Effects of Tetrahydrofuran and Cetyltrimethylammonium Bromide on Carbon Dioxide Hydrate Formation

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The slow formation rate and low conversion of water to hydrates hinder the production of gas hydrate storage and transportation of gas in industry. The presence of Tetrahydrofuran (THF) in the gas hydrate system was discovered that it could reduce the energy required for pressurization or cooling of hydrate drastically. Not only reducing the energy required was very important, but also increasing the rate formation of hydrates. Cetyltrimethyl ammonium bromide (CTAB) was reported to increase hydrate formation rate because of reducing the interfacial surface tension between gas and water. The carbon dioxide hydrate formation in the presence of different THF and CTAB concentrations were investigated in terms of kinetic and thermodynamic. The formation experiment was conducted in the quiescent condition and closed system at 3.5 MPa and 4 °C. The dissociation experiment was carried out after the formation was completed at 2.5 MPa with the driving force of 21 °C. The results showed that the carbon dioxide hydrates formed in the presence of 10 mol% THF, while carbon dioxide hydrates did not form in the presence of CTAB in the quiescent closed system.

1. Introduction

Fossil fuel is the main resource of the world energy. However, combustion of fossil fuel produces carbon dioxide (CO\textsubscript{2}) emission, which is a cause of air pollution and global warming. The rising of CO\textsubscript{2} in the atmosphere leads to increase earth’s surface temperature because CO\textsubscript{2} is a greenhouse gas. It acts as a blanket to trap heat and warm the planet (Letcher, 2013). There are many options to reduce CO\textsubscript{2} emission such as increasing energy usage efficiency, switching to use renewable energy, and developing some technologies to reduce CO\textsubscript{2}. Carbon capture and storage (CCS) technology has been considered to solve this problem. CCS is one of the key technologies to store the generated CO\textsubscript{2} (Ding and Liu, 2014). In a large scale, CCS requires transportation of substantial amounts of CO\textsubscript{2}. Gas hydrates can be used to develop technologies for transportation and storage of CO\textsubscript{2} because hydrate formation provides unique gas storage properties. The hydrates can contain about 150-180 volumes of gas stored by volume of storage vessel (v/v) at standard temperature and pressure. Therefore, gas hydrates become an economical solution for CCS (Hao et al., 2008). Gas hydrates are crystalline solids formed from mixtures of water and light natural gases such as methane, carbon dioxide, ethane, propane, and butane. Its building blocks consist of a gas molecule surrounded by a case of water molecules. Gas hydrates occur under high pressure and low temperature conditions combined to make them stable. However, the utilization of hydrates is restricted because of some disadvantages such as low gas storage density, low formation rate, and long induction time of gas hydrate formation. Attempts have been made to promote hydrate formation. It is expected that gas can be stored and transported in form of hydrates, which is more economical than traditional method. Researchers discovered that adding a surfactant or a thermodynamic promoter can promote gas storage capacity and hydrate formation rate. The surfactant added to natural gas hydrates system can reduce gas-water interfacial tension, which can decrease the inter phase diffusion resistance and solubility of gas molecules in solution. Hence, the

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containing area of gas-liquid is increased, resulting in more likely to generate hydrate crystal nucleus, and increase hydrate nucleation (Dai et al., 2014). Thermodynamic hydrate promoters can significantly reduce the hydrate equilibrium pressures at a given temperature or raise the hydrate equilibrium temperatures at a given pressure (Park et al., 2013). Researchers discovered that tetrahydrofuran (THF) could reduce the equilibrium formation of hydrates drastically, which leads to a reduction in the energy required for pressurization or cooling of the targeted systems (Delahaye et al., 2006). Not only reducing the equilibrium formation of hydrates was very important, but also increasing the rate formation of hydrates was required for reducing the hydrate formation time. Currently many surfactants were used for natural gas hydrate formation rate promoting such as cetyltrimethyl ammonium bromide (CTAB). However, none has been reported on the effect of THF and CTAB in a quiescent closed system on CO₂ hydrate formation. In this research, THF and CTAB were used as hydrate promoters to investigate their effects on CO₂ hydrate formation and dissociation.

2. Experimental

2.1 Experimental Apparatus

Schematic of the experimental apparatus and cross-section of a crystallizer are shown in Figure 1. The experimental apparatus consisted of crystallizer, reservoir, personal computer, data logger, pressure transmitter, external refrigerator, and safety pressure valve. The crystallizer was made of stainless steel cylindrical vessel with an internal volume of 52 cm³. It connected with the reservoir for supplying and collecting gas. The crystallizer and reservoir were immersed in a cooling bath, the temperature of which was controlled by an external refrigerator. Two pressure transducers were used to detect the pressure in the system with the range of 0-21 MPa with 0.13 % global error. The crystallizer had four K-type thermocouples placed in different locations inside it. Thermocouple T1, T2, and T3 was set up at the top. T2 thermocouple T4 was set up at the bottom. A Wisco data logger was connected to a computer to record the data.

![Figure 1: Schematic of the experimental apparatus and cross-section of a crystallizer](image)

2.2 Carbon Dioxide Hydrate Formation

In this research, THF as a thermodynamic promoter, and CTAB, as a cationic surfactant, were selected, and their effects on the hydrate formation were investigated. The thermodynamic promoter was tested with 5, 7, and 10 mol%. The surfactant was tested with 300 and 700 ppm. Solutions were placed in the crystallizer and mixed gently. A rotary vacuum pump was used to evacuate the air in the crystallizer. The crystallizer was then pressurized to 0.5 MPa by the CO₂ gas twice to ensure no more air bubble remained in the system. CO₂ gas was introduced into the crystallizer at the desired experimental condition. The data was recorded every 10 s. Pressure dropped in the crystallizer marked as the gas consumption during the CO₂ hydrate formation. The experiment was stopped when no significantly changed in the pressure. Water to hydrate conversion (mol%) was calculated using following Eq(1) (Kumar et al., 2013).

\[
\text{Water to hydrate conversion (mol%) = } \left( \frac{\Delta n_{H_2O} \times \text{Hydration number}}{n_{H_2O}} \right) \times 100
\]
Where $\Delta n_{H,t}$ = moles of consumed gas for hydrate formation, mol

$n_{H,O}$ = the total number of moles of water in the system, mol

The number of moles of gas consumed for hydrate formation at the end of experiment can calculate following Eq.(2).

$$\Delta n_{H,t} = n_{H,t} - n_{H,0} = \left( \frac{PV}{RT} \right)_{G,t} - \left( \frac{PV}{RT} \right)_{G,0}$$  \hspace{1cm} (2)

Where $\Delta n_{H,t}$ = moles of consumed gas for hydrate formation, mol

$n_{H,t}$ = moles of hydrates at time $t$, mol

$n_{H,0}$ = moles of hydrates at time 0, mol

P = pressure of the crystallizer, atm

T = temperature of the crystallizer, K

V = the volume of gas phase in the crystallizer, cm$^3$

Z = compressibility factor

R = 8.314 J/molK

Subscripts of G,0 and G,t represent the gas phase at time zero and time t, respectively.

As CO$_2$ hydrate forms type I structure, and the unit cell contains 46 water molecules in the basic crystal with 6 large cavities and 2 small cavities, the hydration number can be calculated by following Eq.(3).

Hydration number $= \frac{46}{6θ + 26θ}$  \hspace{1cm} (3)

Cage occupancy value for pure CO$_2$ hydrates obtained by combining results from infrared spectroscopy and gas chromatography were 6θ (fractional occupancy of the small cavities) = 0.81, 6θ (fractional occupancy of the large cavities) = 1.0 leading to a hydration number of 6.04 (Kumar et al., 2013). CO$_2$ hydrates in the presence of THF are type II structure. THF molecule enters into the large cavities then forming the type II structure. After that, CO$_2$ molecules are entrapped into the small cavities of the type II structure. This is the mechanism how the structure changes into SII by adding the THF. The ideal unit cell formula for SII is $8(5^{12}6^4)\cdot16(5^{16})\cdot13\cdot6$H$_2$O, which has 8 large cavities, 16 small cavities and 136 H$_2$O molecules. If all the large cavities are occupied by THF and only the small cavities are occupied by CO$_2$, the hydration number is 5.66 (Sun and Kang, 2015).

2.3 Carbon Dioxide Hydrate Dissociation

The CO$_2$ hydrates were dissociated by thermal stimulation. The pressure in the crystallizer was decreased to the desired pressure and the temperature was increased to the desired dissociation temperature. This point was the time zero for hydrate dissociation experiment. When the temperature in the crystallizer crossed the hydrate phase equilibrium, the CO$_2$ hydrates dissociated. The gas released from the crystallizer was measured by the pressure transducer. The experiment was stopped when there was no change in the pressure. At any given time, the total moles of gas in the system equal to the moles of gas at time zero. The hydrate dissociation can be calculated by Eq.(4) (Kumar et al., 2013).

$$\Delta n_{H,t} = n_{H,t} - n_{H,0} = \left( \frac{PV}{RT} \right)_{G,0} - \left( \frac{PV}{RT} \right)_{G,t}$$  \hspace{1cm} (4)

Where $\Delta n_{H,t}$ = moles of consumed gas for hydrate dissociation, mol

3. Results and Discussion

3.1 Carbon Dioxide Hydrate Formation

Formation of gas hydrate is an exothermic reaction so it can be noticed by the increase in the temperature at the same time with the lowered pressure. Figure 2 shows the formation of CO$_2$ hydrate in the presence of 10 mol% THF at 3.5 MPa and 4 °C. First, the amount of gas uptake increases because of dissolution of CO$_2$ into water. Then, the rate of gas uptake suddenly increases due to the formation of CO$_2$ hydrate in the system. The temperature of all thermocouples rise abruptly at the same time referring to the hydrate formation in different locations almost at the same time and continues to grow until it reaches the maximum formation. Table 1 presents CO$_2$ hydrate formation experimental conditions with the presence of 10 mol% THF at 4°C and 3.5 MPa. The induction time of the experiment confirms that the CO$_2$ hydrate formation in the presence of 10 mol% THF occurs very fast. The average CO$_2$ consumed at the end of experiment is 0.05873 mol/mol of H$_2$O.
Table 1: Carbon dioxide hydrate formation conditions experimental in the presence of 10 mol% THF at 4 °C and 3.5 MPa from three separate experiments

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Water 10 mol% THF</td>
<td>8.00</td>
<td>0.0693</td>
<td>53.00</td>
</tr>
<tr>
<td>2</td>
<td>Water 10 mol% THF</td>
<td>10.00</td>
<td>0.0555</td>
<td>42.45</td>
</tr>
<tr>
<td>3</td>
<td>Water 10 mol% THF</td>
<td>10.00</td>
<td>0.0514</td>
<td>39.31</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.05873 ± 0.0094</td>
<td>44.92 ± 7.17</td>
</tr>
</tbody>
</table>

a Induction Time = time at the first hydrate formation
b no CO₂ hydrates formed during 48 hours of experiment at 4°C and 3.5 MPa

Figure 2: Carbon dioxide hydrate formation at 3.5 MPa and 4°C in the presence of 10 mol% THF.

The CO₂ hydrate formation in the presence of 5 mol% and 7 mol% THF is shown in Figure 3. The temperature profiles during the experiments are relatively constant with a slight decrease in the pressure because of the CO₂ dissolve into the solution. It can be concluded that, in the quiescent closed system, the presence of 5 mol% and 7 mol% THF hardly affects the CO₂ hydrate formation.

Figure 3: Carbon dioxide hydrate formation at 3.5 MPa and 4°C in the presence of A) 5 mol% THF and B) 7 mol% THF

The pressure drop and temperature profiles during the experiment of CO₂ hydrate formation at 3.5 MPa and 4°C in the presence of 300 and 700 ppm CTAB are shown in Figure 4. The amount of CO₂ dissolves into the solution due to the decrease between the gas and water interfacial tension, so the inter phase diffusion resistance is decreased, and solubility of gas molecules into the solution is increased. Zhang et al. (2013) proved that surface tension of surfactants decreased with the increase in the surfactant concentrations; however, it no longer decreased further the above critical micelle concentration (CMC). The CMC of CTAB in water is 1 mM, which equals to 364.5 ppm (Javadian et al., 2013). It was found in this work that the CO₂
hydrate did not form with 300 and 700 ppm CTAB in the quiescent closed system, while the formation of CO₂ hydrates formed in the stirring system at same temperature and pressure (Dai et al., 2014). It may be deduced that the reduction of the interfacial surface tension between gas and water from CTAB alone was not sufficient to form CO₂ hydrates.

Table 2: Carbon dioxide hydrate formation conditions experimental at 4 °C and 3.5 MPa

<table>
<thead>
<tr>
<th>System</th>
<th>Hydrate formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water (quiescent system)</td>
<td>×</td>
</tr>
<tr>
<td>5 mol% THF (quiescent system)</td>
<td>×</td>
</tr>
<tr>
<td>7 mol% THF (quiescent system)</td>
<td>×</td>
</tr>
<tr>
<td>10 mol% THF (quiescent system)</td>
<td>✓</td>
</tr>
<tr>
<td>300 ppm CTAB (quiescent system)</td>
<td>×</td>
</tr>
<tr>
<td>700 ppm CTAB (quiescent system)</td>
<td>×</td>
</tr>
<tr>
<td>300 ppm CTAB (stirring system)</td>
<td>✓</td>
</tr>
<tr>
<td>700 ppm CTAB (stirring system)</td>
<td>✓</td>
</tr>
</tbody>
</table>

3.2 Carbon Dioxide Hydrate Dissociation

The dissociation experiment started after the formation of gas hydrates completes. Thermal stimulation method was used in this research. The pressure in the system was decreased to 2.5 MPa and the temperature to 25 °C, which means the system has a driving force of 21 °C.

When the temperature crosses the hydrate phase boundary, the hydrates will dissociate and CO₂ gas releases. The experiment stopped when the temperature and mol of CO₂ were constant. Figure 5 shows the dissociation of CO₂ hydrates in the system with 10 mol% THF. All thermocouples and water temperature have the same temperature, initially. After that, the temperatures of water and thermocouple are different, which is the result from the dissociation of CO₂ hydrates. Dissociation of hydrates is an endothermic reaction. So, the temperature of thermocouple in the crystallizer is lower than the water temperature during the dissociation process. After the dissociation completes, all temperatures become the same again.
10 mol% THF, the average CO$_2$ consumed at the end of formation experiment was 0.05 mol, while the average CO$_2$ released at the end of dissociation experiment was 0.02 mol. CO$_2$ gas still remains and cannot be recovered.

4. Conclusions
In this research, THF as a thermodynamic promoter and CTAB as a cationic surfactant were selected, and their effects on the CO$_2$ hydrate formation and dissociation were investigated in the quiescent closed system. As the results, the CO$_2$ hydrates formed in the presence of 10 mol% THF, while it was not the case in the presence of 5 mol% and 7 mol% THF. It may be concluded that with the presence of lower than 10 mol% THF hardly affected the CO$_2$ hydrate formation. Even though CTAB was able to decrease the interfacial between gas and water and increase mass transfer in the system, this result showed that the CO$_2$ hydrates did not form.

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