Hydrate Equilibrium Measurements for CH₄ and CO₂/CH₄ Mixture in the Presence of Single 2-Methyl-2-propanol and 1,1-Dichloro-1-fluoroethane

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ABSTRACT: Hydrate phase equilibrium conditions of CO₂/CH₄ + 2-methyl-2-propanol (tBA) + water system, CH₄ + 1,1-dichloro-1-fluoroethane (HCFC-141b) + water system, CO₂ + HCFC-141b + water system, and CO₂/CH₄ + HCFC-141b + water system were measured. The moles fraction of CO₂ in the mixture gases were 0.33 and 0.5, respectively. The mole fraction of HCFC-141b and tBA were 0.056. The measured temperature range is from 283.0 to 294.2 K. The phase equilibrium conditions were tested by an isochoric pressure-search method. Results showed that HCFC-141b has a stronger promotion effect on CH₄ hydrate formation than on CO₂ hydrate. The effect of CO₂ content on the phase equilibrium conditions of CO₂/CH₄ mixture + HCFC-141b + water is weak. tBA also acts as a promoter for CO₂/CH₄ mixture gas. In the presence of tBA, the phase equilibrium conditions of the system with higher CO₂ content moved to higher pressure and lower temperature region compared with the system with lower CO₂ content.

INTRODUCTION

Gas hydrates are ice-like crystalline compounds which capture guest molecules in the cages formed by the hydrocarbon bonding water molecules, and gas molecules like CH₄ and CO₂ interact with water molecules through van der Waals forces.1 Gas hydrates have already attracted wide attention due to their broad application, such as desalination,2,3 gas storage,4,5 and mixture gas separation.6–8 Using the hydrate-based separation, CO₂ can be captured. Flue gas is the most researched gas.9

The other mixture gas is CO₂/CH₄ gas mixture, which is the main component of original natural gas or biogas.9,13,14 However, hydrate-based separation for CH₄ and CO₂ is challenging.9 On one hand, the formation conditions of CH₄ and CO₂ hydrates are harsh. On the other hand, because the difference between the hydrate phase equilibrium of CH₄ and CH₂ is relatively small, both CH₄ and CO₂ molecules may enter the hydrate crystal cavities during the hydrate formation. Therefore, hydrate promoters are used to shift the hydrate equilibrium conditions to the region where hydrates are easier to form or expand the gap between CH₄ and CO₂ hydrate phase equilibrium conditions.15–18

1,1-Dichloro-1-fluoroethane (HCFC-141b) is an air-conditioning refrigerant, which could easily form s-II hydrates at near atmospheric pressure.19,20 Wang et al.21 reported that HCFC-141b could significantly reduce the phase equilibrium pressure and improve the phase equilibrium temperature of CH₄ hydrate and moderate CO₂/CH₄ mixture hydrate formation conditions so that the CO₂/CH₄ separation can be performed under milder conditions.

2-Methyl-2-propanol, also named tert-butanol (tBA), was reported to form s-II hydrates with the presence of gas, such as methane, carbon dioxide, and nitrogen with the inclusion of tBA in s-II large cages.23 With the presence of tBA, the hydrate phase equilibrium conditions of methane moved to the region where hydrates are easier to form, and the hydrate phase equilibrium conditions of CO₂ moved to the region in which hydrates are more difficult to form.23 The effect of tBA on the formation of CH₄ hydrates and CO₂ hydrates was opposite, which might bring unexpected results in CO₂/CH₄ mixture separation based on hydrate technology. But the effect of tBA on the formation of CO₂/CH₄ mixture hydrate is not certain. It is necessary to measure the hydrate formation boundary of CO₂/CH₄ mixture in the presence of tBA.

Though the components of biogas and landfill gas are CH₄ and CO₂, their contents are not same. In this study, the hydrate phase equilibrium conditions of two CO₂/CH₄ mixture (33/67 and 50/50, mole fraction) with HCFC-141b at the concentration of 5.6 mol % were measured. The 5.6 mol % HCFC-141b is the stoichiometric concentration of HCFC-141b molecules and occupies the large cages of s-II hydrates. We also measure the hydrate formation boundary of CO₂/CH₄ mixture gas with tBA at the concentration of 5.6 mol %. These data will be used as essential for CO₂/CH₄ separation based on hydrate formation.

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EXPERIMENTAL SECTION

Materials. Table 1 provided the suppliers and purities of chemicals used in this experiment. The mole fractions of tBA and HCFC-141b solution used in this work are all 5.6% (wtBA = 23.02%, w HCFC-141b = 36.4%, mass fraction), with an uncertainty of ±0.03%. The mixture gases in this work were 50 mol % CO2/CH4 and 33 mol % CO2/CH4.

Experimental Apparatus. Figure 1 shows the schematic diagram of experimental apparatus used in this work, which has a detailed description in previous work.25−27 Major part of the device is a stirred high-pressure stainless steel cell with an effective volume of 300 cm3. Maximum working pressure of the cell is 20 MPa. The stainless steel cell was put in a water bath (Huber CC2-K20B) to control the temperature. Two built-in thermocouples (Westzh WZ-PT100) with ±0.1 K accuracy were installed to monitor temperature of gas and liquid phase in the reactor. A pressure sensor (Senex DG-1300) with an accuracy of ±0.01 MPa was used to measure the system pressure. The data of pressures and temperatures were recorded by data logger (Agilent 34970A) at 10 s intervals.

Experimental Method. In this work, the isochoric pressure-search method was used to measure the phase equilibrium conditions of hydrate.28−31 First, the reactor was evacuated and was rinsed with distilled water. Then approximately 200 mL of experimental solution was inhaled into the reactor and the tested gas was injected into the cell until the desired pressure. Subsequently, the magnetic stirrer (about 600 rpm) and the thermostatic bath started. After the temperature and the pressure of the system were steady at room temperature, the system started to cool down with a rate of 3 K/h. An abrupt drop in pressure and suddenly rise in temperature indicated the formation of hydrate. After forming sufficient hydrate at a constant temperature (at least kept for 3 h), the system heat up with 0.1 K/h. When the temperature closed to the hydrate decomposition temperature, the increasing rate of temperature adjusted to 0.025 K/h. The data of temperature and pressure recorded during all experiments. The hydrate phase equilibrium point was the point at which the slope of the $P-T$ diagram changes drastically.32

RESULTS AND DISCUSSION

To verify the reliability of the experimental method and equipment, the phase equilibrium of hydrate formation conditions of HCFC-141b + CO2 were measured and compared with those reported in literature21 in Figure 2. The measured data listed in Table 2. In this work, the tested system of HCFC-141b + CO2 + H2O consists of three components (HCFC-141b, water, CO2) and four phases (gas, HCFC-141b, H2O, and hydrate). The free degree of the tested system is one according to Gibbs phase rule.21 Therefore, the phase equilibrium conditions of the measured system are independent of the HCFC-141b concentration. As Figure 2 showed, the experimental phase equilibrium data is consistent with that in literature,21 demonstrating that the experimental method and equipment is reliable.

The measured hydrate phase equilibrium conditions of CH4 and CO2/CH4 mixture in the presence of HCFC-141b along with the hydrate phase equilibrium conditions of CH4, CO2, and CO2/CH4 mixture in pure water from literature were plotted in Figure 3 and listed in Table 3. The presence of HCFC-141b significantly decreased the equilibrium pressure of CH4 and CO2/CH4 mixture hydrates at any constant temperature, and a similar phenomenon was also observed for CO2 + HCFC-141b + water system.21 HCFC-141b forms s-II hydrates and occupies the large cages of s-II hydrates,19

Table 1. Materials Used in the Experiments

<table>
<thead>
<tr>
<th>component</th>
<th>purity/mol %</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>99.99</td>
<td>Foshan Kedi Gas Industry Co.</td>
</tr>
<tr>
<td>50 mol % CO2/CH4</td>
<td></td>
<td>Shengying Gas Industry Co.</td>
</tr>
<tr>
<td>33 mol % CO2/CH4</td>
<td></td>
<td>Shengying Gas Industry Co.</td>
</tr>
<tr>
<td>tBA</td>
<td>98.0</td>
<td>JiangSu Yonghua Chemical Technology Co.</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>99.9</td>
<td>Pujiang Jietong Environmental Protection Technology Co.</td>
</tr>
<tr>
<td>water</td>
<td></td>
<td>deionized</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of the experimental apparatus used for the measurement of gas hydrate equilibrium conditions.
whereas CH₄, CO₂ forms s-I hydrate. Therefore, the addition of HCFC-141b in solution converted the CH₄, CO₂ hydrate structure from s-I to s-II. Thus, the gas hydrates formation conditions became mild. In addition, the promotion effect of HCFC-141b on the formation of CH₄ hydrate is stronger than that of CO₂ hydrate. This ascribes to the cage occupancy competition between guest molecules. Because of the size of HCFC-141b molecule, HCFC-141b molecules only occupy the large cages of s-II hydrate. The size of methane molecules is small, and they are very suitable for small cages of hydrates. As for CO₂ molecules, they are prone to occupy large cages because the small cavities are slightly tight for them. CO₂ molecules and HCFC-141b molecules compete with each other to occupy large cages, and numerous small cages are left for CH₄ molecules. Therefore, the hydrate equilibrium conditions of CH₄ + HCFC-141b + H₂O system are milder than that of CO₂ + HCFC-141b + H₂O system. In comparison to the hydrate phase equilibrium of CH₄/CO₂ mixture with those of CH₄ and CO₂ hydrates in the presence of HCFC-141b (Figure 3), both the hydrate phase equilibrium of the 33 mol % CO₂/CH₄ + HCFC-141b + H₂O system and the 50 mol % CO₂/CH₄ + HCFC-141b + H₂O system are located between the phase equilibrium curves of CH₄ + HCFC-141b + H₂O system and CO₂ + HCFC-141b + H₂O system. The phase equilibrium conditions of these two systems are relatively close to the phase equilibrium of the CH₄ + HCFC-141b + H₂O system. This indicates that the content of CO₂ in the mixture has a little effect on the hydrate phase equilibrium conditions of the CO₂/CH₄ mixture + HCFC-141b + water system. Through the above experiments, we can find that HCFC-141b can be used as additive to moderate the CH₄/CO₂ hydrate formation conditions, which is the same as our expectation. But the effect of HCFC-141b on CH₄/CO₂ hydration separation needs further research.

The phase equilibrium conditions for the hydrate formation of 33 mol % CO₂/CH₄ mixture and 50 mol % CO₂/CH₄ mixtures in tBA solution were measured and listed in Table 4. Experimental results are compared with the phase equilibrium data of CH₄, CO₂ in tBA solution, and CO₂/CH₄ mixture in pure water from literature in Figure 4. Seen from Figure 4, tBA + CO₂/CH₄ mixture hydrates confirmed the promotion effect that is signified by a pressure decrease at certain temperature, and the promotion effect of tBA on the hydrate formation of 33 mol % CO₂/CH₄ system was stronger than that of 50 mol % CO₂/CH₄ system. Seo et al. had reported that in the presence of tBA, CH₄ or CO₂ will form s-II hydrate by enclathrating tBA molecules in s-II large cages. Therefore,
molecules are less likely to occupy hydrated cages, preferring hydrogen bonding with water molecules. Therefore, the test system with more CO$_2$ has greater probability of hydrogen bonding between alcohol molecules and hydrates, which weaken the promotion effect of tBA on CO$_2$/CH$_4$ mixture gas hydrate. According to the experimental result, tBA may have the potential to separate CH$_4$/CO$_2$ as a hydration additive but the effect of tBA on hydrate selectivity of CH$_4$/CO$_2$ still needs further study.

### CONCLUSION

This paper reported hydrate phase equilibrium of CH$_4$ + HCFC-141b + water system, CO$_2$/CH$_4$ + HCFC-141b + H$_2$O system, and CO$_2$/CH$_4$ + tBA + H$_2$O system with the mole fraction of HCFC-141b and tBA was 5.6%. The result showed that HCFC-141b acts as a promoter for CH$_4$ and CO$_2$/CH$_4$ mixture. The concentration of CO$_2$ in mixture has little effect on the phase equilibrium conditions of CO$_2$/CH$_4$ mixture + HCFC-141b system. tBA also has promotion effect for CO$_2$/CH$_4$ mixture gas hydrate, but the promotion effect on 50 mol % CO$_2$/CH$_4$ mixture was weaker than that on 33 mol % CO$_2$/CH$_4$ mixture. The result demonstrated that the promotion effect of tBA on CO$_2$/CH$_4$ mixture gas depends on the composition of CO$_2$/CH$_4$.

### REFERENCES

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