimental data for the kinetics of pure methane and ethane hydrates formation in a semi-batch and stirred cell. They also used the particle size analyzer for their experiments. By using experimental pressure, temperature, and particle size distribution, they determine the kinetics of pure methane and ethane hydrates formation. ZareNezhad and Varaminian (2012) used the chemical affinity model for hydrate formation rate in the isothermal-isochoric cell for different gas hydrates containing CH₄ (methane), C₂H₆ (ethane), C₃H₈ (propane), CO₂ (carbon dioxide) R-22 (hydrochlorofluorocarbon-22) and Xe (xenone). Mohebbi et al. (2012) conducted experimental and modeling study on methane hydrate formation rate in a stirred cell. They also applied a mass transfer model based on Skovborg and Rasmussen (1994) model.

In this work, the modeling and experimental studies are conducted on the kinetics of methane and carbon dioxide hydrates in a stirred cell under constant volume and temperature conditions. Subsequently, the hydrate formation rate is described in terms of mass transfer through gas–liquid interface so that the kinetic model of Skovborg and Rasmussen (1994) is expressed according to the concentration of hydrate former in the interface phase. In the model of Skovborg and Rasmussen (1994), the interfacial mole fraction of hydrate former was set equal to mole fraction (solubility) of hydrate former in the bulk liquid phase which is not true. Therefore, to improve the kinetic model of Skovborg and Rasmussen (1994), the mole fraction of hydrate former in the interface phase is computed by using the parachor model based on the work of Tjahjono and Garland (2010) and the interfacial properties. It should be mentioned that this investigation is just valid when gas hydrate forms in pure water.

2. Experimental

2.1. Materials

Methane and carbon dioxide are supplied by Technical Gas Services. These two hydrate formers have purities about 99.99%. The information of hydrate formers and water used in experiments has been listed in Table 1.

2.2. Apparatus

In this work, as it is shown in Fig. 1, the kinetic experiments of hydrate formation were done in the cylindrical and stainless steel cell.

Table 1
Materials used for experiments.

Component	Chemical formula	Purity	Supplier
Carbon dioxide	CO ₂	99.99%	Technical gas services
Methane	CH ₄	99.99%	Technical gas services
Water	H ₂ O	Deionized-distilled	Bahrezolal, Iran

The total capacity of the cell was 600 cm³. The hydrate formation cell had a four-blade mixer. It was also capable of operating in the pressures ranged (0–100) bar and the temperatures ranged (253.15–373.15) K. The mixture of (water + ethylene glycol) was used as a coolant which was circulated by using a circulation pump through the jacket of the cell. This controllable circulator was utilized for adjusting the temperature of the high pressure cell with the accuracy of ± 0.1 K. A PT100 thermometer (Pro-Temp Controls, Santa Ana, California, United States) that had an accuracy of ± 0.1 K was used for measuring the temperature of the high pressure cell. Furthermore, a BD-Sensors-Str.1 pressure transmitter that had an accuracy of ± 0.1 bar was used for measuring the pressure of high pressure cell. The hydrate formation cell had a data acquisition system.

2.3. Experimental procedure

Prior to conducting any hydrate formation experiment, the high pressure cell was rinsed with de-ionized water for two times. Then the high pressure cell was evacuated with a vacuum pump. The high pressure cell was charged with 300 cc of de-ionized water. Subsequently, at each specified temperature, the high pressure cell was pressurized up to 5 bar under the equilibrium pressure of methane or carbon dioxide hydrate formation. The constant temperature bath was turned on. After the high pressure cell reached the constant specified temperature, the high pressure cell was pressurized up to the specified pressure. This specified pressure was selected between the saturation pressure of the hydrate former (gas) and the equilibrium pressure of hydrate formation. The initial operational and equilibrium conditions of hydrate formation are shown in Figs. 2 and 3 for methane and carbon dioxide hydrates, respectively. Then the stirrer started to work at the specified speed and pressure of high pressure cell was recorded during the hydrate formation process until the pressure of high pressure cell reaches to equilibrium pressure of hydrate formation. Similar to the work of (Li et al., 2009; Mohebbi et al., 2012; Karimi et al., 2014), based on the pressure drop in the cell and vapor phase, the amount of hydrate former (gas) consumed during the formation process was computed by using Eq. (1):

$$n_{ci} = n_o - n_i = \left(\frac{PV}{ZRT} \right)_o - \left(\frac{PV}{ZRT} \right)_i \quad (1)$$

In Eq. (1), n_{ci} is the consumed moles of hydrate former, n_o is the initial mole of hydrate former, n_i is the mole of hydrate former at any time, P is the pressure, T is the temperature, Z is the compressibility factor, V is the volume of hydrate former and R is the universal constant of gases. Subscripts o and i show the initial condition and the condition at any time, respectively.

In this study, the VTSRK EOS (Lin et al., 2006) was applied for computing compressibility factor of methane or carbon dioxide. In the high pressure cell, as it is shown in Eq. (2), the rate of gas consumption during hydrate formation is considered as the difference between initial condition of hydrate former and the condition of the hydrate former at any time.

$$\frac{\Delta n}{\Delta t} = \frac{n_o - n_i}{\Delta t} = \frac{\left(\frac{PV}{ZRT} \right)_o - \left(\frac{PV}{ZRT} \right)_i}{\Delta t} \quad (2)$$

In Eq. (2), t is the time.

3. The description of model

3.1. Kinetic model

As it is mentioned in the introduction part, different driving forces can be considered for hydrate formation process. In this

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