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Hydrate Equilibrium Measurement of Single CO₂ and CH₄ Hydrates Using Micro DSC

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Abstract: In this study, the simple gas hydrate equilibrium conditions of methane and carbon dioxide in water were measured by using high pressure micro DSC (why is the advantage). The technique was chosen because it is economic, fast and accurate. In this study, the methane hydrate equilibrium conditions were measured at pressure between 35-112 bar and temperature between 276-288 K. In addition, the carbon dioxide hydrate equilibrium conditions were measured at pressure between 15-37 bar and temperature between 274-282.5 K. The measured data was compared to the available literature data and the AADT % between the measured data and predicted model was calculated. Good agreements were obtained between the measured and literature data. The AADT% between the measured data and predicted models is less than 0.07% for CH₄ hydrate and 0.15% for CO₂ hydrate.

Key words: Micro DSC, natural gas, average absolute deviation percentage, THI

INTRODUCTION

Oil and natural gas are the most powerful, attractive and vital supply of energy in the world. To satisfy the world's increasing demand for energy, oil and gas companies continue developing and extracting reserves in more challenging environments. The new developments involve longer transport distances, colder areas, deeper waters and more complex fluid compositions.

Flow assurance was listed as a major technical problem in offshore energy development. It seeks to prevent or mitigate some problems like slugging, surge volumes, wax deposition, gelling, hydrates, etc. Hammerschmidt (1934) reported that the hydrate formation causes plugging the gas pipelines which can lead to catastrophic economic losses and ecological risks.

Natural gas hydrates are termed "Clathrates" this means there is a network of cages. Host (water) molecules can trap small guest molecules, such as methane, ethane and propane. The hydrate is formed under high pressure, low temperature and sufficient amount of water. The water molecules connected through hydrogen bonding, forming a cage-like structure that completely encapsulates another molecular species (Englezos, 1993). Natural gas compounds have three

common types of hydrate structures, cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH) (Ripmeester *et al.*, 1994).

Various methods were developed to mitigate the formation of gas hydrate. The techniques include system heating and/or depressurization, water removal and inhibition. Under many circumstances, the hydrate inhibition by adding inhibitors is the very feasible. These inhibitors are divided into two main groups: Thermodynamic Hydrate Inhibitors (THI) and Low Dosage Hydrate Inhibitors (LDHI). Thermodynamic inhibitors shift the equilibrium hydrate dissociation curve, i.e., the Hydrate-aqueous Liquid Vapor Equilibrium (HLVE) curve, to lower temperature and higher pressure, thus avoid the hydrate formation. Methanol, glycols and sodium chloride are example on THIs which are used normally around 10-60 wt% (Dholabhai *et al.*, 1992; Koh, 2002). Two kinds of LDHIs the first one is a Kinetic Hydrate Inhibitors (KHIs), they slow down the rates of hydrate nucleation and growth, this type of inhibitor delays hydrate formation to time longer than the residence time of the fluid in the hydrate-prone section of pipeline, but eventually KHIs allow hydrate formation (Sloan and Koh, 2008). Kinetic Hydrate Inhibitors (KHIs) are water-soluble polymers such as Poly N-vinyl Pyrrolidone (PVP) and Poly N-vinyl Caprolactam (PVCap). It used

normally at low dosages <2wt%. The other type of (LDHs) is anti-agglomerants (AAs) which prevent the hydrate crystals from agglomerating and accumulating into large masses but do not inhibit the hydrate formation. Recently, Xiao and Adidharma (2009) introduced ionic liquids as another class of gas hydrate inhibitors which are called “Dual function inhibitors”.

It is important to know hydrates formation conditions for gas industry. Data for various phase equilibria help to study how we can prevent or mitigate the formation of gas hydrates. Natural gas with high carbon dioxide (CO₂) concentrations is encountered in various areas such as Gulf of Thailand, so in this study, measurement of hydrate dissociation temperature of pure carbon dioxide and methane are tested by using micro DSC.

MATERIALS AND METHODS

Gases: Pure methane and carbon dioxide with purity 99.99% were used which supplied by Gas Walker. To form hydrates deionized water is used with these gases.

Apparatus: High pressure μ DSC7 evo provided by SETARAM is used in this study Fig. 1. The DSC is a thermoanalytical technique in which the difference between the sample and the reference at the same temperature is recorded as a function of temperature. It uses Peltier cooling and heating principle. The main advantage is that no refrigerating fluid, such as liquid nitrogen is needed for cooling the instrument. The minimum temperature that can be reached is -45°C and the maximum temperature is 120°C. The gas tight high pressure vessels are designed to work upto 400 bar and to

contain 0.33 mL of sample. They are made of Hastelloy C276 which allows the analysis of corrosive fluids such as drilling fluids. The screwed top is equipped with a doughnut ring coupled to an antiextrusion ring. Controller pressure works upto 200 bar supplied from SETARAM is used with an accuracy of ± 1 bar. It measures pressure gauge so we add atmospheric pressure to the value which shown on the panel.

Procedures: Fifty milligram of sample solution is introduced in the Hastelloy cell and placed inside the calorimetre; the reference cell was left empty. Gas pressure is applied to both the sample and reference cell via the pressure controller. Only the cells are under pressure, the DSC detector remains at atmospheric pressure. A flow of nitrogen gas is maintained over the samples to create a reproducible and dry atmosphere to avoid ambient moisture condensation. Non-isothermal mode is used to determine the onset temperature of hydrate dissociation. The thermal cycle includes cooling step, in which the temperature is decreased from 20°C to -15 and -20°C for methane and carbon dioxide, respectively with cooling rate 1°C min⁻¹ followed by an isothermal process for 10 min to ensure the hydrates are formed then heating step in which the temperature is brought back to 20°C with very low heating rate 0.01°C min⁻¹ to obtain more accurate results (Xiao *et al.*, 2010). The pressure rang for methane hydrate study is between 35-112 bar and for carbon dioxide is 15-37 bar. Hydrate dissociation temperature can be determined from the DSC thermogram (heat flow, temperature) for each value of pressure, the intersection of the returning line of the hydrate dissociation peak with the baseline represents the dissociation temperature, as shown in Fig. 2.

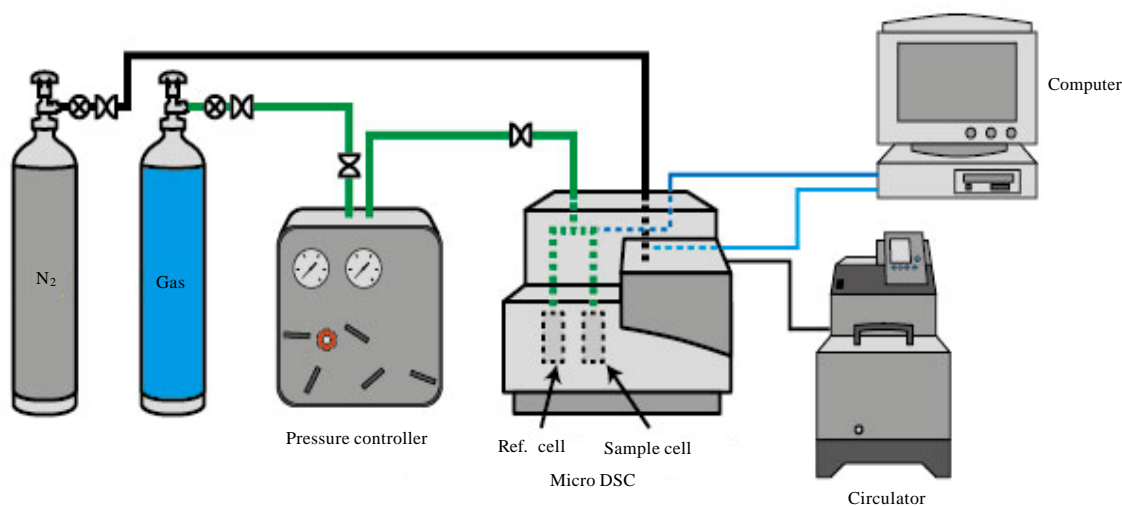


Fig. 1: Experimental apparatus

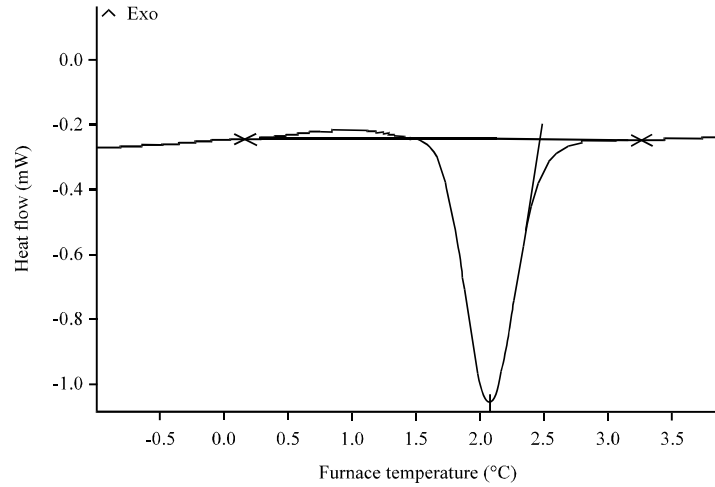


Fig. 2: Hydrate dissociation peak

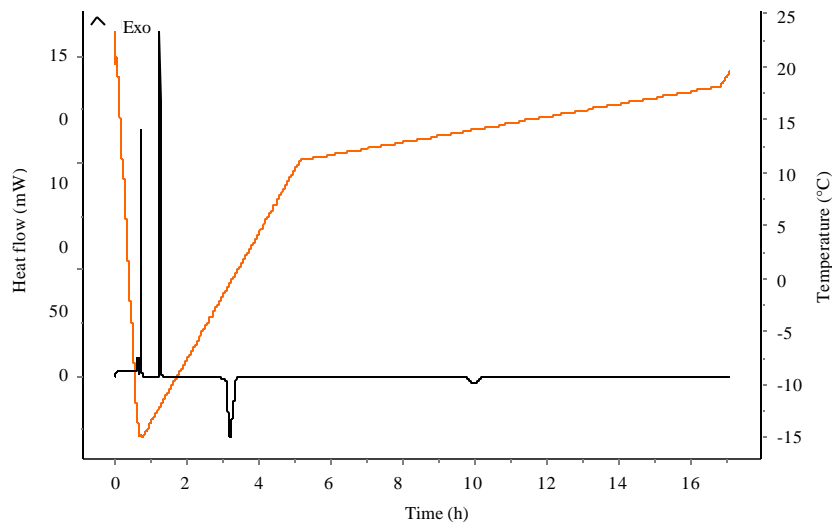


Fig. 3: DSC thermogram of methane hydrates at about 111 bar

RESULTS AND DISCUSSION

The DSC thermogram for methane hydrate is shown in Fig. 3. Two exothermic peak can be observed for hydrates and ice formation then two endothermic peaks for ice and hydrate dissociation. The result exhibited as HLVE curve (Fig. 4) and a good harmony can be observed in comparison with predicted data by CSMGem software and pervious study.

In carbon dioxide case DSC thermogram shows in addition to ice and hydrates peaks some other peaks which are attributed to solubility of carbon dioxide in

water and formation the carbonic acid (Fig. 5). The results of this study are shown as HLVE curve with some literature values in Fig. 6.

To evaluate the reliability of the present experimental methods, the Average Absolute Deviation percentage (AADT%) of the present dissociation temperature measurements of pure methane and carbon dioxide hydrates from the predicted data was measured by using the following model:

$$AADT (\%) = \left(\frac{1}{ND} \right) \sum_{i=1}^{ND} \frac{|T_{i,exp} - T_{i,cal}|}{T_{i,exp}} \times 100$$

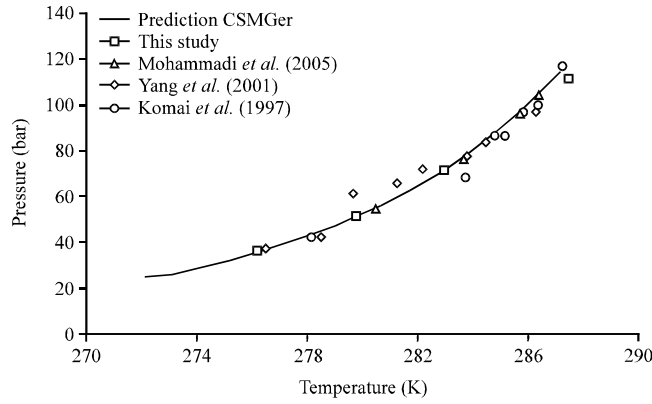


Fig. 4: Dissociation points of methane hydrates

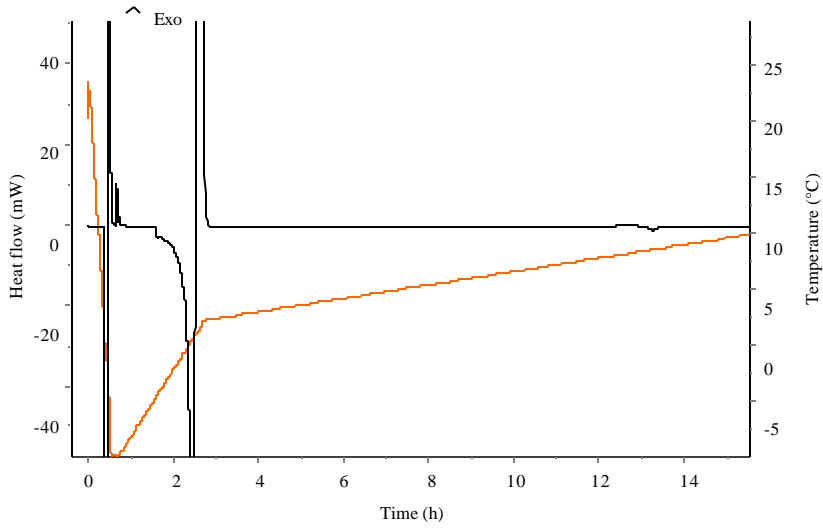


Fig. 5: DSC thermogram of carbon dioxide hydrates at pressure about 36 bar

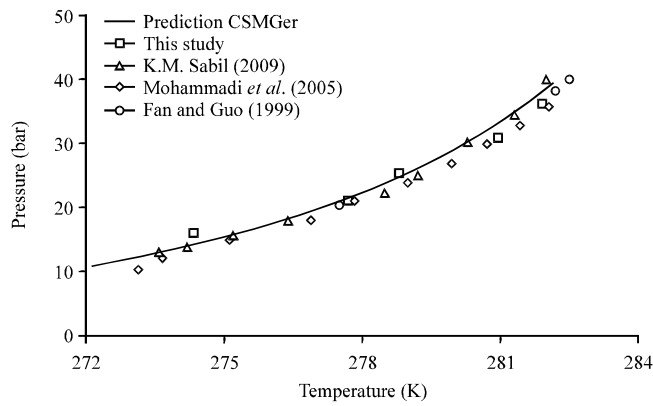


Fig. 6: Dissociation points of carbon dioxide hydrates

Table 1: Average absolute deviation percentage between predicted and measured hydrate equilibrium dissociation temperatures at different operating pressures

CH ₄		CO ₂	
Data	AADT (%)	Data	AADT (%)
This study	0.07	This study	0.15
Mohammadi <i>et al.</i> (2005)	0.02	Sabil <i>et al.</i> (2010)	0.21
Yang <i>et al.</i> (2001)	0.20	Mohammadi <i>et al.</i> (2005)	0.09
Komai <i>et al.</i> (1997)	0.14	Fan and Guo (1999)	0.05

where, $T_{i,cal}$ and $T_{i,exp}$ are the predicted and measured hydrates equilibrium dissociation temperature, respectively and ND is the number of data points. The deviations of our results and some previous data from predicted data by CSMGem shown in Table 1.

CONCLUSION

Based on present results μ DSC is good technique to determine the dissociation temperature of gas hydrates and has some advantages like it is economic and accurate method. Also a good agreement of the present results can be observed comparing with literature data and CSMGem software which has been proved by calculation the Average Absolute Deviation percentage (AADT%).

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