CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652027

Effects of Tetrahydrofuran and Cetyltrimethylammonium Bromide on Carbon Dioxide Hydrate Formation

Soravis Limvisitsakul[a], Katipot Inkong[a], Atsadawuth Siangsai[a],
Pramoch Rangsunvigit*[,a,b], Santi Kulprathipanja [c]

[a]The Petroleum and Petrochemical College, Chulalongkorn University
[b]Center of Excellence on Petrochemical and Materials Technology
[c]UOP, A Honeywell Company, Des Plaines, USA
pramoch.r@chula.ac.th

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_2) emission, which is a cause of air pollution and global warming. The rising of CO_2 in the atmosphere leads to increase earth's surface temperature because CO_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_2 emission such as increasing energy usage efficiency, switching to use renewable energy, and developing some technologies to reduce CO_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_2 (Ding and Liu, 2014). In a large scale, CCS requires transportation of substantial amounts of CO_2. Gas hydrates can be used to develop technologies for transportation and storage of CO_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

Please cite this article as: Limvisitsakul S., Inkong K., Siangsai A., Rangsunvigit P., Kulprathipanja S., 2016, Effects of tetrahydrofuran and cetyltrimethylammonium bromide on carbon dioxide hydrate formation, Chemical Engineering Transactions, 52, 157-162 DOI:10.3303/CET1652027

contacting 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 CO_2 hydrate formation. In this research, THF and CTAB were used as hydrate promoters to investigate their effects on CO_2 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 cm^3. 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.

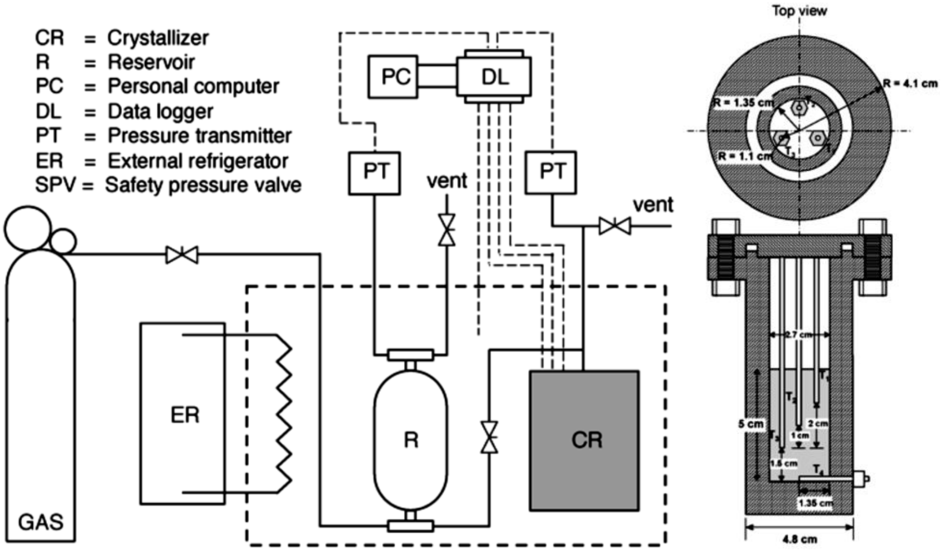

Figure 1: Schematic of the experimental apparatus and cross-section of a crystallizer

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 CO_2 gas twice to ensure no more air bubble remained in the system. CO_2 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 CO_2 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).

$$\text{Water to hydrate conversion (mol\%)} = \frac{\Delta nH\downarrow \times \text{Hydration number}}{nH_20} \times 100 \tag{1}$$

Where $\Delta n_{H,\downarrow}$ = moles of consumed gas for hydrate formation, mol
n_{H_2O} = 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).

$$\Delta n_{H\downarrow,} = n_{H,0} - n_{H,t} = \left(\frac{PV}{zRT}\right)_{G,0} - \left(\frac{PV}{zRT}\right)_{G,t} \quad (2)$$

Where $\Delta n_{H,\downarrow}$ = 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 = 82.06 $cm^3\cdot atm/mol\cdot K$

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).

$$\text{Hydration number} = \frac{46}{6\theta_L + 2\theta_S} \quad (3)$$

Cage occupancy value for pure CO_2 hydrates obtained by combining results from infrared spectroscopy and gas chromatography were θ_S (fractional occupancy of the small cavities) = 0.81, θ_L (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 $8(5^{12}6^4)\cdot16(5^{12})\cdot13\cdot6H_2O$, which has 8 large cavities, 16 small cavities and 136 H_2O 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).

$$\Delta n_{H,\uparrow} = n_{H,t} - n_{H,0} = \left(\frac{PV}{zRT}\right)_{G,t} - \left(\frac{PV}{zRT}\right)_{G,0} \quad (4)$$

Where $\Delta n_{H,\uparrow}$= 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_2O.

Table 1: Carbon dioxide hydrate formation conditions experimental in the presence of 10 mol% THF at 4 ℃ and 3.5 MPa from three separate experiments

Exp. No.	System	[a] Induction Time [min]	CO_2 Consumed [mol/mol of H_2O]	Water Conversion to Hydrate [mol%]
Ref.	Water	[b]	-	-
1	10 mol% THF	8.00	0.0693	53.00
2	10 mol% THF	10.00	0.0555	42.45
3	10 mol% THF	10.00	0.0514	39.31
		Average	0.05873 ± 0.0094	44.92 ± 7.17

[a] Induction Time = time at the first hydrate formation

[b] no CO_2 hydrates formed during 48 hours of experiment at 4°C and 3.5 MPa

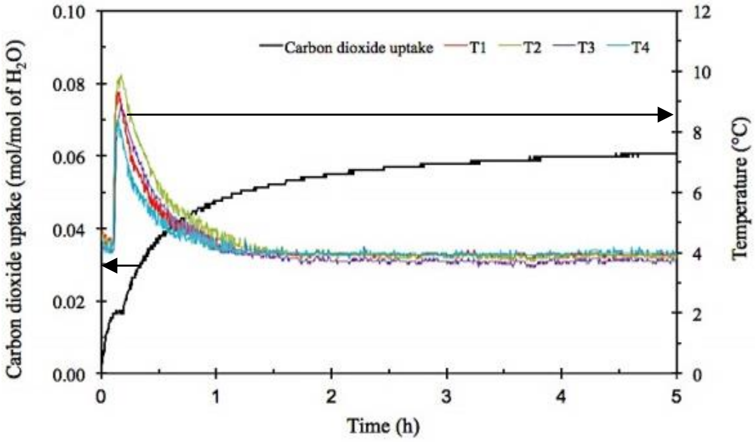

Figure 2: Carbon dioxide hydrate formation at 3.5 MPa and 4°C in the presence of 10 mol% THF.

The CO_2 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 CO_2 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 CO_2 hydrate formation.

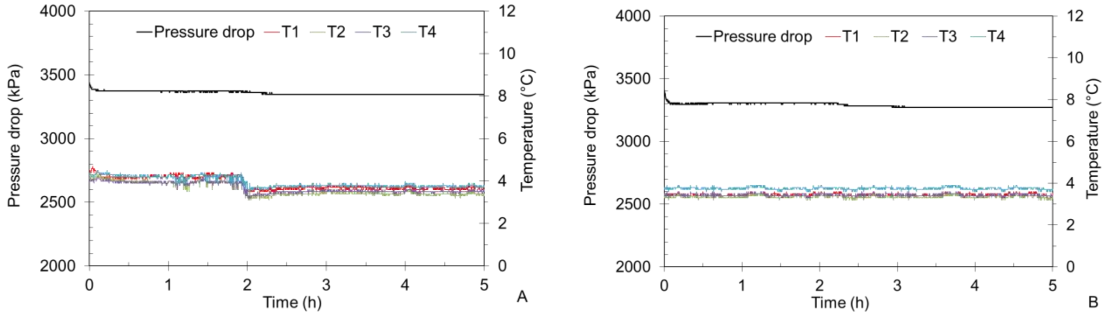

Figure 3: Carbon dioxide hydrate formation at 3.5 MPa and 4 °C in the presence of A) 5 mol% THF and B) 7 mol% THF

The pressure drop and temperature profiles during the experiment of CO_2 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 CO_2 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 CO_2

hydrate did not form with 300 and 700 ppm CTAB in the quiescent closed system, while the formation of CO_2 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 CO_2 hydrates.

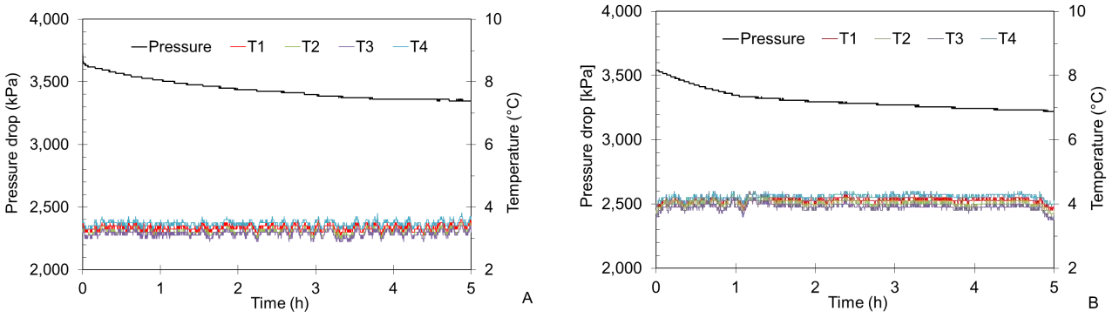

Figure 4: Carbon dioxide hydrate formation at 3.5 MPa and 4 °C in the presence of A) 300 ppm CTAB and B) 700 ppm CTAB

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

System	Hydrate formation
Pure water (quiescent system)	✗
5 mol% THF (quiescent system)	✗
7 mol% THF (quiescent system)	✗
10 mol% THF (quiescent system)	✓
300 ppm CTAB (quiescent system)	✗
700 ppm CTAB (quiescent system)	✗
300 ppm CTAB (stirring system) (Dai et al., 2014)	✓
700 ppm CTAB (stirring system) (Dai et al., 2014)	✓

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.

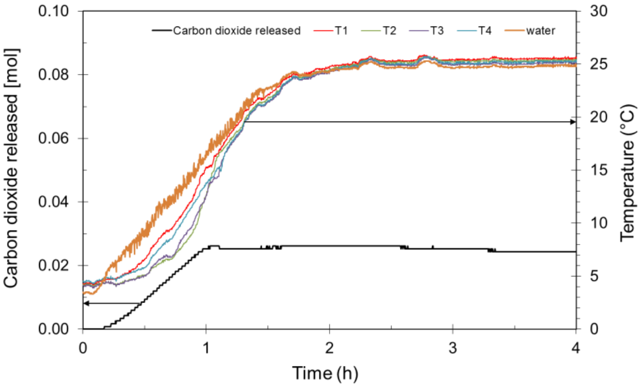

Figure 5: (a) Carbon dioxide hydrate formation at 3.5 MPa and 4°C in the presence of 10 mol% THF

When the temperature crosses the hydrate phase boundary, the hydrates will dissociate and CO_2 gas releases. The experiment stopped when the temperature and mol of CO_2 were constant. Figure 5 shows the dissociation of CO_2 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 CO_2 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. With the presence of

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.

Acknowledgments

The authors would like to sincerely thank the The 90th Anniversary of Chulalongkorn University Fund and Grant for International Integration: Chula Research Scholar, Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University, Thailand; The Petroleum and Petrochemical College, Chulalongkorn University, Thailand; Center of Excellence on Petrochemical and Materials Technology, Thailand; and UOP, A Honeywell Company, USA, for providing support for this research work.

References

Dai Y., Zhong X., Jiang X., Wang S., 2014. Experiment of New Additives Effect on Gas Hydrate Formation. Energy and Power Engineering, 6(06), 133.

Delahaye A., Fournaison L., Marinhas S., Chatti I., Petitet J.P., Dalmazzone D., Fürst W., 2006. Effect of THF on equilibrium pressure and dissociation enthalpy of CO2 hydrates applied to secondary refrigeration.Industrial & engineering chemistry research, 45(1), 391-397.

Ding T., Liu Y., 2014. Simulations and analysis of hydrate formation during CO 2 injection into cold saline aquifers. Energy Procedia, 63, 3030-3040.

Hao W., Wang J., Fan S., Hao W., 2008. Evaluation and analysis method for natural gas hydrate storage and transportation processes. Energy conversion and management, 49(10), 2546-2553.

Javadian S., Ruhi V., Heydari A., Asadzadeh Shahir A., Yousefi A., Akbari, J., 2013. Self-assembled CTAB nanostructures in aqueous/ionic liquid systems: effects of hydrogen bonding. Industrial & Engineering Chemistry Research, 52(12), 4517-4526.

Letcher T.M. ed., 2013. Future Energy: Improved, Sustainable and Clean Options for Our Planet. Elsevier.

Kumar A., Sakpal T., Linga P., Kumar R., 2013. Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics. Fuel, 105, 664-671.

Park S., Lee S., Lee Y., Lee Y., Seo Y., 2013. Hydrate-based pre-combustion capture of carbon dioxide in the presence of a thermodynamic promoter and porous silica gels. International Journal of Greenhouse Gas Control, 14, 193-199.

Sun Q., Kang Y.T., 2015. Experimental correlation for the formation rate of CO 2 hydrate with THF (tetrahydrofuran) for cooling application. Energy, 91, 712-719.

Zhang L., Zhou S., Wang S., Wang L., Li J., 2013. Surfactant Surface Tension Effects on Promoting Hydrate Formation: An Experimental Study Using Fluorocarbon Surfactant (Intechem-01)+ SDS Composite Surfactant