

Dissociation behavior of (CH₄ + C₂H₄) hydrate in the presence of sodium dodecyl sulfate

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Abstract: Separation of a mixture of CH₄+C₂H₄ gas by forming hydrate in ethylene production has become of interest, and the dissociation behavior of (CH₄+C₂H₄) hydrate is of great importance for this process. The hydrate formation rate could be increased by adding a small amount of sodium dodecyl sulfate (SDS) into water. In this work, the kinetic data of CH₄(18.5 mol%)+C₂H₄(81.5 mol%) hydrate decomposition in the presence of 1000 mg·L⁻¹ SDS at different temperatures and pressures were measured with the depressurizing method using a sapphire cell apparatus. The experimental results show that the dissociation rate of (CH₄+C₂H₄) mixed gas hydrate was large at high temperature and low pressure, and temperature had great influence on the dissociation rate at high pressure. A kinetic model for hydrate dissociation was proposed and the calculated results from the kinetic model were in good agreement with the experimental data. The activation energy for dissociation of the (CH₄+C₂H₄) mixed gas hydrate was determined to be 43.9 kJ·mol⁻¹, which is lower than that of methane (81.0 kJ·mol⁻¹) and ethane (104.0 kJ·mol⁻¹) hydrate in water (Clarke and Bishnoi, 2004). As the similar molecular dimensions between ethane and ethylene, the close activation energy need to be provided for ethylene hydrate dissociation. The obtained activation energy of the (CH₄+C₂H₄) mixed gas hydrate dissociation indicates that the dissociation of the (CH₄+C₂H₄) mixed gas hydrate is easier than that of pure CH₄ or C₂H₄ gas hydrate.

Key words: Methane, ethylene, hydrate, dissociation, SDS

1 Introduction

Gas hydrates are nonstoichiometric crystalline compounds, which are formed when water molecules form cages through hydrogen-bond and enwrap small gas molecules (such as CH₄, C₂H₄, C₂H₆, and C₃H₈) at suitable temperature and pressure. In recent decades, a number of technologies based on hydrate were developed for industrial application, such as the separation of gas mixtures (Sun et al, 2007a; Vorotyntsev et al, 2001; Zhang et al, 2004; Luo et al, 2007), the desalination of seawater (Javanmardi and Moshfeghian, 2003), the deep sea sequestration of CO₂ (Brewer et al, 1999; Haugan and Drange, 1992) and storage and transportation of natural gas (Wang et al, 2008; Khokhar et al, 1998). When a gas mixture partially forms hydrate, the relative concentration of each component in the hydrate solid phase and in the residual vapor phase are likely to be different, the component that can form hydrate more easily will be enriched in hydrate phase (Zhang et al, 2006a). Since methane and ethylene are two major components of refinery gases or cracking gases

in ethylene plants, their separation has attracted increasing attention. Much research has demonstrated that the presence of sodium dodecyl sulfate (SDS) can drastically accelerate hydrate formation (Kalogerakis et al, 1993; Gayet et al, 2005; Zhong and Rogers, 2000; Sun et al, 2007b; Lin et al, 2004).

Separating gas mixtures safely and economically by forming hydrate requires knowledge of the thermodynamics and kinetics of hydrate formation and dissociation. In thermodynamics, the hydrate phase equilibrium of (CH₄+C₂H₄) system has been investigated by many researchers (Ma et al, 2001; Ma et al, 2008; Sugahara et al, 2003). However, reports on the dissociation of (CH₄+C₂H₄) hydrate are rarely seen. Kim et al (1987) developed a model for the intrinsic rate of CH₄ hydrate decomposition and determined the rate constant from experimental data. Sun and Chen (2006) performed methane hydrate dissociation above 0 °C and below 0 °C, and suggested that the methane hydrate dissociation rate is controlled by an intrinsic dissociation reaction at temperatures higher than 0 °C. Clarke and Bishnoi (2001) measured the dissociation rate of methane+ethane hydrate in a semi-batch stirred-tank reactor, and determined the intrinsic rate constant and activation energy for methane in structure II hydrate. Additionally, Rovetto et al (2007)

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determined the dissociation behavior of $(\text{CH}_4+\text{C}_2\text{H}_6)$ and $(\text{CH}_4+\text{CO}_2)$ binary gas hydrates with structure I using NMR spectral analysis, and the results indicated that the gas composition did not change after hydrate dissociation.

Ethylene is the major component of cracking gas in ethylene plants, and is usually accompanied by a small amount of methane gas. In order to decrease the pressure loss in separating gas mixtures by forming hydrate, the dissociation of the mixed gas hydrate needs to take place at high pressure and a suitable temperature. The purpose of this work is to measure the kinetic data of CH_4 (18.5 mol%)+ C_2H_4 (81.5 mol%) hydrate dissociation at different temperatures and three fixed pressures 1.0, 2.0 and 3.0 MPa using a transparent sapphire cell, and to investigate the dissociation behavior of $(\text{CH}_4+\text{C}_2\text{H}_4)$ hydrate.

2 Experimental

2.1 Material and preparation of samples

Analytical grade methane (99.99%) and ethylene (99.5%) supplied by Beijing AP Beifen Gases Industry Company, Limited, China were used to prepare the gas mixture of CH_4 (18.5 mol%)+ C_2H_4 (81.5 mol%). This mixed gas sample was analyzed by a Hewlett-Packard gas chromatograph (HP6890). The critical micelle concentration (CMC) at different temperatures and pressures for (methane+SDS+water) system and (ethylene+SDS+water) system has been reported by Peng et al (2006) and Luo et al (2006), respectively. Surfactants with a content below their CMC did not influence the thermodynamic equilibrium of hydrate (Kalogerakis et al, 1993; Gayet et al, 2005). In this work, the SDS concentration is lower than its CMC, so the equilibrium condition of the $(\text{CH}_4+\text{C}_2\text{H}_4)$ mixed gas hydrate is regarded as the same as in pure water, and can be calculated by using the Chen-Guo

hydrate model (Chen and Guo, 1998), and the calculated result is shown in Fig. 1. The water used in experiment was twice-distilled water and its conductivity was less than $10^{-4} \text{ S}\cdot\text{m}^{-1}$. The SDS, with a purity of 99.5%, was supplied by Beijing Chemical Reagents Company, China. An electronic balance with a precision of $\pm 0.1 \text{ mg}$ was used for preparing aqueous solution with a SDS concentration of $1000 \text{ mg}\cdot\text{L}^{-1}$.

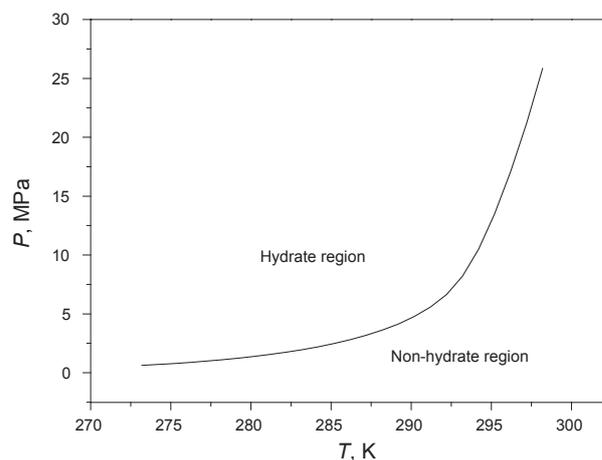


Fig. 1 Equilibrium diagram of mixed CH_4 (18.5 mol%)+ C_2H_4 (81.5 mol%) hydrate

2.2 Apparatus and procedures

The experimental apparatus used in this work has been described in detail in the previous papers from our laboratory (Lin et al, 2004; Sun et al, 2006). It was also used for measuring the hydrate formation conditions of (methane+ethylene+tetrahydrofuran+water) systems (Zhang et al, 2006b). Fig. 2 shows the schematic diagram of the

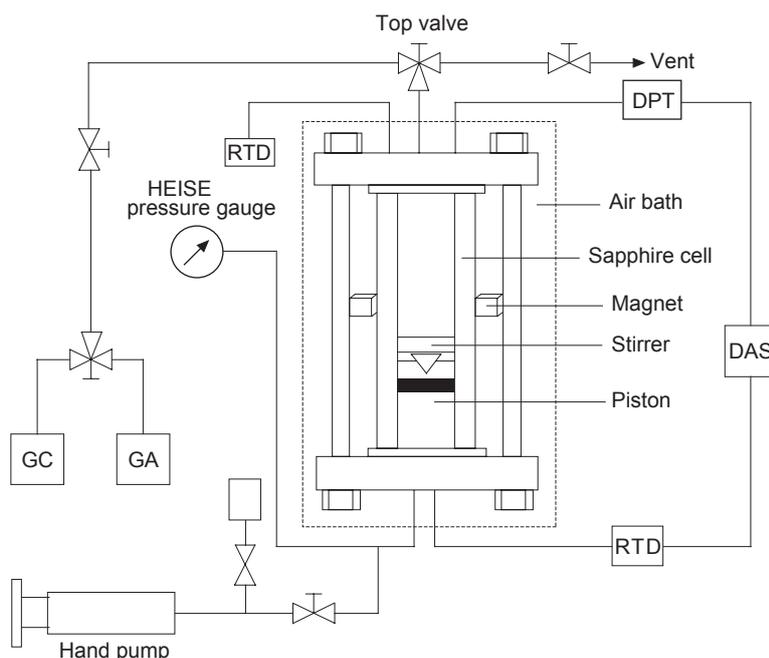


Fig. 2 Schematic diagram of the experimental apparatus
RTD – resistance thermocouple detector; DPT – differential pressure transducer;
GC – gas cylinder; GA – gas aerometer; DAS – data acquisition system

experimental apparatus. It consists of a cylindrical transparent sapphire cell (with an inner diameter of 2.54 cm and a maximum workspace of 78 cm³) installed in an air-bath and equipped with a magnetic stirrer for accelerating the equilibration process. The formation/dissociation of the hydrate crystals in the solution can be observed directly through the transparent cell. A gasometer, manufactured by RUSKA Instrument Corporation, U.S.A, with a volume of 2 L and a precision of 0.1 mL, was used to collect the dissociation gas. The accuracy of temperature and pressure measurement was ± 0.1 K and ± 0.025 MPa, respectively.

About 30 mL of water+SDS (1000 mg·L⁻¹) solution was injected into the high pressure sapphire cell and then the sapphire cell was evacuated. Then the mixed gas CH₄(18.47 mol%)+C₂H₄(81.53 mol%) was introduced to the cell until the desired pressure (1.0, 2.0 or 3.0 MPa) was attained, which is above the three-phase (gas, liquid and hydrate phase) equilibrium pressure. When both pressure and temperature became stable, stirring was started and the hydrate was formed with continuous gas consumption. After the majority of the water was converted into hydrate, the cell was depressurized to a pressure about 0.05 MPa above the equilibrium pressure by releasing gas to atmosphere. When the system was stable, the cell was further depressurized to the hydrate dissociation pressure, and the pressure was maintained by moving the piston. The temperature of the cell was maintained by the air bath. The gas from the cell was collected using an aerometer and the dissociation time was also recorded.

3 Modeling of hydrate dissociation

Water is released from the destruction of the clathrate host lattice at the surface of a hydrate particle and desorption of the guest molecules from the surface of hydrate particles (Kim et al, 1987). Since the dissociation temperature in this work is higher than 0 °C, the mass transfer resistance can be ignored (Sun et al, 2006). It might be assumed that the dissociation temperature of (CH₄+C₂H₄) mixed gas hydrate at the surface of solid hydrate is equal to the temperature in the bulk gas phase. Temperature is an important variable in separating gas mixtures by forming hydrate. The difference between the equilibrium temperature of the (CH₄+C₂H₄) mixed gas hydrate at dissociation pressure and the bulk gas phase temperature was used as the driving force of hydrate dissociation. We also assume that the hydrate particles are spherical, and the hydrate dissociation is then recognized as an intrinsic reaction (Sun et al, 2006; Clarke and Bishnoi, 2001). Thus the rate of hydrate dissociation is written as

$$-\frac{dn_H}{dt} = k_d(4\pi r_c^2)(T_{eq} - T) \quad (1)$$

where K_d is the apparent dissociation rate constant; r_c is the hydrate particle radius at time t ; T_{eq} and T are the equilibrium temperature of the (CH₄+C₂H₄) mixed gas hydrate at the dissociation pressure and the bulk gas phase temperature, respectively; n_H is the moles of (CH₄+C₂H₄) mixed gas in the hydrate. The hydrate dissociation rate can also be expressed by the following equation

$$\frac{dn_H}{dt} = -4\pi r_c^2 \rho_s \frac{dr_c}{dt} \quad (2)$$

where ρ_s is the gas density in hydrate phase. Substituting Eq. (2) into Eq. (1), we can obtain

$$\frac{dr_c}{dt} = k_d(T_{eq} - T) / \rho_s \quad (3)$$

Integrating Eq. (3) and substituting the initial condition of $t = 0, r_c = r_0$, gives

$$1 - \frac{r_c}{r_0} = Kt \quad (4)$$

where

$$K = k_d(T - T_{eq}) / (\rho_s r_0) \quad (5)$$

r_0 is the hydrate particle radius before dissociation. The relationship of the remaining hydrate amount (x) during dissociation and $\frac{r_c}{r_0}$ can be expressed by the following form

$$x = \frac{n_H}{n_0} = \frac{4/3\pi r_c^3}{4/3\pi r_0^3} = \left(\frac{r_c}{r_0}\right)^3 \quad (6)$$

where n_0 is the number of moles of (CH₄+C₂H₄) mixed gas in the hydrate before dissociation.

Substituting Eq. (6) into Eq. (4), we can get

$$1 - x^{1/3} = Kt \quad (7)$$

Eq. (7) can thus be used to describe the experimental data of x for an isothermal–isobaric experiment.

4 Results and discussion

According to the experimental method mentioned above, the dissociation rate of CH₄(18.5 mol%)+C₂H₄(81.5 mol%) mixed gas hydrate in the presence of 1000 mg·L⁻¹ SDS was obtained at the pressure of 1.0, 2.0 and 3.0 MPa and temperature range from 283.2 K to 292.2 K. During the hydrate dissociation, the possible change of gas composition during the hydrate dissociation was ignored (Clarke and Bishnoi, 2001). It was also assumed that the heat conductivity of the sapphire cell is excellent, i.e., the temperature of bulk gas phase is always equal to that of the air bath throughout the hydrate dissociation. The experimental data were correlated by Eq. (7), in which only one adjustable parameter K is contained. The experimental result and calculated result are shown in Figs. 3 to 5 for comparison.

From Figs. 3 to 5, it can be seen that the agreement between the calculated values and the experimental data is satisfying. When the pressure is specified, the proportion of remaining (CH₄+C₂H₄) hydrate during dissociation at the same time decreased with an increase of temperature, indicating that the dissociation rate increased with increase of temperature at a specified pressure. However, the decomposition time of the (CH₄+C₂H₄) mixed gas hydrate was shorter at low pressure than that at high pressure at the same temperature. That is to say that the larger dissociation rate can be obtained at higher temperature and lower

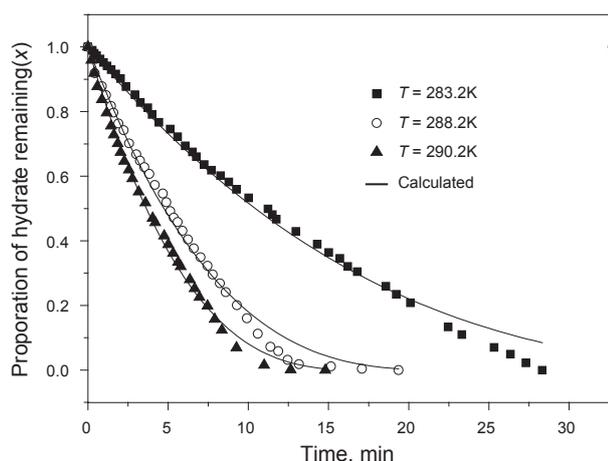


Fig. 3 Relationship of the proportion of (CH₄+C₂H₄) hydrate remaining during dissociation with time at 1.0 MPa

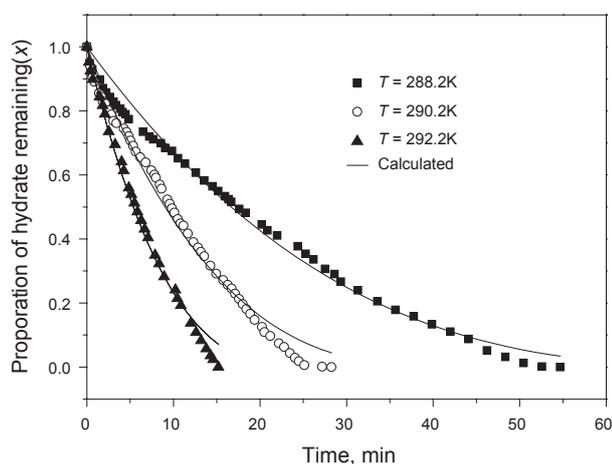


Fig. 4 Relationship of the proportion of (CH₄+C₂H₄) hydrate remaining during dissociation with time at 2.0 MPa

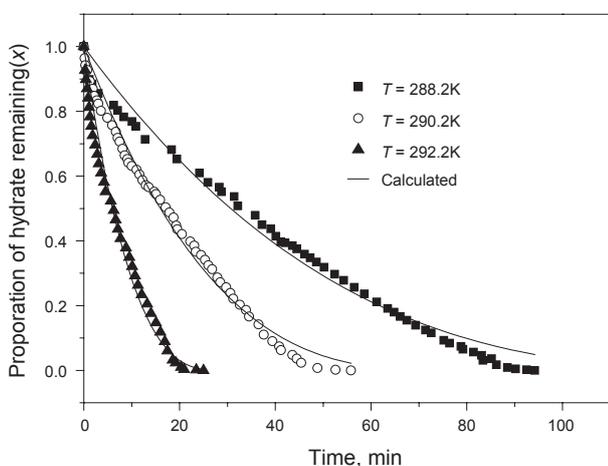


Fig. 5 Relationship of the proportion of (CH₄+C₂H₄) hydrate remaining during dissociation with time at 3.0 MPa

pressure. This is ascribed mainly to the large driving force for hydrate dissociation at high temperature and low pressure. In addition, the time for complete dissociation of (CH₄+C₂H₄) mixed gas hydrate at different temperatures and pressures are listed in Table 1. As shown in Table 1, the time for complete dissociation at different temperatures almost decrease with half of the previous dissociation time at 2.0 MPa and 3.0 MPa, indicating that temperature has a great effect on the dissociation rate at high pressure.

Table 1 The time for complete dissociation of (CH₄+C₂H₄) mixed gas hydrate at different temperatures and pressures

Pressure, MPa	Temperature, K	T, min
1.0	283.2	28
	288.2	19
	290.2	15
2.0	288.2	55
	290.2	28
	292.2	15
3.0	288.2	94
	290.2	56
	292.2	25

The rate constant K in Eq. (7) at different temperatures and pressures could be determined by the experimental data. From Eq. (5), it suggests that

$$K = k' \Delta T \tag{8}$$

Eq. (8) means that a linear relationship exists between the rate constant K and the driving force ΔT of hydrate dissociation, and thus the Arrhenius equation can be used for k' :

$$k' = k_0 e^{-\Delta E / RT} \tag{9}$$

where ΔE is the activation energy for dissociation of (CH₄+C₂H₄) mixed gas hydrate, k_0 is the pre-exponential factor. The average value of k' of hydrate dissociation at one temperature was used to find the relationship between $\ln k'$ and $1/T$ (Fig. 6). Therefore, the activation energy ΔE for CH₄(18.5 mol%)+C₂H₄ (81.5 mol%) binary gas hydrate dissociation in aqueous solution of 1000 mg·L⁻¹ SDS can be obtained by fitting the relationship between $\ln k'$ and $1/T$.

The activation energy for dissociation of (CH₄+C₂H₄) mixed gas hydrate determined from Fig. 6 is 43.9 kJ·mol⁻¹, which is lower than that of methane (81.0 kJ·mol⁻¹) and ethane (104.0 kJ·mol⁻¹) hydrate in pure water (Clarke and

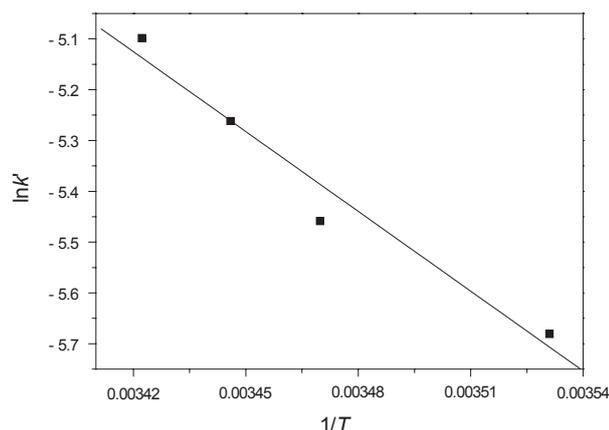


Fig. 6 The relationship between $\ln k'$ and $1/T$

Bishnoi, 2004). As the presence of SDS has little effect on the activation energy of decomposition (Liang et al, 2005), the decrease of the activation energy was mainly attributed to the mixture gas. According to the viewpoint of Kim et al (1987), the process of hydrate decomposition consist of destruction of the clathrate structure and desorption of guest molecules from the clathrate surface, and it can be accomplished only when sufficient energy is available to make the vibration between molecules vigorous enough to overcome the van der Waals force and to break the hydrogen bonds (Kim et al, 1987). It is well known that the smaller molecular methane always occupies the small cavity of structure I, and the diameter ratio of methane molecular to 5^{12} (pentagonal dodecahedron) cavity is 0.86, while ethane only fits into the $5^{12}6^2$ (tetrakaidecahedron) cavity of structure I, and the diameter ratio of ethane to the $5^{12}6^2$ cavity of structure I is 0.94 (Sloan and Koh, 2008). Therefore, there need to provide larger energy to break the hydrogen bonds for ethane because of its high diameter ratio. The close energy for ethylene should also be provided because the simliar molecular dimensions between ethane and ethylene (Sugahara et al, 2000), Nevertheless, for $(\text{CH}_4+\text{C}_2\text{H}_4)$ mixed gas, after the hydrogen bond is broken by the vibration of methane molecules, the vibration of ethylene molecules can provide more energy to overcome the van der Waals force and to break the other hydrogen bonds, so the dissociation process of the mixed gas hydrate need less energy than that of pure methane or ethylene gas hydrate. Therefore, the obtained activation energy in this work indicated that $(\text{CH}_4+\text{C}_2\text{H}_4)$ mixed gas hydrate dissociation is easier than that of pure CH_4 or C_2H_4 gas hydrate.

5 Conclusions

In this work, we had measured the kinetic date of $\text{CH}_4(18.5\text{mol}\%)+\text{C}_2\text{H}_4(81.5\text{mol}\%)$ mixed gas hydrate dissociation in the presence of $1000\text{ mg}\cdot\text{L}^{-1}$ SDS by using the depressurizing method. The results demonstrated that temperature had great influence on the dissociation rate at high pressure. A kinetic model based on the hydrate dissociation controlled by an intrinsic dissociation reaction was proposed and good agreement between the calculated result and the experimental data was obtained. The calculated

activation energy for $(\text{CH}_4+\text{C}_2\text{H}_4)$ mixed gas hydrate dissociation indicated that $(\text{CH}_4+\text{C}_2\text{H}_4)$ mixed gas hydrate dissociation is easier than that of pure CH_4 or C_2H_4 gas hydrate.

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