

**Study of Ionic Liquid as Low Dosage Hydrate Inhibitor**

by

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Dissertation submitted in partial fulfillment of  
the requirement for the  
Bachelor of Engineering (Hons)  
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,



( Dr Khalik Bin Mohamad Sabil )



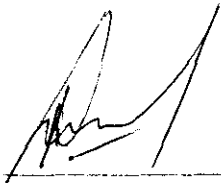
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2012

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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**NORDIYANA BT MUHAMMAD SOFFIAN WONG**

## ABSTRACT

This report constitutes of study of ionic liquid as low dosage hydrate inhibitor. The objectives of this project are to screen, to test the performance and investigate ionic liquids compatibility as low density hydrate inhibitor candidates. This study focused on experimental measurement to obtain fundamental thermodynamic behavior of methane hydrate and the kinetic of formation of methane hydrate systems. This measurement is essential to analyze the performance of ionic liquid towards inhibiting hydrate formation. In this work , three concentrations for each ionic liquid have been studied at 1 wt%, 0.5 wt% and 0.1 wt%. EMIMCl and OHC<sub>2</sub>MIMCl are two ionic liquids that have been screened and tested in order to study their performance. This measurement has been measured with Hydreval, which is one type of PVT equipments. All the data obtained from the experiment were recorded by data acquisition system. Significant gas consumption reduction has been observed in the presence of ionic liquids. However, the result shows insignificant thermodynamic effect toward hydrate formation for binary system of methane and water.

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“There are two ways of spreading light: to be the candle or the mirror that reflects it”.

- Edith Wharton

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# CHAPTER 1

## INTRODUCTION

### 1.1 Project Background

Gas or clathrate hydrate were discovered almost two century ago by Sir Humphrey Davy in 1810. In early days, interest in gas hydrates was mainly focused on the discovery of new hydrated formers, mainly inorganic chemicals and the composition of these hydrate [Sloan, 1998]. After the discovery of the occurrence of hydrate in oil and gas production by Hammerschmidt in 1934 [Hammerschmidt, 1934], the research shift towards more industrial hydrate research focusing on hydrocarbons based hydrate has been carried out to fulfill the needs of oil and gas production.

Hydrate formation has severe implication to industry as it can cause blockage of the pipelines and equipments. Pressure control, temperature control, chemical injection, water supply removal and hydrate former supply removal are practices in industry application to mitigate gas hydrate formation. These practices are described as below:

#### a) Pressure control

Pressure control is achieved by designing and by operating the system with pressure low enough to maintain the fluids outside of hydrate region. This practice is often impractical for normal operation since the pressure required for transportation of production fluids would usually exceed hydrate formation pressure at ambient temperature. However, for removal of hydrates as the result of unplanned shutdowns, pressure control is a common practice [Pickering et al., n.d]. The pressure control method is also applied where normally chemicals could not be easily delivered to plug location. The objective of this method is to remove the plug. Once the pressure has been established, it is possible to flood the system with thermodynamic inhibitor to

accelerate the dissociation process, and stabilize the resultant mixture in preparation for cleanup operations [Sloan et al., 2011].

b) Temperature Control

Temperature control approach is maintaining the temperature of production fluids by either passive insulation or active heating in order to prevent the system entering the hydrate envelope. The usage of insulation is an established approach to hydrate formation during normal operating condition, particularly in black oil systems [Pickering et al., n.d]. However, temperature control by passive insulation is only suitable for normal operation. Following the shutdown, production fluids will cold down and will enter the hydrate region. Under this circumstance, depressurisation of the system is the approach to solve this problem [Mehta et al., 2001].

c) Water Supply Removal

Hydrate formation is prevented by removing supply of water by using separation and dehydration. This approach has been proved as a preferred practice for the export of sales gas but impractical for subsea application [Sloan et al., 1998]. For example, dehydration tank is used to prevent formation of hydrate for export of sales gas purpose before transported to storage tank.

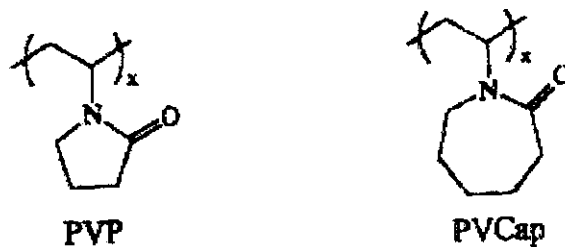
d) Hydrate Former Supply Removal

Gas-liquid separation is a common practice in term of removing supply of hydrate former. This approach has been proposed by subsea operation where gas and liquids are separated and transported to the processing facilities in separate pipelines. The gas pipelines still require hydrate inhibition but the liquid pipelines which containing oil and water is able to operate without forming hydrate due to the absence of hydrate formers.

e) Chemical Inhibitors Injection

Chemical inhibitors injection into system will modify the kinetic/morphology of hydrate formation. The chemical inhibitors has also found as widespread application. Three types of commercial inhibitor available in the market are Thermodynamic Hydrate Inhibitor (THIs), Kinetic Hydrate Inhibitor (KHIs) and Anti Agglomerate Inhibitor (AAs). THIs are high dosage consumption and the inhibition effect are not time dependent. It inhibits gas hydrate formation by shifting phase aqueous and gas hydrate equilibrium toward lower temperature and higher pressure. Main representatives of this inhibitor are water-soluble electrolyte salt such as calcium chloride and low molecular-weight alcohols such as methanol and monoethylene glycol, diethylene glycol, and triethylene glycol. Among these inhibitors, methanol is the common practice in industry [Semenov et al., 2011].

KHIs has been in commercial use in oil and gas for about 14 years [Kelland, 2006]. The main criteria that determine KHIs performance is induction time. Induction time in field operation is depends upon the subcooling ( $\Delta T$ ) in the system. Higher subcooling, lower the induction time. Commercial KHIs are water soluble polymer. Two main classes of polymer are (1) homopolymers and copolymer of vinyl caprolactam and (2) hyperbranched polyester amide. AAs on the other hand, prevents hydrate from agglomerating and forming blockage.



**Figure 1. Example of KHIs chemical structure [Lederhos, 1995]**

Low Dosage Hydrate Inhibitors (LDHIs) are time dependent inhibitor which requires smaller concentration than conventional thermodynamic inhibitors. Due to high dosage consumption of thermodynamic inhibitor during the operation, hydrate research has undergone the transition from thermodynamic inhibitors to low dosage inhibitor (LDHIs). KHIs and AAs are types of LDHIs.

## **1.2 Problem Statement**

Low Dosage Hydrate Inhibitors (LDHIs) are the time dependent inhibitor which require smaller concentration than conventional thermodynamic inhibitors. Nowadays, LDHIs is a common practice in industry due to their potential savings factors. Besides of low dosage consumption, other saving factors involve are include smaller storage capacity and smaller pumps for chemical injection process. Currently, ionic liquid has been discovered as potential LDHI due to their tuneable cation and anion criteria for hydrate mitigation [Xiao-Sen et al., 2011]. However, there is still limited evidence regarding ionic liquid efficiency as potential LDHIs.

## **1.3 Scope of Study**

This study covers the kinetic study of hydrate and thermodynamic of hydrate formation. In term of kinetic, the study will focus on the effect of ionic liquids to reduce consumption of hydrate during hydrate formation and induction time. Therefore, the study of phase behavior of methane hydrate formation act as basic knowledge as well as to lead to better understanding of this project.

## **1.4 Objective**

- a) To screen ionic liquid as candidates of LDHIs.
- b) To test the performance of ionic liquids as LDHIs.
- c) To study and investigate operation compatibility of ionic liquid as LDHIs.

### **1.5 Relevancy of Project**

As previously mentioned, LDHs has huge potential market in industry. Since LDHs require low dosage for each injection, it saves cost. Induction time is one of the criteria when evaluating LDHI performance. It is defined as the time between the absence of crystal and the appearance of the first crystal of the material being crystallized. By improving the criteria, it can promote towards better alternative for LDHs practice in industry.

### **1.6 Feasibility of the Project**

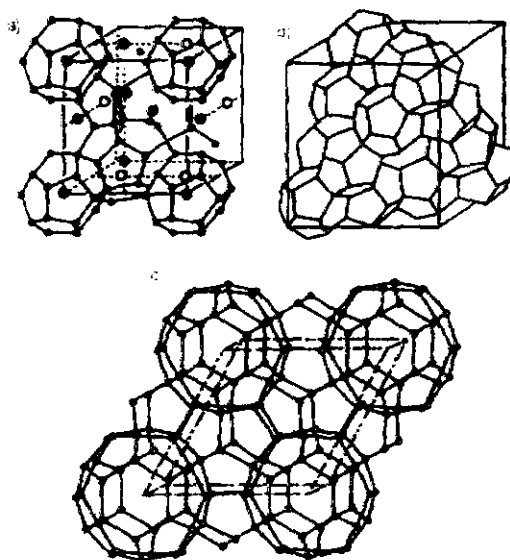
In University Technology Petronas, a research team has been established specifically in ionic liquid research and development. Therefore, equipments, chemicals and guidance are available for this research to be completed within the time framework.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Gas hydrate

Natural gas hydrates or clathrates hydrates are crystalline solid compounds that are formed in mixtures of water and non or slightly polar molecular gases. Formation of hydrate is promoted at high pressure and low temperature conditions. Hydrate is formed when hydrogen-bonded form cage like structures, known as cavities in the crystalline lattice. In order to stabilize gas hydrate structure, these cavities has to be filled at least partially filled with hydrate forming molecules. Depending on type and size of hydrogen bonded molecules, different structure of gas hydrate can be formed. Common structure are structure I, II and H. However, only structure I and II are typically found in oil and gas production. The largest cavities structure is structure H followed by structure II and structure I.



**Figure 2 - Unit cells of hydrate structure I(a), II(b) & H(c) [modified from Sloan, 1998]**

In order for stable hydrate crystal to form, four essential elements must be available such as forming guest molecules, access to supply of water, low temperature and



high pressure [Parmar, 2009]. Hydrate can be inhibited by removing at least one of these elements.

## **2.2 Hydrate formation and Dissociation**

Hydrate formation and dissociation can be related to experimental pressure-temperature trace for hydrate formation and dissociation as shown as in Figure 3 and Figure 4. Figure 3 indicate methane hydrate equilibrium formation condition. Hydrate equilibrium line represents the pressure and temperature boundary at which hydrate is stable. The hydrate equilibrium condition is depends on types of hydrate itself. Hydrate formation varies at different pressure and temperature condition at which it can be determined via hydrate equilibrium line. Figure 4 represents the graph which is plotted based on typical isochoric experiment of a vessel containing water and gas. Starting at point 1, the system is cooled at constant rate until the onset of hydrate formation is observed by indication of drastic decrease in pressure (point 2) which caused by concentration of gas in hydrate phase. At point 2 to 3, the temperature is maintained constant until rapid hydration formation end. The system is slowly heated at constant rate (point 3 to 1) to dissociate the hydrates.

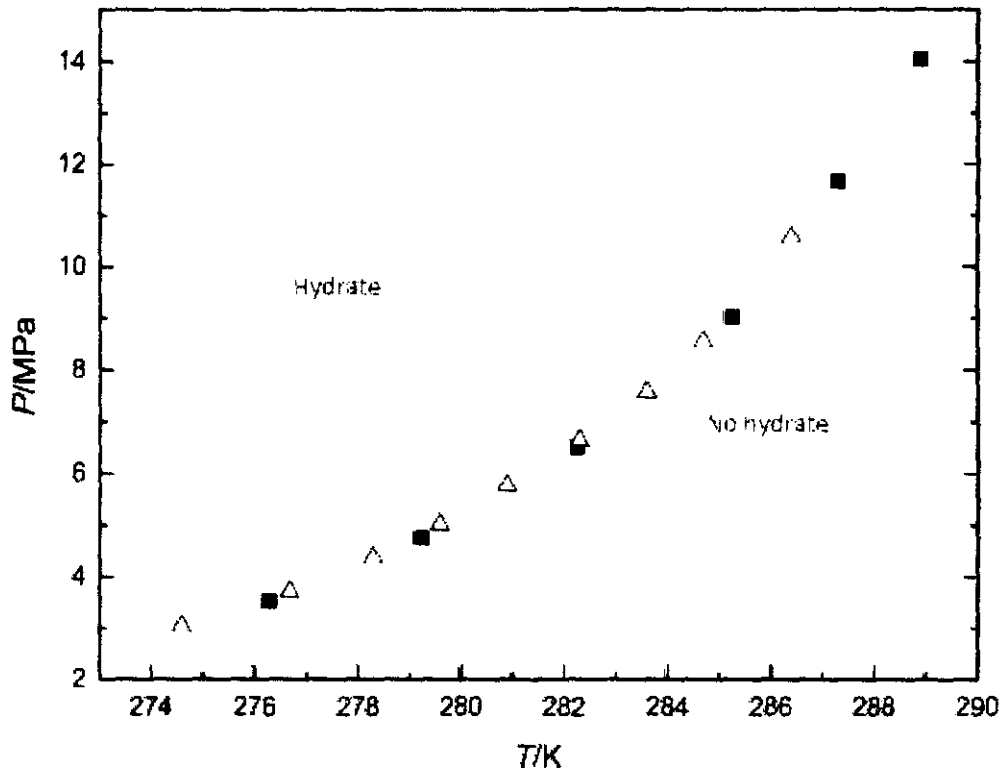


Figure 3 - Equilibrium hydrate formation for methane + water mixtures,  $\Delta$ Xiao-Sen et al;  $\blacksquare$  Adisasmito et al.(modified from Xiao-Sen,2011)

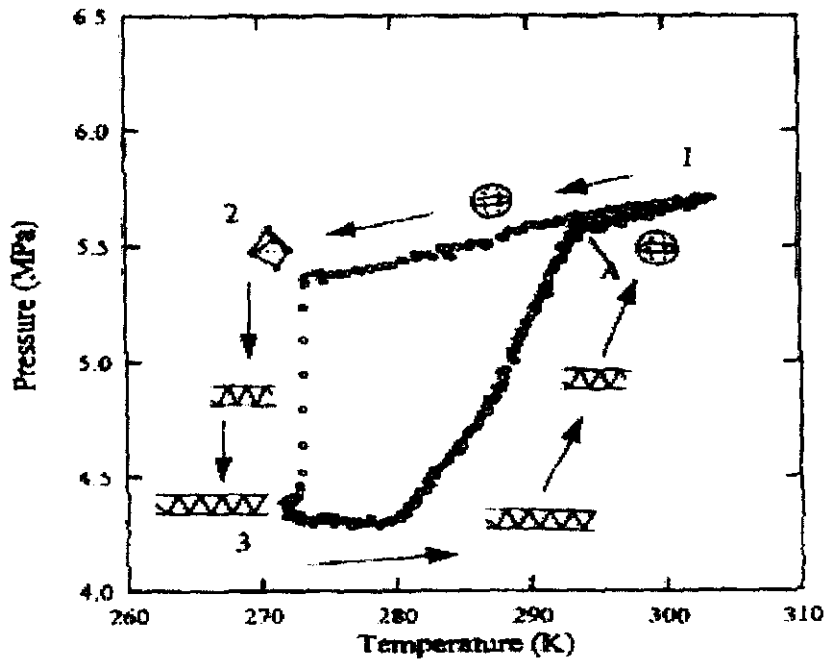


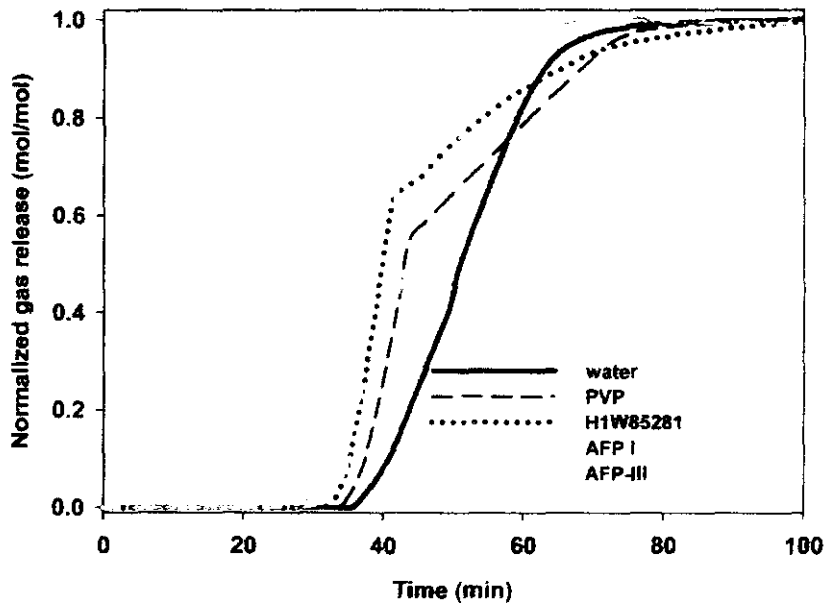
Figure 4 - Hydrate formation mechanism species superimposed on a pressure temperature traced [ Lederhos, 1995].

The formation of gas hydrates is generally divided into two processes, the nucleation process and the stable growth process [Vysniskas and Bishnoi, 1983; Englezos et al.,1987; Skovborg et al.,1993].The nucleation processes refer to the formation and grow of hydrate nuclei to a critical size. The growing clusters of gas and water molecules are acting as the precursors to hydrate nuclei formation. The growing hydrate nucleus that attains the critical size is a stable nucleus and leads to formation of crystal hydrate.

The formation of gas hydrate required supersaturated environment in order to occur. When gas molecules dissolved in water, it create supersaturated environment throughout the liquid phase or near the gas water interface. The nuclei will grow if sufficient gas present in water environment. Vapour-liquid interface is preferred for hydrate formation not only due to the lowering of Gibbs free energy of nucleation but also due to high concentration of water and guest molecules. The hydrate growth process is referred to growth of stable hydrate nuclei as solid hydrates. Mass and heat transfers play important roles in hydrate growth. The growth is dependent on interfacial area, pressure, temperature and subcooling.

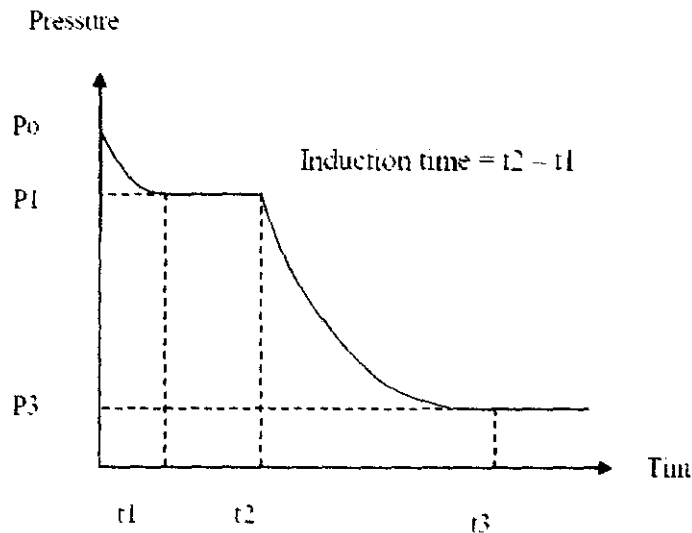
Hydrate formed in the presence of inhibitors were decomposed by heating, which resulted in consistent melting. Without hydrate formation, pressure increase due to the gas expansion as temperature increased with high pressure associated with dissociation of hydrate. The presence of commercial inhibitor has made decomposition of hydrate appeared in two stages and maximum pressure were not achieved until the control sample has decomposed [Daraboina et al.,2011]. Although KHIs can prolong the hydrate formation, long shut-in period can result in formation and plugging of pipelines. In these cases, decomposition of hydrate in the presence of inhibitors is an important consideration. Daraboina et al paperwork has shown biological inhibitors not only delays nucleation and inhibit hydrate growth, but when conditions change, hydrate formation in the presence of AFPs show complete decomposition at an earlier time, an advantages and valuable attribute to

KHIs.



**Figure 5 - Effect of inhibitors on hydrate growth for experiment conducted at 8.1 MPa and 275.15K [Daraboina et al.,2011]**

Important parameter use to characterize hydrate nucleation is the induction time. The induction time is the time elapsed during the nucleation processes which include formation of gas-water cluster and their growth to stable nuclei with critical size. The induction time can be obtained from pressure-time relationship for hydrate formation. In Figure 6 the dissolution of gas in the liquid causes initial pressure to drop. After the steady state is achieved, the pressure stabilized until sudden pressure drop is detected due to hydrate formation. The pressure keeps decreasing as gas is consumed during hydrate formation process. The induction time is calculated as  $t_1 - t_2$ .



**Figure 6 - Schematic Diagram of Pressure Changes with Time during Hydrate Formation [Khalik, 2009]**

Hydrate dissociation is an endothermic process. For hydrate to dissociate, heat must be supplied externally to break the hydrogen bonds between water molecules and the van der Waals interaction forces between the guest and water molecules of the hydrate lattice in order to decompose the hydrate into water and gas. Hydrate decomposition may be viewed as two step process which are the destruction of clathrate host lattice at the particle surface followed by desorption of guest molecule from the surface [Kim et al., 1987].

### **2.3 Gas Hydrate in Industry Application**

Hydrate formation has severe implication to industry as it can cause blockage of the pipelines and equipment. Hydrate can form at pressure and temperature found in natural gas and oil pipelines and cause blockage, especially when temperatures fall significantly such as chocked flowing gas condition [Pickering et al., n.d ].

Safety issues are also others important issue concerning hydrate formation. The presence of hydrate can cause severe implication to drilling operation. Under prevail condition during drilling operation , hydrates can form in the drilling risers and blowout the preventers [Edmond et al., 2001]. Occurrence of hydrates which close to the surface can also present a serious hazard during drilling by releasing gas into borehole leading to well control difficulties and the potential for blowout. In offshore industry, the difficulties associated with hydrate formation become more significant. The fluids from deep water reservoir tend to be relatively at low temperature and high pressure which hydrates tend to form. Two properties of hydrates that can cause them to be hazard are [Sloan et al., 2011]:

- a) They are denser than the fluids with which they are associated, giving them momentum and subsequent impact when they are dislodged from the pipe wall.
- b) They contain significant amounts of gas, so that if they are dissociated in a confined space, they will generate significant amounts of pressure.

Methane hydrate are volatile compounds, which are are stable in the extreme cold and crushing weight of deepwater, but are extremely dangerous when they build up inside the drill column of a well. If methane hydrate was destabilized by heat or a decrease in pressure, methane hydrates can quickly expand to 164 times their volume. Therefore, strategies for hydrate mitigation and control are crucial in order to ensure safety and reduce operating problems.

#### **2.4 Hydrate Mitigation and Remediation**

Currently, common practice of hydrate inhibition is by injecting chemical inhibitor. Three types of inhibitors available in the market are Thermodynamic Inhibitor (THIs), Kinetic Inhibitor (KHIs) and Anti-Agglomerating Inhibitor (AAs). KHIs and AAs is categorized as LDHI due to low dosage inhibitor consumption.

In a growing number of flow assurance applications, hydrate risk management is more economical than avoidance of the hydrate formation. Thus, LDHIs has been widely practised in industry compared to THIs. Therefore, currently there are extensive researches regarding new class of LDHI as alternative to commercial LDHIs. Lately, there is a new discovery of ionic liquids ability as gas hydrate inhibitor. Ionic liquid are composed solely of cations and anions. Due to tunable organic cations and anions properties, research has been carried out to find compatibility of ionic liquids as LDHIs candidate [Xiao-Sen et al., 2011].

#### **2.4.1 Thermodynamic Hydrate Inhibitors (THIs)**

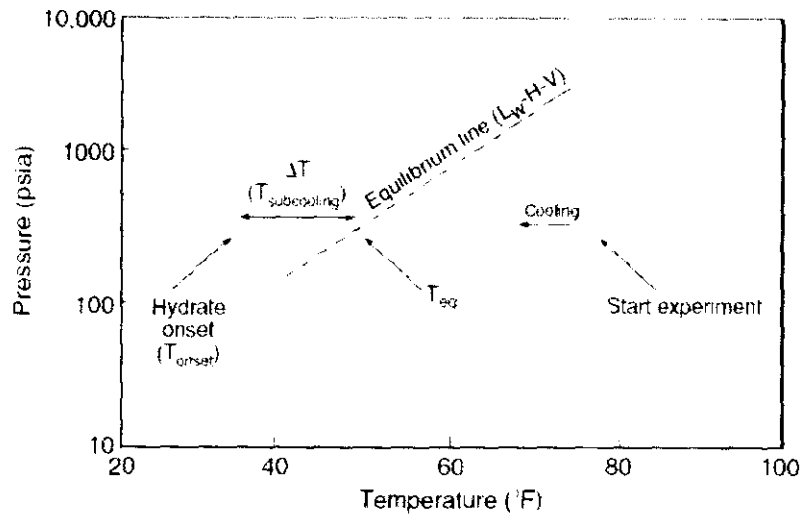
This inhibits hydrate by shifting hydrate formation region to higher pressure and lower temperature. THIs hydrate inhibition effects is independent of time. More inhibitor added to the system, more water molecules is prevented from participating in the hydrate structure. Therefore, higher pressures and lower temperatures are required for hydrate formation from the remaining uninhibited water.

#### **2.4.2 Kinetic Hydrate Inhibitors (KHIs)**

Unlike THIs, KHIs inhibition effect is time dependent. KHIs slow down hydrate formation by slowing down gas hydrate promoter access to hydrogen bonded molecules. The inhibitor molecules adsorbed on the surface of the growing crystal and forcing the hydrate surface to grow past the polymer backbone barrier anchored to its surface. When KHIs chains are closer, the subcooling is greater because it is more difficult for the hydrate crystal to grow between the polymer chains that are closer together. This will slow down the hydration formation. KHIs retard and elongated hydrate formation at 1% to 2% wt concentration. Thus, KHIs are expected to have economic advantages.

Sub-cooling is one of the criteria that determine the kinetic hydrate inhibitor performance. Sub-cooling is the different of equilibrium temperature and temperature

of onset of hydrate formation. The equilibrium line is the pressure and temperature boundary at which the hydrate is stable. As the system is cooled at relatively constant pressure, it must not be cooled beyond the hydrate onset temperature marked  $T_{\text{onset}}$  in Figure 2.5. At lower temperature and higher pressure, without KHIs, hydrates will form.



**Figure 7 - Subcooling temperature chart [Sloan, 2011]**

### 2.4.3 Anti Agglomerating Inhibitors (AAs)

AAs on the other hand, prevent hydrate from agglomerating and forming blockage. They are surface active chemicals that help to stabilize hydrate crystal that prevent it from agglomerate. They absorb on the surface. Anti-agglomerant element cause small, hair like of hydrate to protrude into the oil phase so that the two particles attractive forces are smaller than pure spherical particles. Therefore, the hydrate particles are kept suspended in the oil phase. In this way, anti-agglomerants can be considered as bridge compounds that keep apart the normally aggregated hydrate particles in which they are suspended in the oil phase without aggregation. Typical anti-agglomerants are quaternary ammonium salts, which the end of the molecules attached to the hydrate structure, and the other end of the long chain dissolve in oil phase [Kelland, 2006].



## 2.5 Tuning Ionic Liquid for Hydrate Inhibition

Adidharma and Xiao first identified ILs as methane hydrates inhibitor [Kim et al., 2011]. However, they just tested on imidazolium cation-based ILs without optimising combination of cation and anion. Via Kim et al.[2011] work, they have adopted systematic approach to tune ionic liquid as hydrate inhibitor. Their development work is base on two hypotheses, ILs must be hydrophilic in order for them to access water molecules and functional group has to be introduced since that would create intermolecular hydrogen bonding with hydroxyl groups of water molecules leading to disturbance among water molecules. In addition, shorter alkyl substituent in ILs reduce steric hindrance effect for functional group to create intermolecular hydrogen bonding with water molecules [Xiao et al., 2010]. Though functional group has enhancing inhibiting effect on hydrates formation, alkyl substituent length has bigger impact on inhibitor performance. For example, equilibrium hydrate formation for dialkylimidazolium and tetraalkylammonium based ionic liquid for methane hydrate has been investigated at 10 wt% of ionic liquid. Through the result, each cations of ionic liquid exhibit inhibition effect as THIs. From 5 studied ionic liquids, tetraalkylammonium-based given more promising result compared to dialkylimidazolium based ionic liquid due to steric hindrance effects of alkyl substituent. Even though anion has less significant effect compared to cation in inhibiting hydrate, optimum combination of anion and cation leads to good LDHIs. Example of anion that compatible with hydrate inhibition purpose is halides group [Xiao, 2010]. Ionic liquids with higher electrical conductivity show higher inhibition effects.

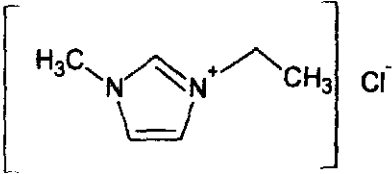
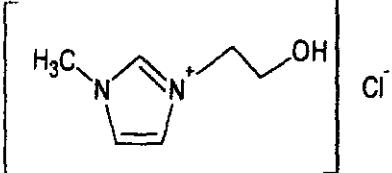
## CHAPTER 3

### METHODOLOGY/WORK FLOW

#### 3.1 Materials

All chemicals will be used in this work are shown in Table 1. These chemicals are used without any further purification process. The dialkylimidazolium based ionic liquids with the short alkyl and hydroxyl groups are taken into account in this work. All ionic liquids are water soluble and were purchased from Sigma-Aldrich with mass purity 99.8%. Methane gas with mole purity 0.9995 was supplied by Merck. To obtain different concentration, in term of weigh percentage, wt% all the ionic liquids were diluted with distilled water.

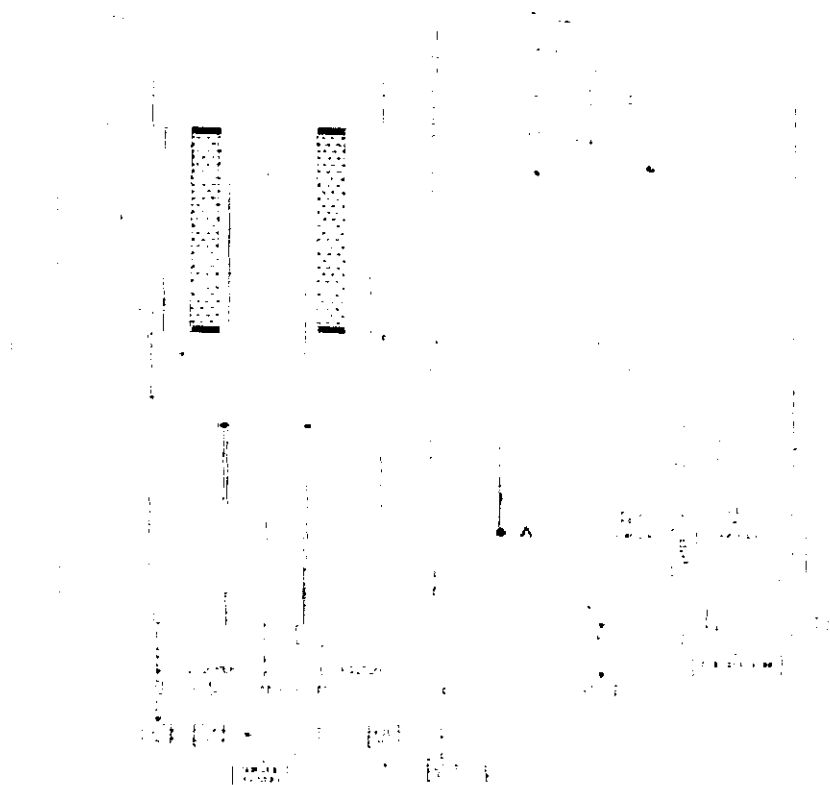
**Table 1 - Ionic Liquids Studied in This Work**

Symbol	Chemical Name	Chemical Structure
[EMIM]-Cl	1-ethyl-3-methyl-imidazolium chloride	
[OH-C <sub>2</sub> MIM]-Cl	1-hydroxyethyl-3-methyl-imidazolium chloride	

## 3.2 Apparatus and Procedure

### 3.2.1 Apparatus

The schematic diagram of the experimental procedure is shown in Figure 8. Hydreval is based on motor driven PVT cell. The chamber is closed at one end of the piston and at the other end is cell head made of titanium alloy, with maximum titanium cell capacity of 80cc. Maximum operating pressure of hydreval is 200 bar and temperature range of  $-20^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . This equipment is also equipped with magnetic driven. All parameters such as pressure, cell volume and temperature can be regulated by using computerized visualization. External pump will be used to pump gas and liquid into the sapphire cell.



**Figure 8 - Illustration of Flow Schematic of Hydreval [adapted from Hydreval Operation and Maintenance Manual,n.d]**



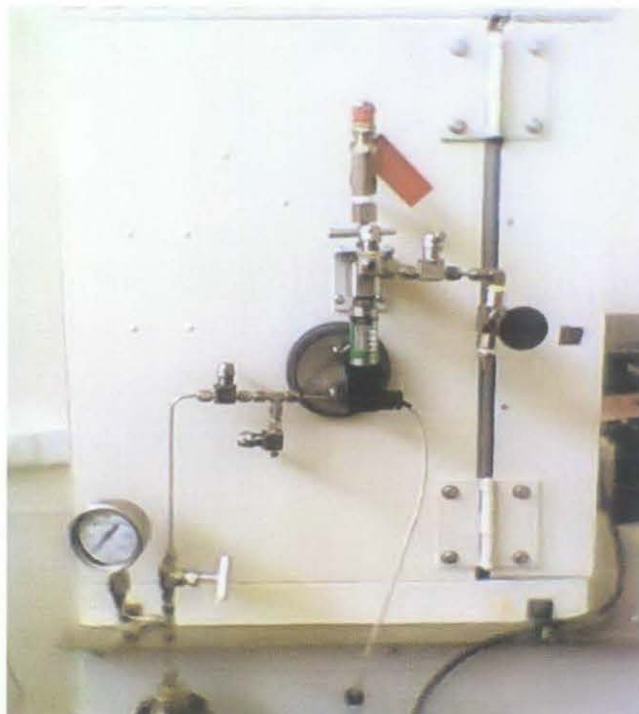
**Figure 9 - Hydreval**



**Figure 10 - External Pump**



**Figure 11 - Liquid accumulator**



**Figure 12 - Gas Inlet**

### 3.2.2 Sample Preparation

Initially, 10 grams of ionic liquid was dissolved in 990 ml of water to produce 1 wt% concentration. There are three ionic liquid concentrations that will be used in this study which are at 1 wt%, 0.5 wt% and 0.1 wt%. Therefore, 1 wt% aqueous will be diluted in water in order to produce 0.5 wt% and 0.1 wt% concentration. Equation below is used to calculate the required 1 wt% of ionic liquid concentration to produce 0.5 wt% and 0.1 wt% ionic liquid concentration.

$$M_1 V_1 = M_2 V_2 \quad (1)$$

Where,  $M_1$  and  $M_2$  are the concentration of first solution and desired concentration. Meanwhile,  $V_1$  is the volume of initial solution to produce desired concentration with  $V_2$  volume.

Prior to the experiments, the liquid accumulator was filled with water or desired ionic liquids by using external pump. This liquid later will be transferred to the sapphire cell by using the same external pump.

### 3.2.3 Hydrate Equilibrium Points Measurement

The equilibrium hydrate formation points were measured by isochoric method. The sapphire cell was then washed using distilled water and vacuumed. 40 ml of ionic liquid solution at desired concentration was injected into sapphire cell by using external pump. Then, the temperature was cooled down 2-3K above hydrate equilibrium. Subsequently, the cell was flushed with methane gas to ensure it was air-free. The gas was then supplied into the cell until the desired pressure is achieved at temperature where hydrate can not form. After the temperature and pressure of the system remained constant, the stirrer was switched on and the temperature was slowly lowered to form hydrate. The hydrate formation in the vessel was detected by visual observation. The temperature was then increased slowly. In this way, a pressure-temperature diagram was obtained for each experiment run.

### 3.2.4 Kinetics of Hydrate Formation Measurement

This experiment was measured by an isobaric method in order to investigate total of methane gas consumed during experiment with and without ionic liquid effect. Ionic liquid solution at desired concentration is loaded into the sapphire cell. Subsequently, the cell with the solution is flushed with methane gas at least 4 times to ensure it was air free. While flushing, the stirrer the stirrer is switched off to prevent solubility of methane in the aqueous samples. The methane gas was then supplied into the cell until desired pressure is achieved which is 70 bar. The loading of the gas is conducted at initial temperature 2-3K higher than the hydrate equilibrium temperature. The system temperature must be above the equilibrium temperature of methane hydrate formation which is about 3K higher in order to avoid instant hydrate formation when loading of methane is taking place. When the pressure and temperature are relatively constant, the stirrer is switched on and the rate of stirring is kept at 600 rpm. This value is chosen as the stirring rate is sufficient to remove the clathrate hydrate from gas-liquid interface and to keep hydrate particles as small crystal but not high enough to induce excessive bubble entrapment by vortex [Vysniauskas et al., 1983]. When pressure regains its stability, the temperature is slowly reduced to 7°C below equilibrium line. Constant cooling rate should be applied to the system in order to reduce stochastic of hydrate formation [Sloan and Koh, 2008]. In this work, equation of real gas can be used to calculate concentration of methane gas at initial, saturated and at specific time. Pressure (P) and temperature (T) measurement were used to calculate number of moles of gas consumed by following equation:

$$PV = nZRT \quad (2)$$

In term of mol of gas calculation, equation (2) will become,

$$n = \frac{PV}{ZRT} \quad (3)$$

In term of concentration, equation (2) will become,

$$C = \frac{P}{zRT} \quad (4)$$

where  $n$  if mole of methane gas to form hydrate and dissolved in water at time  $t$  and time  $0$ ,  $z$  is the compressibility factor calculated by Pitzers's correlation and  $V$  is the volume of methane gas in sapphire cell at time  $t$ .

Percentage of moles of gas consume during hydrate formation is calculated based on moles of gas at calculated at that specific point. By using hydreval, volume of total ionic liquid and gas can be recorded. By assuming ionic liquid is incompressible, total gas consumed can be calculated based on equation below,

$$\% \text{ mol consume} = \left( \frac{n_t - n_f}{n_i} \right) \times 100 \quad (5)$$

where,  $n_i$  is initial mol of methane gas at beginning of experiment and  $n_f$  is the mol of methane gas at time  $t$ .

In this work, the compressibility factor,  $z$  is calculated from Pitzer's correlation as shown below.

$$z = z^0 + \omega z^1 \quad (6)$$

Where,  $z^0$  and  $z^1$  are functions of both the reduced temperature ( $T_r$ ), reduced pressure ( $P_r$ ) and accentric factor of methane ( $\omega$ ). The values of  $z^0$  and  $z^1$  are obtained from Lee/Kesler Generalized Correlation Table presented in Appendix E in Smith et al. [2001]. Meanwhile, the value of  $\omega$  is obtained from Don et al. [2008].



In this work, the rate consumption of methane during hydrate formation with presence of ionic liquid will also be studied. Thus, rate consumption of methane gas during hydrate formation is calculated from below equation.

$$\frac{dn}{dt} = \frac{n_1 - n_2}{t_2 - t_1} \quad (7)$$

Where,  $\frac{dn}{dt}$  is the consumption rate of methane gas. Meanwhile,  $n_1$  and  $n_2$  are mol of gas from previous point and point of interest for methane gas consumption.  $t_1$  and  $t_2$  are the time at previous point and at point of interest for methane consumption.

In order to obtain apparent rate constant ( $k$ ), the concentration profile must be constructed. Since the formation of clathrate hydrate of methane can be assumed as 1<sup>st</sup> order reaction, the concentration profile can be plot by using equation below,

$$\frac{dC_h}{dt} = k(C - C_s) \quad (8)$$

Equation 8 result in following equation after being integrated.

$$\ln \left[ \frac{C_0 - C_s}{C - C_s} \right] = kt \quad (9)$$

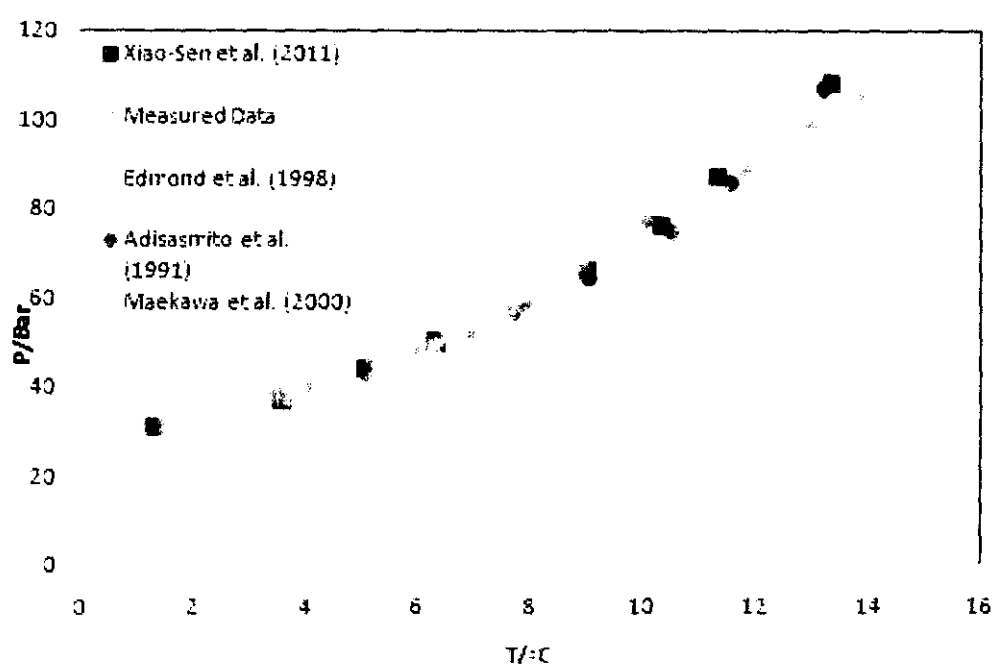
Where,  $C_0$ ,  $C$  and  $C_s$  are initial concentration of methane (mol/L), concentration at time  $t$  (mol/L) and saturated concentration of methane at the stationary point (mol/L). Meanwhile,  $k$  and  $t$  are apparent rate constant ( $\text{min}^{-1}$ ) and time taken for hydrate formation.

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Phase Behavior in the Hydrate Forming Region

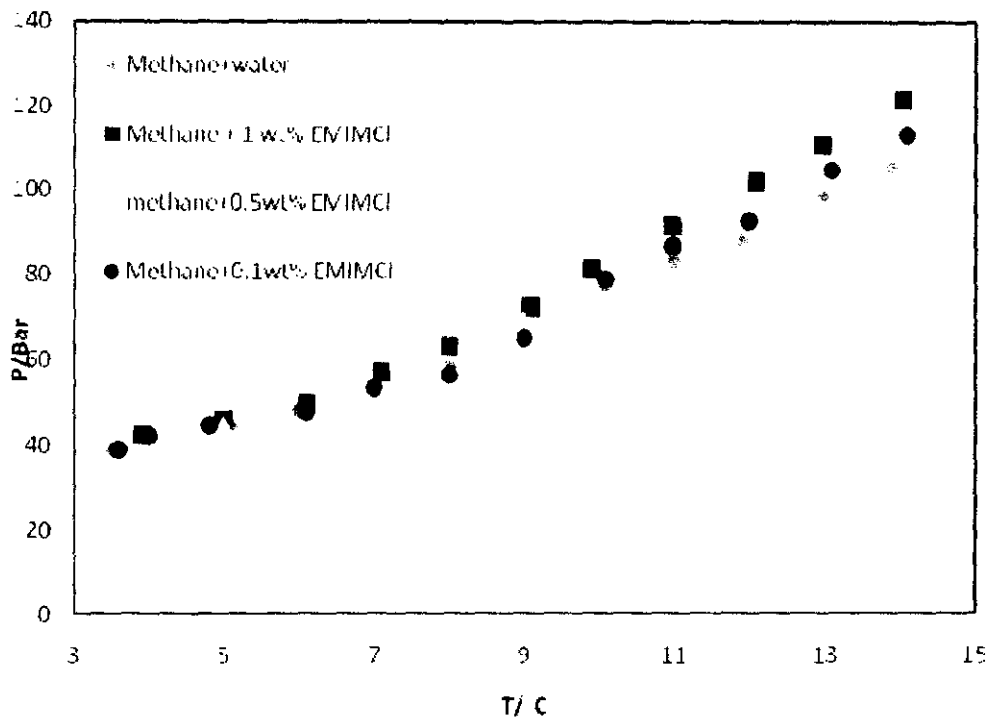
Prior to the experiments, methane hydrate formation are obtained and compared with the data from various literatures. As shown in Figure 13, the H-L<sub>v</sub>-V data obtained in this work are agree very well with various literatures review as below, which are obtained from direct measurement.



**Figure 13 - Equilibrium hydrate formation condition for methane + water**

The phase equilibrium data for Ethyl Methyl Imidazolium Chloride, EMIMCl at different low concentration are shown in Figure 14. Hydrate equilibrium data for methane and water are also shown in this figure for comparison purpose with EMIMCl solution at 1wt%, 0.5 wt% and 0.1 wt%. Even though at higher concentration, EMIMCl has shown potential as kinetic and thermodynamic inhibitor [Xiao-Sen et al., 2011], it has shown insignificant thermodynamic effect toward hydrate formation at lower concentration condition. Based on Figure 14, all EMIMCl ionic liquids show higher thermodynamic effect at higher pressure condition. This

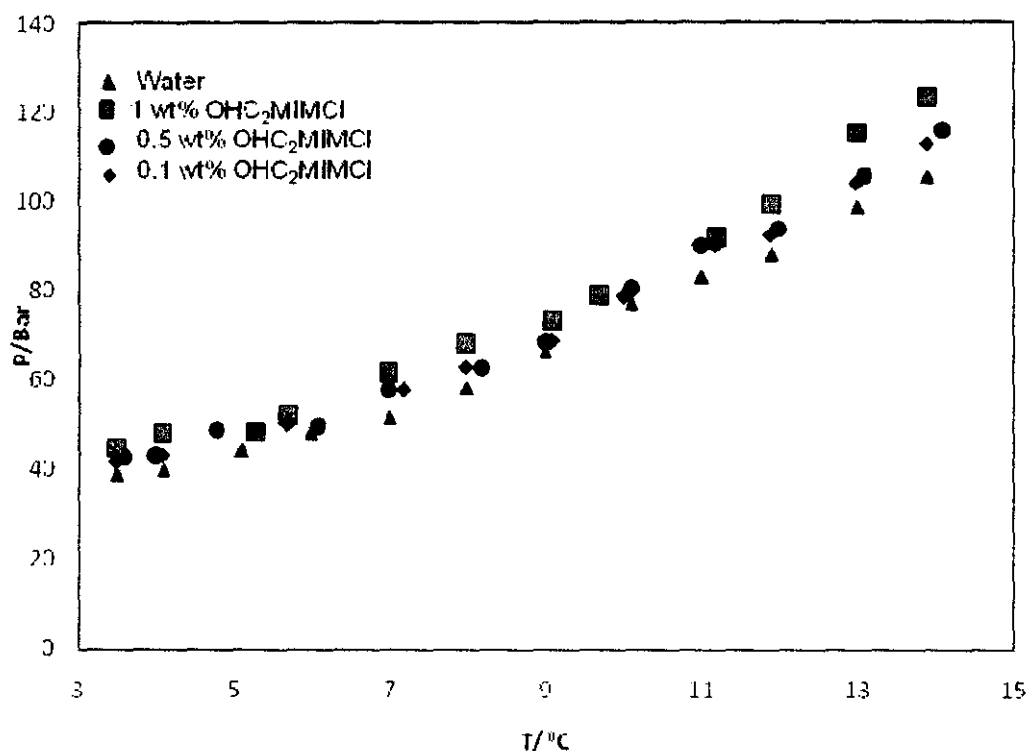
suspected due to salting out effect, which reduce solubility of methane in water by creating mass transfer resistance that prolong nucleation of hydrate in the presence of electrolyte. It is observed that, at lowest concentration, 0.1 wt%, the equilibrium line is similar to 0.5 wt% of EMIMCl. This condition indicates the similar repulsive electrostatic interaction of resulting in stability of hydrate at lower temperature for regardless of ionic liquid concentration for EMIMCl concentration less than 0.5 wt%. up to 0.1 wt%.



**Figure 14 - Equilibrium hydrate formation condition for EMIMCl**

The phase equilibrium data for OHC<sub>2</sub>MIMCl at different low concentration are shown in Figure 15. Hydrate equilibrium data for methane and water are also shown in this figure for comparison purpose with OHC<sub>2</sub>MIMCl solution at 1wt%, 0.5 wt% and 0.1 wt%. Compared to EMIMCl aqueous solution, equilibrium phase of methane hydrate have shown inconsistent data. This might occurs due to impurity of the ionic liquids. All imidazolium chloride based ionic liquids are hygroscopic where the available sample of OHC<sub>2</sub>MIMCl has partially turned into liquid. Based on Figure 14 and Figure 15, both ionic liquids have shown insignificant thermodynamic

effect on methane hydrate at low concentration.



**Figure 15 - Equilibrium of hydrate formation condition for OHC<sub>2</sub>MIMCI**

#### 4.2 Massive Hydrate Growth

Massive hydrate growth process is considered from turbidity point at which the starting point of hydrate formation to maximum methane gas consumption is observed. Two types of graph in term of percentage of gas consumed and consumption rate of gas have been plotted to study the relationship with time and temperature. Graph of  $\ln(C_0 - C_s / C - C_s)$  vs. time has been plotted to identify rate constant of hydrate formation.

Before sudden decrease of volume of gas occurs due to hydrate formation, slight decrease of gas volume is observed. This situation occurs due to solubility of methane in water at high pressure. Percentage of methane consumed during this process for hydrate formation is plotted in Figure 16. For all hydrate forming system, the maximum of methane gas consumed in the system is dependent on initial

pressure of methane in the system which related to initial mol of methane gas in the sapphire cell. Higher the initial mole of methane in sapphire cell, higher the gas consumption to form hydrate.

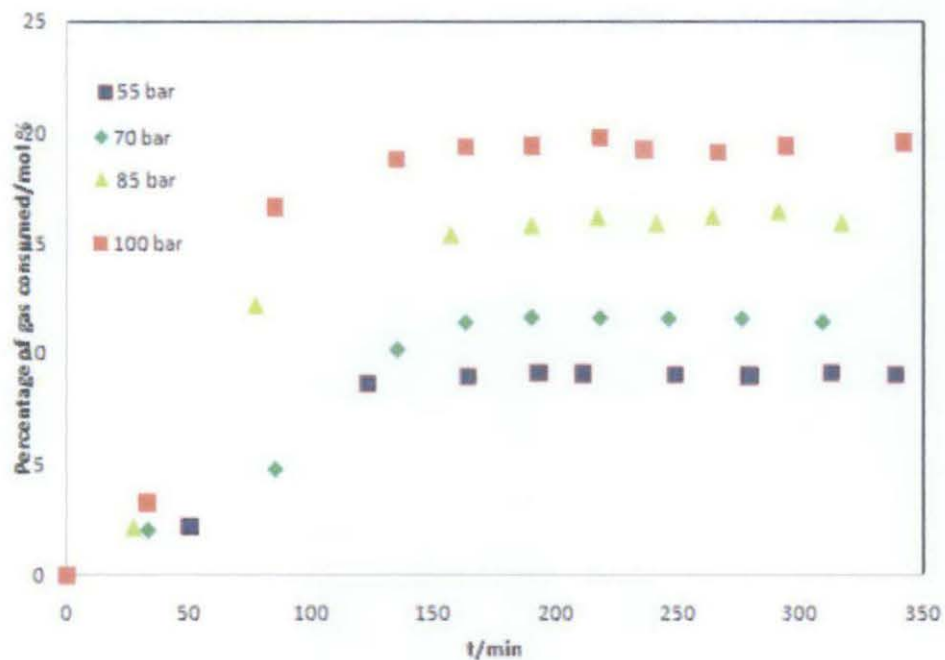


Figure 16 - Percentage of gas consumed at various pressure

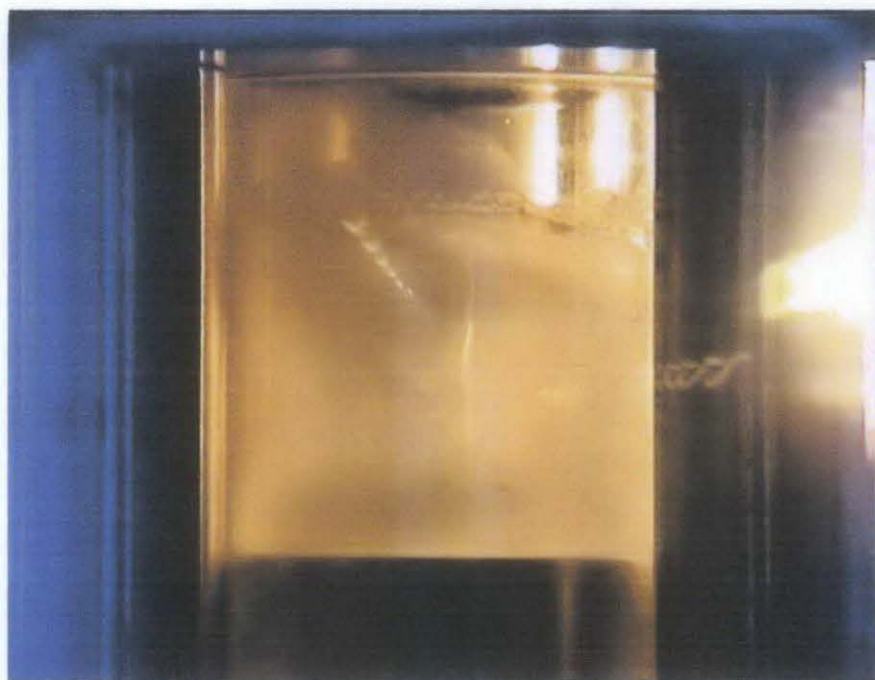


Figure 17 - Hydrate formed at 100 bar

#### **4.2.1 Percentage of Gas Consumed During Hydrate Formation**

As shown in figure 18, presence of ionic liquid, EMIMCl at different concentration is found to be able to reduce methane consumption during hydrate formation. Ions of EMIMCl act to minimize the water-accessible surface area of methane gas. The initial adsorbed methane molecules unfold to become flatter than methane molecules in salt free solution due to ionic liquid enhance the molecules dehydration effects. As adsorption continues and the electronic repulsion between methane molecules becomes greater, chloride ion induce refolding which cause island formation of methane in water in presence of EMIMCl. This salting out effect is greater with increasing of ionic liquid concentration.

For short ethyl alkyl group, hydroxyl group found to have significant effect towards ionic liquid performance. Low steric hindrance effect of short alkyl group causes higher tendency of hydroxyl to form hydrogen bond with methane molecules.

This condition creates a disturbance for interaction of methane and water molecules to form hydrate. Based on Xiao-Sen work, [2011], the results suggest ionic liquid with short alkyl group performs better inhibition effect than those with long alkyl group. The inhibition effectiveness of dialkylimidazolium based ionic liquid weakens with increasing of alkyl length. Longer length and bigger size of molecules create higher steric hindrance effect which made the hydroxyl group become less significant than in presence of short alkyl group of ionic liquid.

From these result, it is found that 1 wt % of ionic liquid gives the best result as LDHs. At this concentration, the gas consumption rate is the lowest, followed by 0.5 wt% and 0.1 wt%. With reduction of gas consumption, less hydrate will be formed.

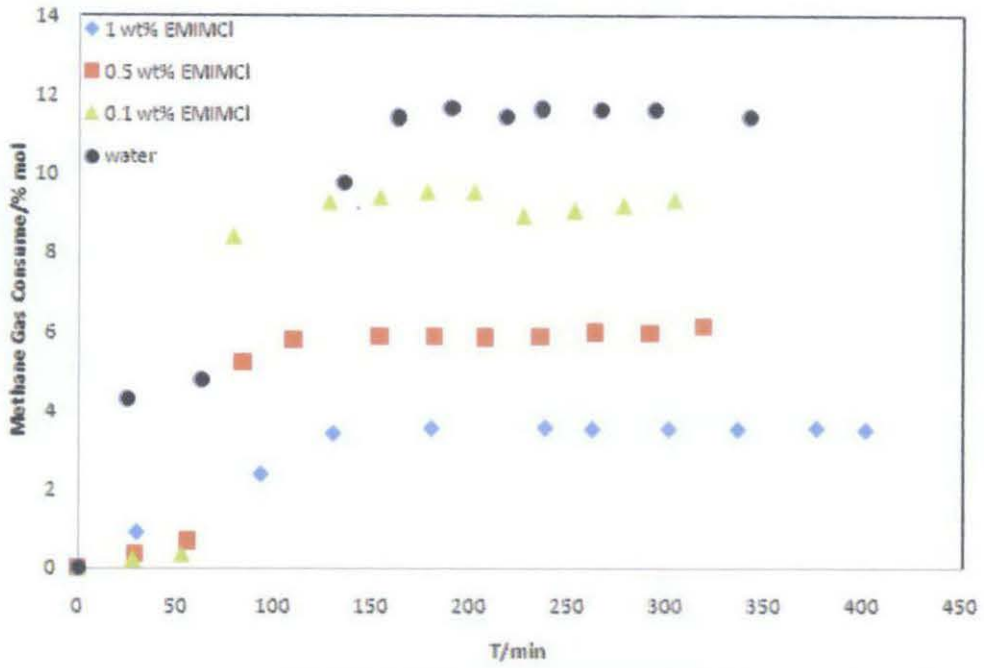


Figure 18 - Percentage of gas consumed at various EMIMCl concentration

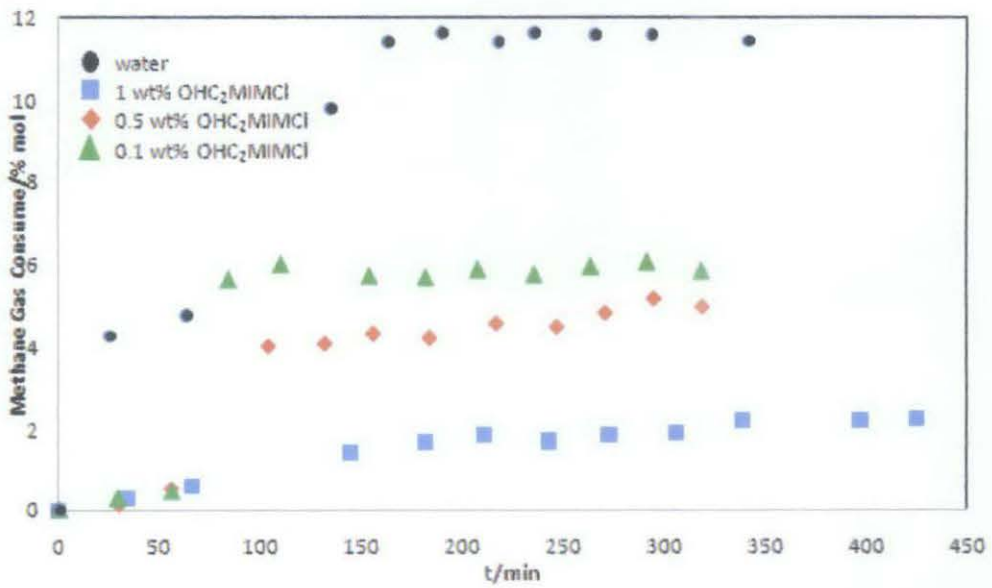


Figure 19 - Percentage of gas consumed at various OHC<sub>2</sub>MIMCl concentration

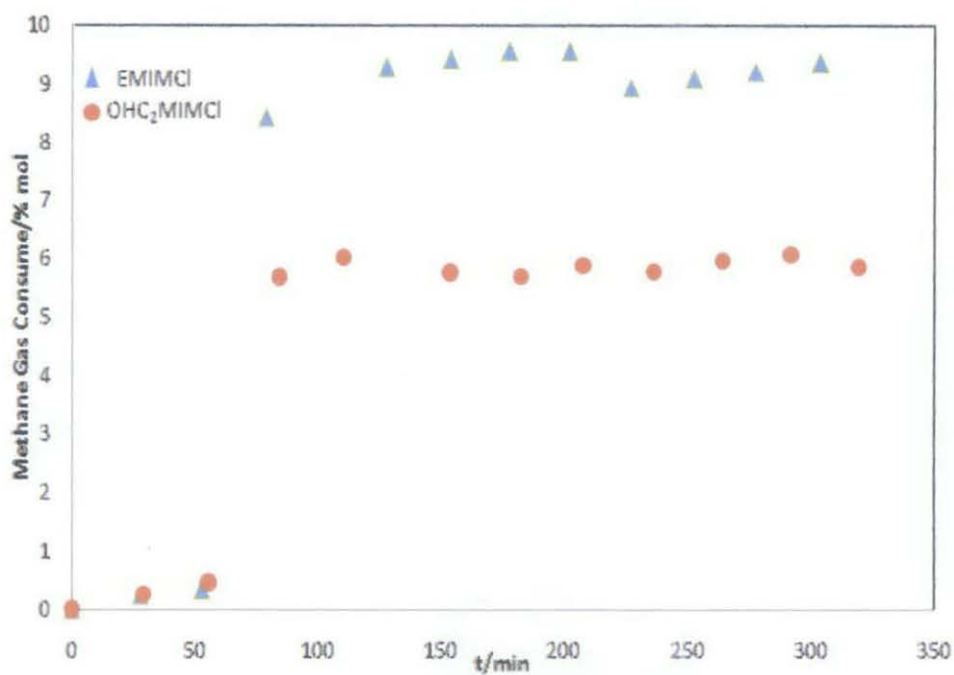


Figure 20 - Percentage of gas consumed at 0.1 wt% concentrations

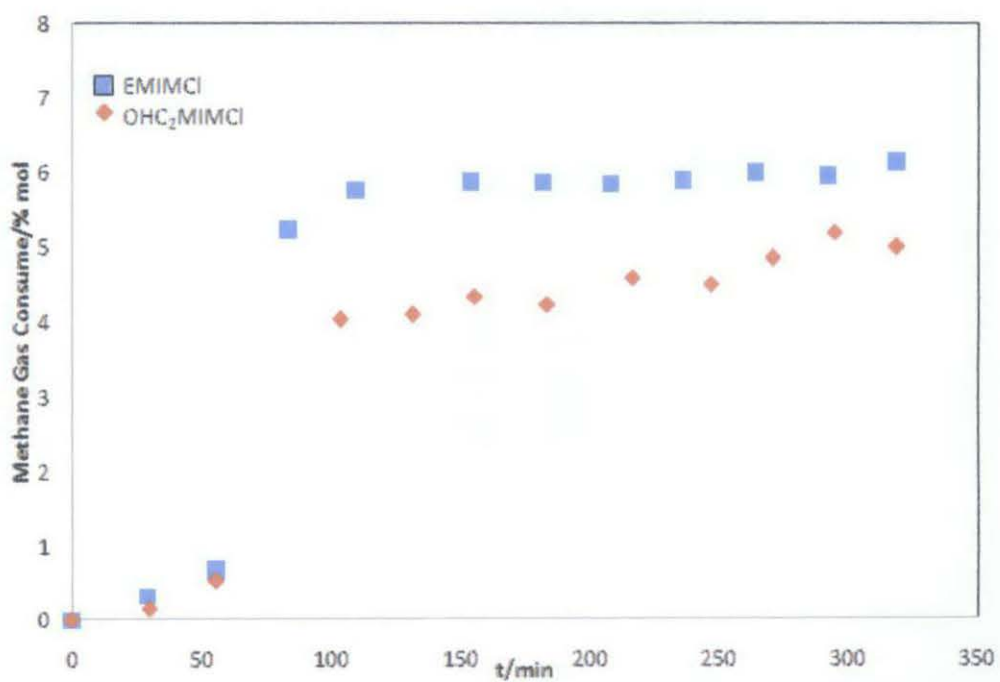
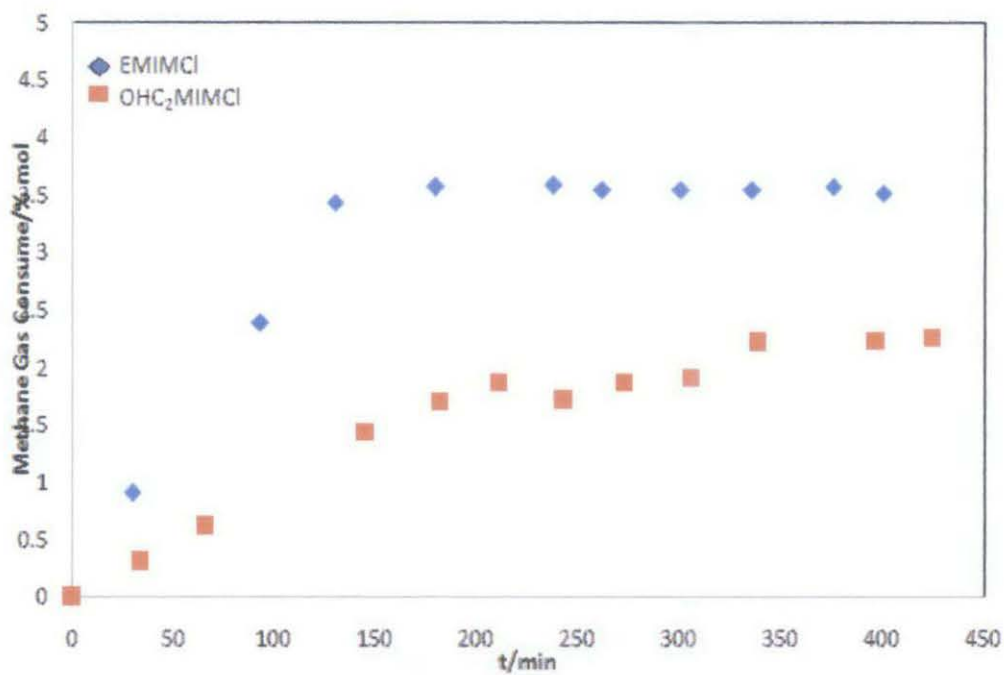
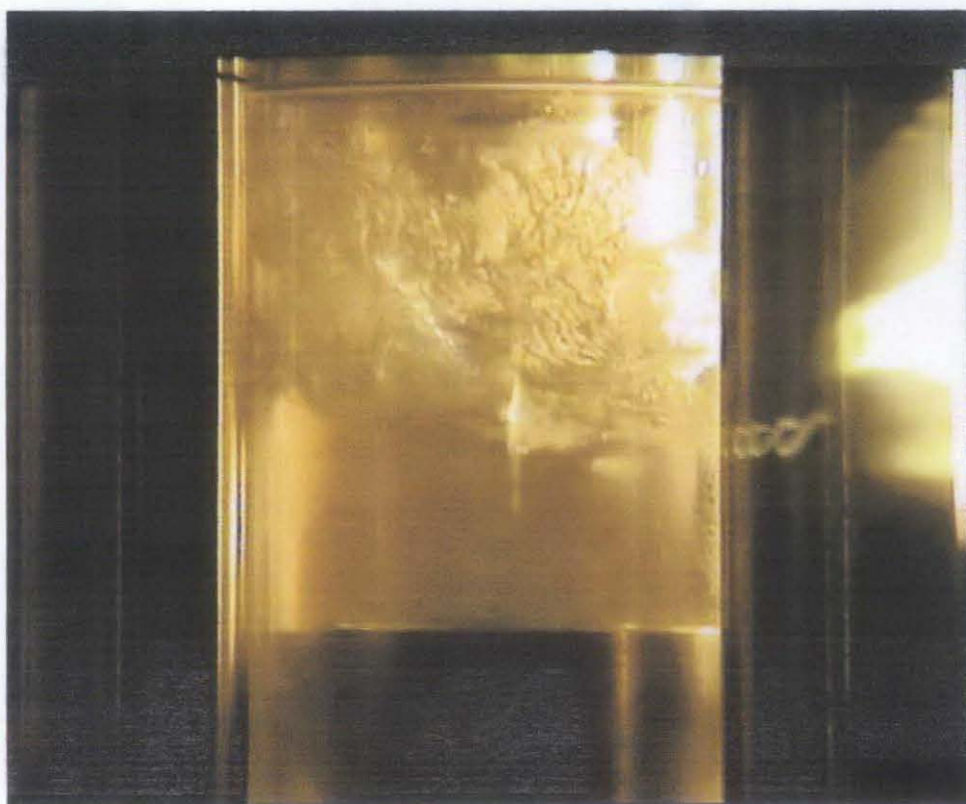


Figure 21 - Percentage of gas consumed at 0.5 wt% concentrations





**Figure 22 - Percentage of gas consumed at 1 wt% concentrations**



**Figure 23 - Hydrate formed in presence of 1 wt% OHC<sub>2</sub>MIMCI at 70 bar**

#### 4.2.2 Consumption Rate of Methane Gas during Hydrate Formation

Sudden increase of consumption rate by decreasing of temperature indicates the hydrate formation. Hydrate formation is the result of attraction between hydrogen bonded molecules and the gas guest molecules. Enthalpy of hydration is always exothermic because it involves attraction, and therefore bonding between guest molecules and water molecules. When bonding occurs, energy is released. Based on figure 24, it is observed the consumption rate of methane gas is depends on initial mol of gas. Huge declination of gas consumption rate is observed by decreasing pressure. Due to different setting of pressure, hydrate is formed at different temperature based on phase equilibrium property. For figure 25 to 27, hydrate is detected to form almost at the same temperature due to the same setting of pressure. However, different rate consumption has been observed due to presence of different types of ionic liquids at different concentration.

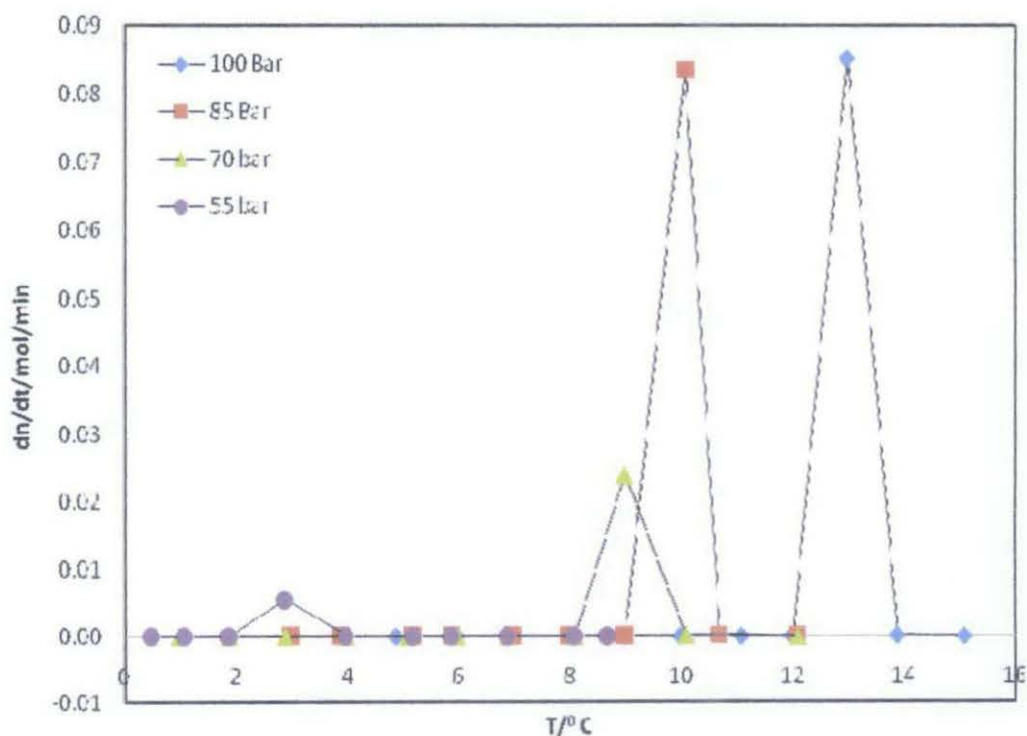
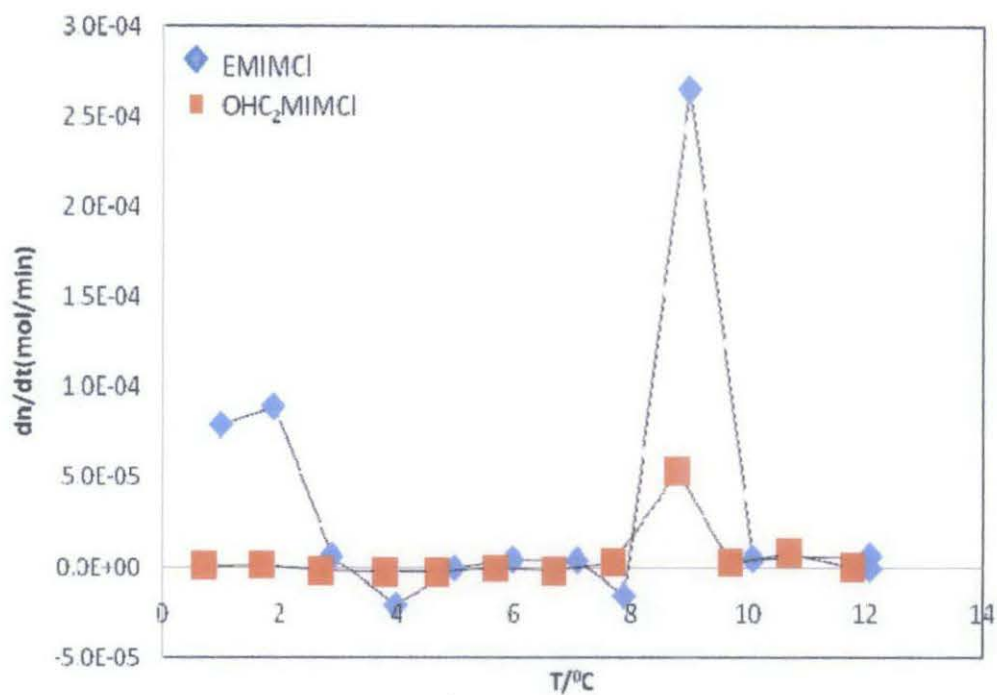
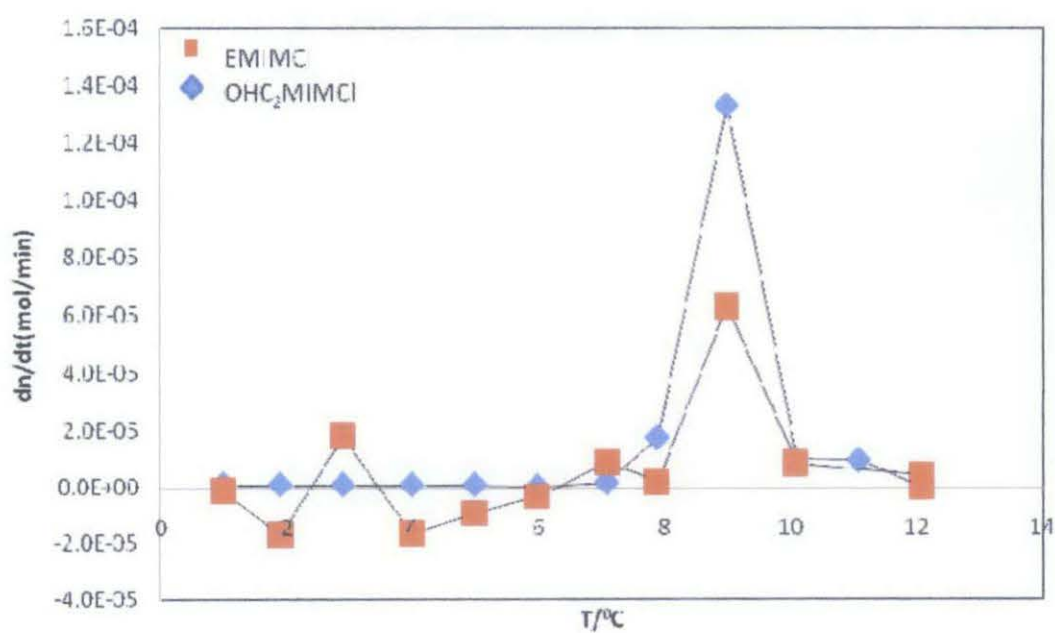


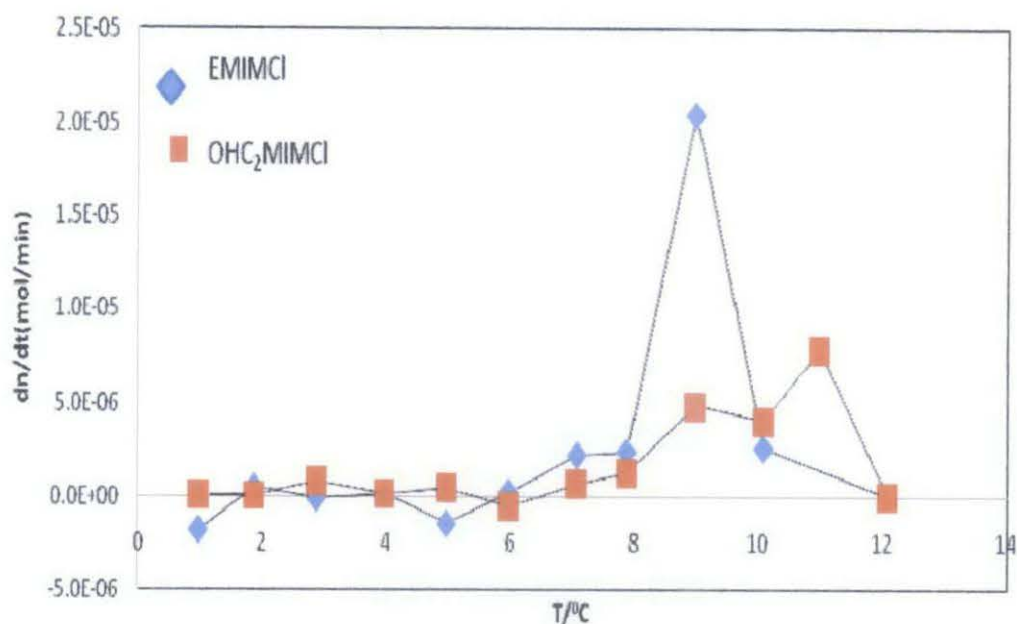
Figure 24 - Consumption rate of methane+ water at various pressure



**Figure 25 - Consumption rate of methane+ water at 0.1wt%**



**Figure 26 - Consumption rate of methane at 0.5 wt%**



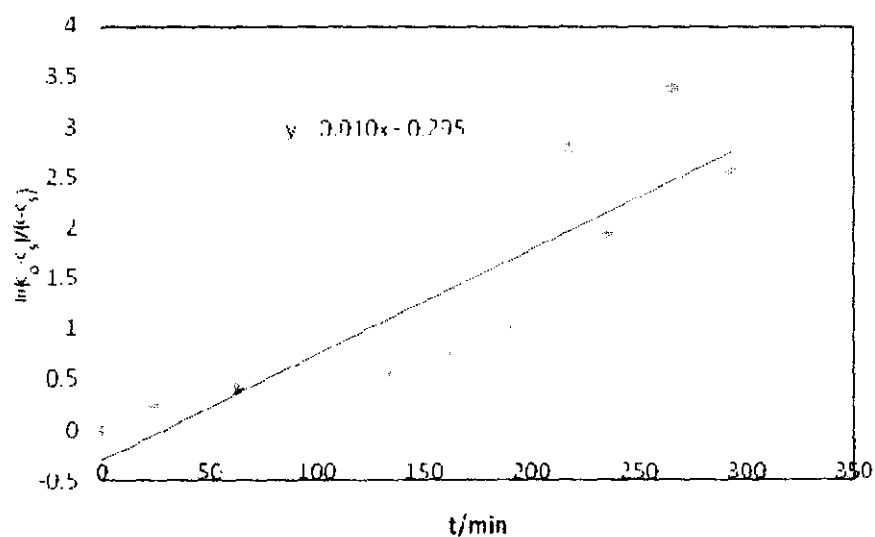
**Figure 27 - Consumption rate of methane at 1wt%**

#### 4.2.3 Rate constant

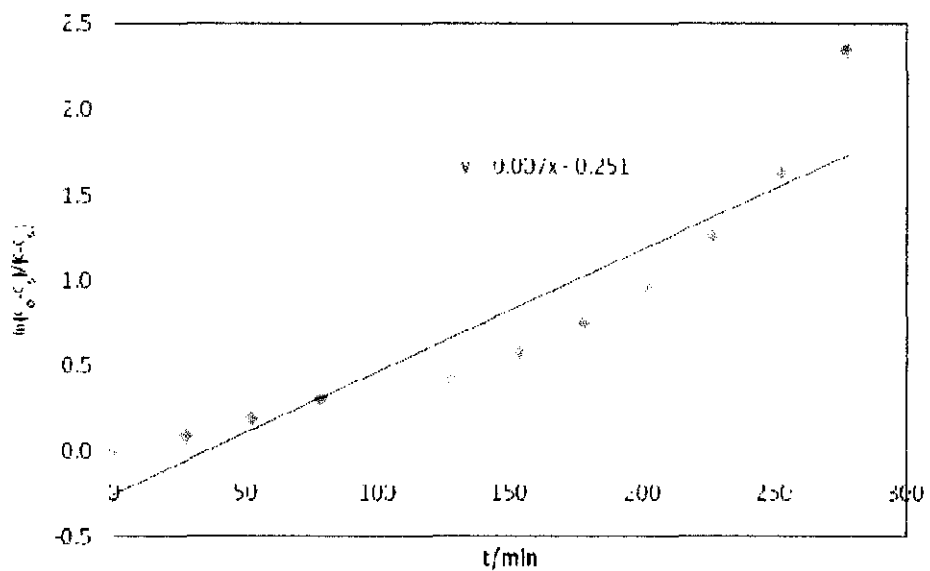
Presence of both ionic liquids reduces the kinetic rate constant for hydrate formation. From these plot, the apparent rate constant is calculated from the slope of each line and the data are tabulated in Table 2. Presences of both ionic liquids reduce the kinetic rate constant for hydrate formation. From the table, the highest reductions of rate constant are observed with presence of OHC<sub>2</sub>MIMCl and EMIMCl which are 0.002/min and 0.008/min. The trend applied for both ionic concentration at 0.5 wt% and 0.1 wt%. For OHC<sub>2</sub>MIMCl, there is obvious reduction of constant rate from 0.010/min to 0.002/min. Compared to OHC<sub>2</sub>MIMCl, the rate constant of EMIMCl is higher, indicating weaker inhibition effect. However, rate constant at 0.5 wt% of OHC<sub>2</sub>MIMCl observed to be higher than 0.5 wt% of OHC<sub>2</sub>MIMCl. This might occur due to inconsistent stirring rate that effect the solubility of methane in water.

**Table 2 - Rate constant of EMIMCl and OHC<sub>2</sub>MIMCl at various concentration.**

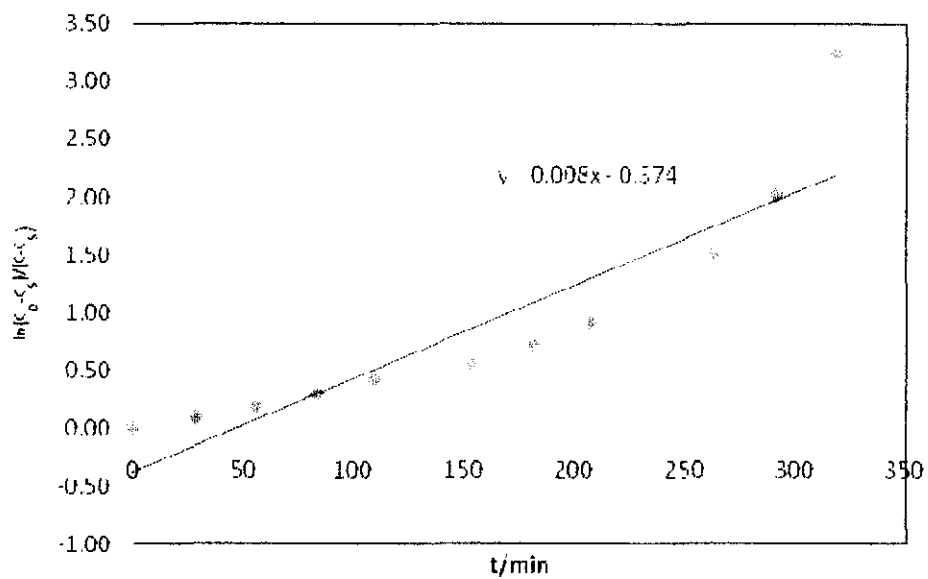
Concentration/wt%	k/min <sup>-1</sup>	
	EMIMCl	OHC <sub>2</sub> MIMCl
0.1	0.007	0.005
0.5	0.008	0.009
1	0.006	0.002
0	0.010	0.010



**Figure 28 - Graph ln(C<sub>0</sub>-C<sub>s</sub>/C-C<sub>s</sub>) for methane + water**



**Figure 29 - Graph  $\ln(C_0 - C_s / C - C_s)$  for EMIMCl at 0.1wt%**



**Figure 30 - Graph  $\ln(C_0 - C_s / C - C_s)$  for EMIMCl at 0.5wt%**

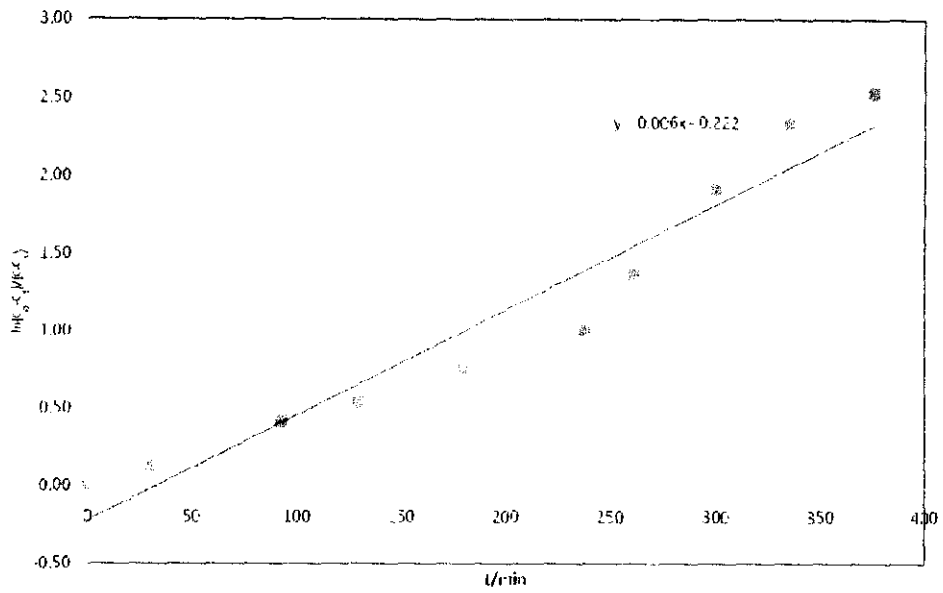


Figure 31 - Graph  $\ln(C_0 - C_s / C - C_s)$  for EMIMCl at 1wt%

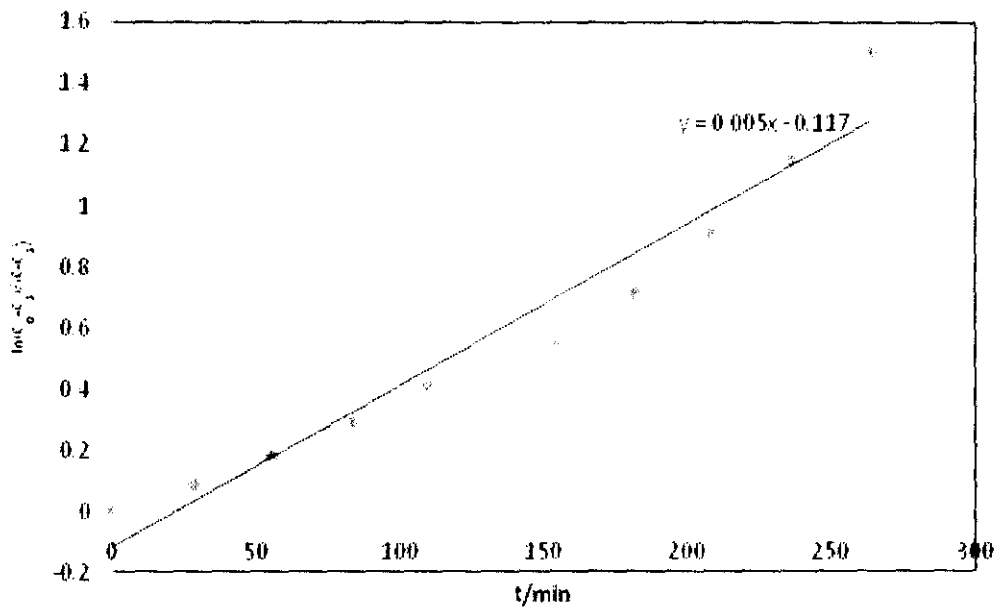
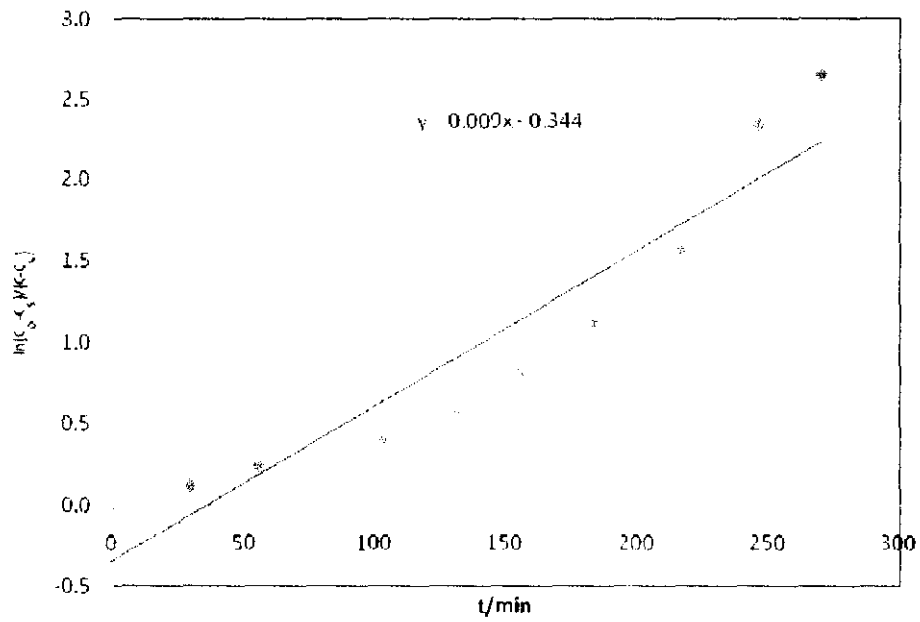
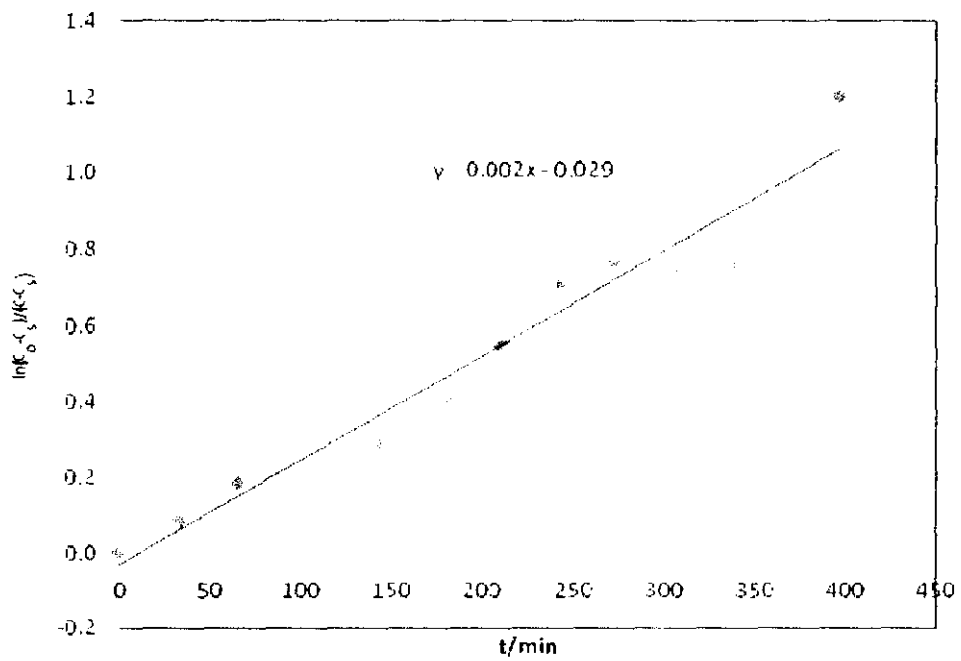


Figure 32 - Graph  $\ln(C_0 - C_s / C - C_s)$  for OHC<sub>2</sub>MIMCl at 0.1wt%



**Figure 33 - Graph  $\ln(C_0 - C_t / C_0 - C_s)$  for  $\text{OHC}_2\text{MIMCl}$  at 0.5wt%**

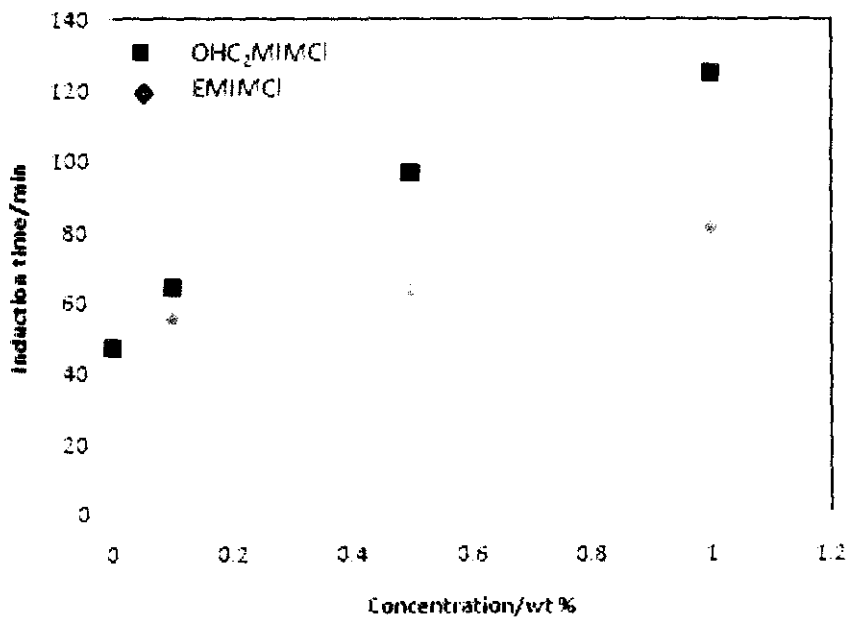


**Figure 34 - Graph  $\ln(C_0 - C_t / C_0 - C_s)$  for  $\text{OHC}_2\text{MIMCl}$  at 1wt%**

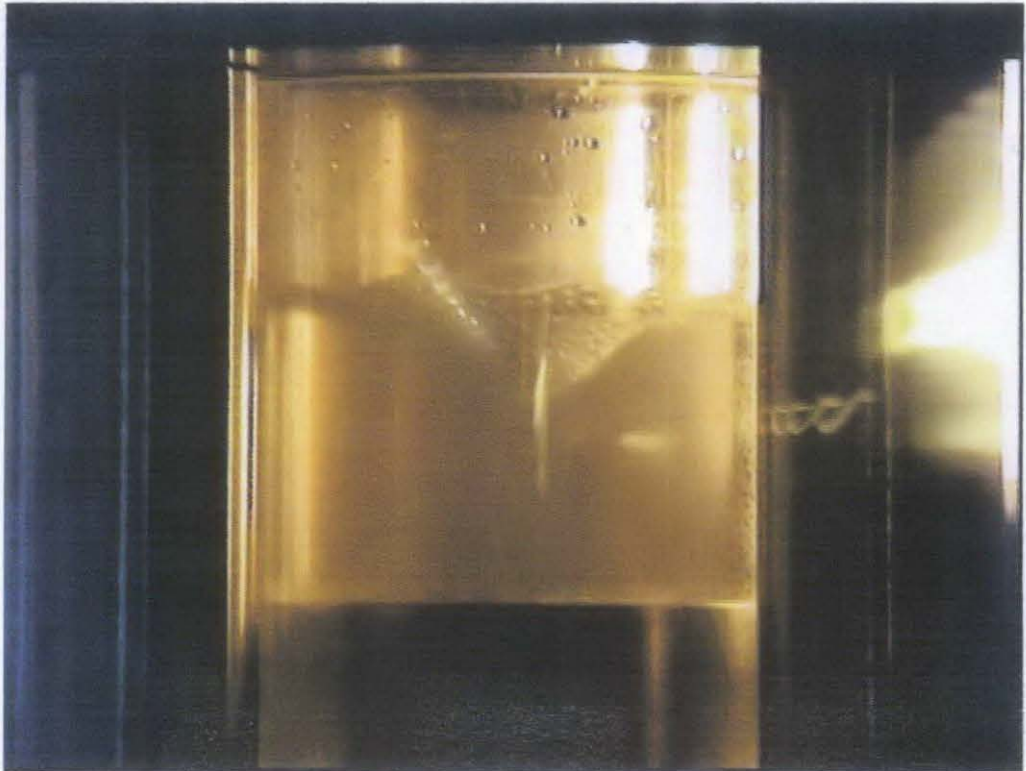


### 4.3 Induction Time

Induction time determines inhibitors performance. The pressure and temperature were recorded with time and consequently the induction time was decided by visual observation. For comparison with methane hydrate formation without presence of ionic liquid, the induction time for EMIMCl at 1 wt%, 0.5 wt% and 0.1 wt% were measured. From Figure 28, it is observed that the induction time for hydrate formation increasing with increasing of ionic liquid concentration. The presence of EMIMCl prolong the induction time in methane hydrate forming system. This occurs due to presence of ion in the aqueous phase hinders hydrate formation due to clustering with of water molecules with ions.  $\text{OHC}_2\text{MIMCl}$  causes lower gas consumption rate compared to EMIMCl. This condition occurs due to presence of hydroxyl group which create higher mass transfer resistance that prolongs nucleation of hydrate.



**Figure 35 - Induction time for various EMIMCl and  $\text{OHC}_2\text{MIMCl}$  concentration**



**Figure 36 - Initial formation of hydrate in presence of 0.5wt% OHC<sub>2</sub>MIMCl**

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

Two series of experiment was conducted to obtain equilibrium line and kinetic data of hydrate formation in methane and water system. The equilibrium hydrate formation condition in the presence of aqueous solution of EMIMCl and OHC<sub>2</sub>MIMOH at 1 wt%, 0.5 wt% and 0.1 wt%, have been investigated. The data was measured from 4 bar to almost 120 bar. For low concentration, the thermodynamic effect for both ionic less significant compared to their kinetic performance. For kinetic study of methane hydrate, kinetic of hydrate formation measurement was applied in order to screen ionic liquid effect on the induction time and gas consumption during hydrate formation. It has been found that both ionic liquid has significantly delayed hydrate nucleation and reduced the hydrate growth even at low concentration. From the result, it is also indicate the higher concentration of ionic liquid result in higher inhibition of hydrate. Presence of hydroxyl group in OHC<sub>2</sub>MIMOH has shown tremendous effect toward hydrate formation inhibition. It has shown significant reduction of methane gas consumption compared to EMIMCl. At lowest studied concentration, 0.1 wt%, it has capability to reduce methane consumption up to 5% gas consumption which similar to 0.5 wt% of EMIMCl's performance. Even though, low concentration ionic liquid is less significant as dual function inhibitor, it has shown high potential as good KHI. Therefore, ionic liquid is a good LDHI candidate.

It is recommended to conduct the study by using more various ionic liquid concentrations in order to have better understanding on concentration effect on hydrate formation. This study can also can be expanded by studying ionic of different alkyl length with presence of hydroxyl group and at various pressure. Due to equipment limitation, the lowest cooling rate for this experiment is 0.1°C/min. It is recommended to conduct experiment lower than 0.1°C/min to reduce stochastic effect on data accuracy.

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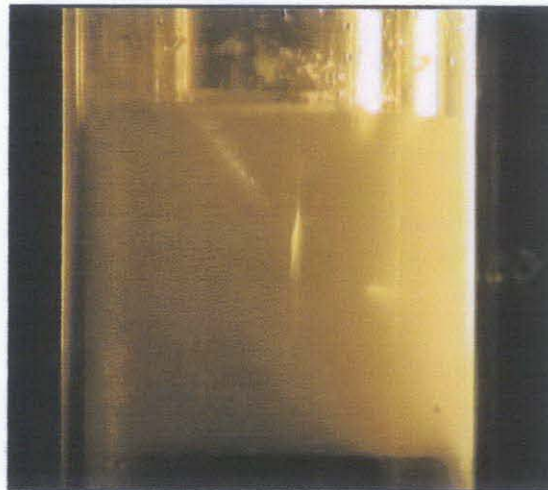
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## APPENDICES

### APPENDIX A: VISUAL OBSERVATION OF HYDRATE FORMATION

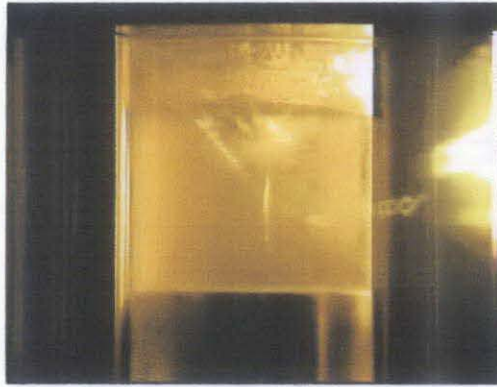


**Figure 37 - Hydrate formed at 85 bar**

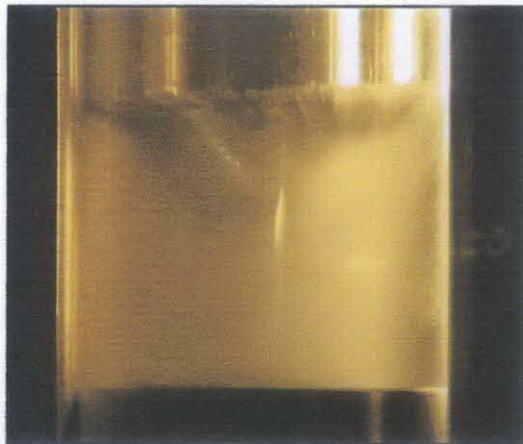


**Figure 38 - Hydrate formed at 70 bar**

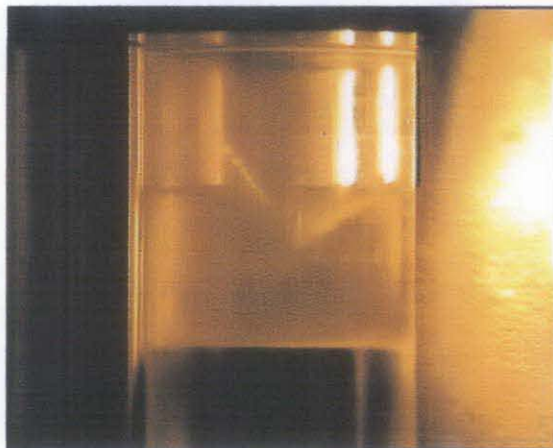




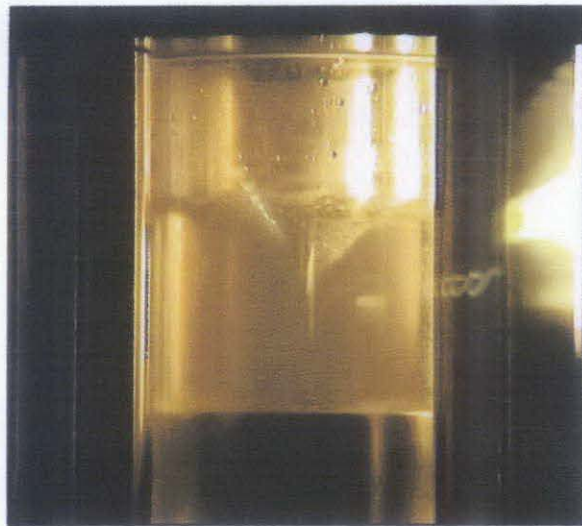
**Figure 39 - Hydrate formed at 55 bar**



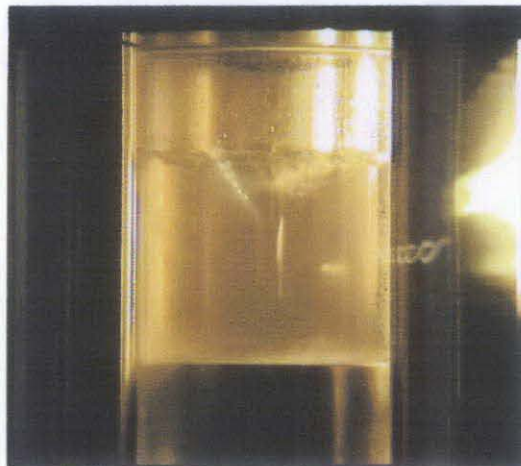
**Figure 40 - Initial formation of hydrate in presence of 1wt% OHC<sub>2</sub>MIMCl**



**Figure 41 - formation of hydrate in presence of 0.5wt% EMIMCl**



**Figure 42 - Initial formation of hydrate in presence of 0.1 wt% OHC<sub>2</sub>MIMCl**



**Figure 43 - Initial formation of hydrate in presence of 0.1wt% EMIMCl**