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# Evaluation of Tetraethylammonium Chloride on Methane Gas Hydrate Phase Conditions

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**Abstract:** In this work, hydrate liquid vapor equilibrium conditions for methane (CH<sub>4</sub>) gas is measured in the absence and presence of different aqueous TEACl concentrations. The temperature cycle (T-cycle) method has been used for the hydrate equilibrium temperature of CH<sub>4</sub> + H<sub>2</sub>O + TEACl system measurement within the pressure ranges of 3.90 – 8.30 MPa. Results reveal that, for 10 wt% aqueous TEACl average of suppression temperature ( $\Delta T$ ) (inhibition effect) appeared of 0.9 K for CH<sub>4</sub> hydrate. Additionally, the enthalpy of dissociation for methane gas hydrate with and without the present of inhibitor is calculated using Clausius-Clapeyron equation.

## 1. Introduction

In oil and gas industry, gas hydrate is one of the major challenges as exploration and production facilities are moving towards application of game-changer technologies with operating condition at extremely low temperature and high pressure in such conducive condition for hydrate formation [1,2]. Gas hydrates are crystalline compound consist of water cage structure and stabilized with gases as guest molecules under thermodynamically driven conditions [3]. Normally, small guest molecules occupying the water cages are light hydrocarbons such as methane (CH<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>), besides other gas carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). There are three gas hydrate structures namely structure I (sI), structure II (sII) and hexagonal structure H (sH) primarily subject to the size of the guest molecules. Gas hydrate issues in offshore production facilities has caused plugging and interrupted production line thus causing disastrous economic, inefficient operation and safety issue [2,3]. Occurrence of hydrate at low temperature and high pressure environment has made offshore production in deeper oceans such as North Sea, Gulf of Mexico and Alaska exposed to hydrate plugging issues. Remediation due to hydrate flow assurance issues, industry required exorbitance cost annually depending on the severity and location. The conventional hydrate remediation strategy includes dehydration of free water, depressurization, insulation or heat tracing and chemical inhibition [3]. However, chemical inhibition is considered as the most efficient hydrate prevention strategy existed in the industry [3]. Chemical inhibitor that works by shifting hydrate curve to the left were identified as thermodynamic hydrate inhibitor (THI). Among known THI are methanol and mono ethylene glycol (MEG) and they were used at very high concentration 20-50% by volume depending on aqueous phase in the system [4]. As the gas production and exploration moves to deeper seas large amount of THI need to be injected as the pressure and temperature conditions become more conducive for hydrate formation. Although THI is effective, factors such as economic, operational health & safety and product quality has forced oil and gas industry to develop low dosage hydrate inhibitor (LDHI) that commonly injected at very low dose 0.1- 2.0wt % [5]. There are two types of LDHI namely kinetic hydrate inhibitor (KHI) and anti-agglomerant (AA). KHI typically a water soluble polymer delayed the hydrate formation by slowing down the growth of hydrate crystallization in the pipelines and processes unit while AA inhibitors allowed hydrate formation, this surface active molecules attach to and disperse hydrate particles that can still be transported in slurry form [6]. When tiny hydrate particle began to form, AA will bind to particles and makes it slightly hydrophobic, thus prevented from hydrate cluster to grow [7]. However, AA performance are only effective at low to



moderate water cut resulting industry to further research more effective hydrate inhibitor. Despite being in the industry for years, both THI and KHI (as well as AA) are still far from satisfactory to give an economic solution [8]. In previous research activity, it is admitted that the combined effect of thermodynamic and kinetic inhibitors would be able to promise an improved solution to the current issue [5]. Recently, more efforts has been conducted to define effective operability of new-kind inhibitors than the current commercial chemical inhibitors [9].

Among the earliest discovery of a new category of inhibitors, known as ionic liquids (ILs) is by Xiao and Adidharma [10] and Xiao et al [4]. It has been found that ILs can powerfully function as both THI and KHI. As of now, commonly studied are imidazolium bases ionic ILs [4], [11], [12]; therefore insufficient work is done to study the effects of other group of ILs as hydrate inhibitor, especially ammonium-based ionic liquid (AILs) [13]. Tariq et al. [13] have evaluated that AILs worked as dual function hydrate inhibitor. Govinda et al. [14] has studied the applications of AILs in several research area such as carbon capture and storage, fuel cells, corrosion inhibition included flow assurance applications. AILs have been claimed to possess a better eco-friendly properties as compared to imidazolium based ILs group as AILs are commonly found to be used as the food stabilizers [15]. Li et al. [16] have studied that tetramethylammonium chloride (TMACl) as gas hydrate inhibitor and it is found TMACl produce better THI in comparison to imidazolium group ILs. Consequently, Keshavarz et al [17] has assessed the influence of tetraethylammonium chloride (TEACl) with other imidazolium-based ILs and discovered that all investigate ILs shows inhibition performance as high as 0.9 K [17–20].

As limited understanding in literature on the inhibition performance of AILs, this study are obliged to further investigate the thermodynamic inhibition performance of one of the AILs group named tetraethylammonium chloride (TEACl) on the hydrate equilibrium conditions of methane ( $\text{CH}_4$ ) hydrates at 1, 5 and 10 wt% concentrations of TEACl.

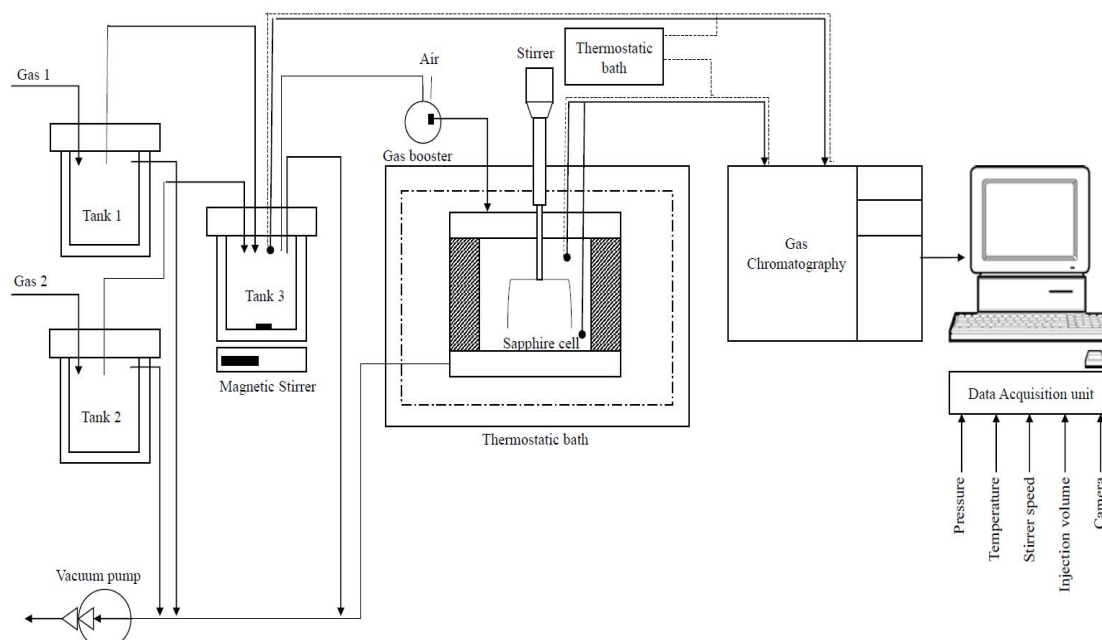
## 2. Methodology

### 2.1 Material

Materials used in this study are TEACl (95%) and acquired from Merck milli-pore company Germany.  $\text{CH}_4$  gas is supplied by Air Products PTE LTD. Ultra-purified deionized water is used to dilute the TEACl to intended concentration.

### 2.2 Experimental apparatus

Experimental set-up consists of fixed volume Saphhire glass cell is used in this work for determining the hydrate phase equilibrium conditions of  $\text{CH}_4$  gas in the absence and presence of TEACl. The set-up was furnished with an internal cell with 60  $\text{cm}^3$  in volume with design pressure up to 20 MPa and design temperature in the range of 253 – 333 K. The temperature, pressure and volume are measured in evert two seconds with an accuracy of  $\pm 0.1$  K,  $\pm 0.01$  MPa and  $\pm 0.001$   $\text{cm}^3$ , respectively. The glass cell is submerged in a ethanol coolant bath where temperature is controlled by means circulating the coolant in Lauda + DLK45 thermostats. The scientific equipment setup used in this work, depicted in Figure 1. The temperature in the equilibrium cell both in liquid and gas phase are measured by means of platinum-resistance (Pt100) thermometer probes and it is calibrated by Laboratoire National d'Essais Paris. The pressure in the equilibrium cell is measured by stable pressure transducer pressure calibrated by Armines-Mines Paristech Research Centre. The glass cell is equipped with magnetic stirrer in order to promote homogenous state of sample, which can be operated at maximum operating speed of 2000 rpm. Tank 1 or Tank 2 is used as a collecting tank for the gas sample prior entering Tank 3 which act as mixing tank. The gas sample is pressurized to the cell via Haskel AG-303 air driven gas booster compressor. Liquid water is transferred into the equilibrium cell using the manual syringe pump provided in this set up. Alternatively, images and video of sample in the equilibrium cell can be observed via a camera attached at the front of the thermostat bath.



**Figure 1.** Schematic diagram of experimental set-up.

### 2.3 Experimental Procedure

Thermodynamic equilibrium measurements for  $\text{CH}_4$  gas in this work used a traditional T-cycle method. Prior to the measurements, Sapphire cell is systematically washed with ultra-purified deionized water and subsequently vacuumed to ensure the cell is air free. The equilibrium cell is first charged with 10 ml of aqueous sample of TEACl followed by gas sample. The cell then is charged with  $\text{CH}_4$  gas and pressurized to the desired conditions (within the range of 3.9 – 8.3 MPa). Once the system stabilized, the mixture is stirred at 300 rpm. The temperature is reduced by applying rapid cooling method to enhance hydrate formation. The length of each cooling step varies from 2 to 4 hours maximum. Hydrate formation is observed both visually along with the sudden pressure drop. Once the gas mixture has fully encapsulated and hydrate has fully formed with no further pressure drop being observed, the equilibrium cell then is heated slowly for complete dissociation. Pressure-temperature trace is plotted in a graph, the first point where heating curve meets with the cooling curve is taken as hydrate equilibrium conditions.

### 3. Results and discussion

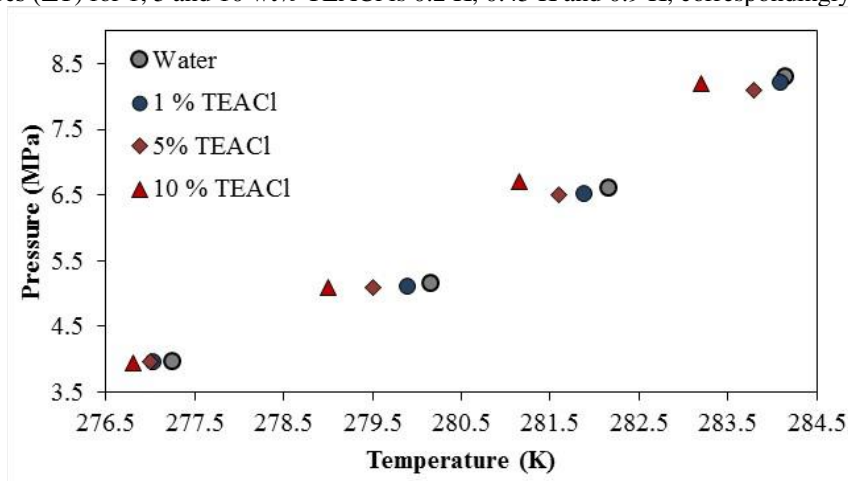
#### 3.1 Measurement of Hydrate Equilibrium Pressure and Temperature of Methane Hydrate

Table 1 shows the experimental results from the measurement of CH<sub>4</sub> hydrates equilibrium pressure and temperature in the absence and presence of TEACl. The experimentals were measured from 3.9 to 8.3 MPa pressure range.

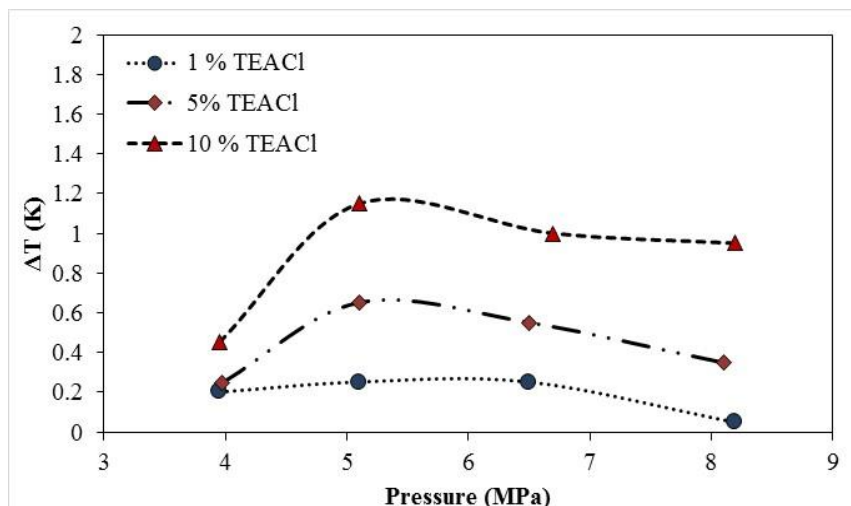
**Table 1.** Hydrate equilibrium pressure and temperature of CH<sub>4</sub> hydrates with and without the TEACl

System	TEACl Concentration in the solution							
	0		1wt%		5 wt%		10 wt%	
	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
CH <sub>4</sub> +TEACl+H <sub>2</sub> O	277.25	3.97	277.05	3.95	277	3.97	276.8	3.95
	280.15	5.16	279.9	5.1	279.5	5.1	279	5.1
	282.15	6.62	281.9	6.5	281.6	6.5	281.15	6.7
	284.15	8.3	284.1	8.2	283.8	8.1	283.2	8.2

The hydrate equilibrium pressure and temperature of CH<sub>4</sub>+H<sub>2</sub>O and CH<sub>4</sub>+TEACl+ H<sub>2</sub>O system at different concentrations of aqueous solution are presented in Figure 2. From Figure 2, it is evident that the presence of TEACl at different concentrations shift the CH<sub>4</sub> hydrate formation curves to higher pressure and lower temperature condition, which indicates the influence of TEACl is resulting a hydrate inhibition effect. Interestingly, the inhibition performance are found to be concentration driven, an increase in TEACl concentrations enhance the THI performance of TEACl. Figure 3 describes the influence of  $\Delta T$  over experimental pressure of studied TEACl system. It is also observed that, the inhibitions effect is more potent at pressure value of 5 MPa for 5 and 10 wt% of TEACl concentrations. The findings are in line with the earlier AILs studies [21,22]. The average suppression temperatures ( $\Delta T$ ) for 1, 5 and 10 wt% TEACl is 0.2 K, 0.45 K and 0.9 K, correspondingly.

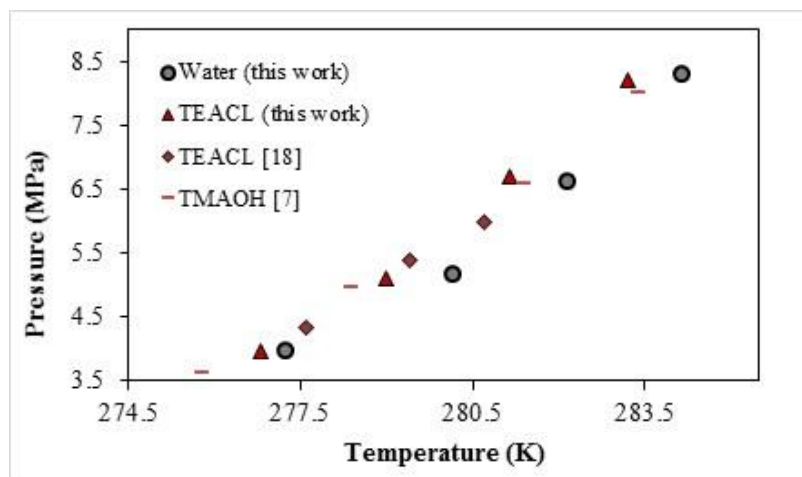


**Figure 2.** Hydrate phase equilibrium conditions for CH<sub>4</sub>+TEACl+H<sub>2</sub>O at 1, 5 and 10 wt%.



**Figure 3.** Average suppression temperature ( $\Delta T$ ) of  $\text{CH}_4 + \text{TEACl} + \text{H}_2\text{O}$  at 1, 5 and 10 wt%.

The inhibition effects of TEACl on  $\text{CH}_4$  hydrate in this work is compared to TEACl and other works related to ammonium based ionic liquid which; tetramethylhydroxide (TMAOH). The comparison of previous work is as per presented in Figure 4. In Figure 4, at 10 wt%, TEACl study in this work is found to be low in inhibition performance in comparison to studied AILs reported by Khan et al [22] at pressure of 5 MPa. However, the inhibition effect of 10 wt% TEACl is almost equivalent to the value testified by others [17] at pressure values higher than 5 MPa.



**Figure 4.** Hydrate equilibrium condition of  $\text{CH}_4 + \text{TEACl} + \text{H}_2\text{O}$  system with different type of ammonium based ionic liquids at 10 wt% concentration.

### 3.2 Enthalpy of dissociation

As hydrate forming and dissociation reaction The heat required to decompose hydrate crystals into liquid and hydrate-forming gas phase is known as dissociation enthalpy. The enthalpy of dissociation ( $\Delta H_{diss}$ ) would rely on the type of gas-guest molecule, size of the molecules and type of hydrate structure [23]. For example, typical sII hydrate formers such as propane occupy large cage and was reported with enthalpy of dissociation of 129 kJ/mol [19]. As for CH<sub>4</sub> gas which formed sI hydrate, it is occupying small cavity with  $\Delta H_{diss} = 58.88$  kJ/mol as reported in various literature [17,26].

In this work the enthalpy of dissociation is calculated by using the Clausius-Clapeyron equation [19–21, 23–25]. Enthalpy of dissociation is predicted by utilising the CH<sub>4</sub> hydrate equilibrium pressure and temperature measured in this study, while  $z$  is gas compressibility factor and  $R$  is universal gas constant.

$$\frac{d \ln P}{d \left( \frac{1}{T} \right)} = \frac{\Delta H_{diss}}{zR} \quad \text{Eq. 1}$$

The calculated values for  $\Delta H_{diss}$  for CH<sub>4</sub> + TEACl + H<sub>2</sub>O system is as per listed in Table 2. Assumption is made that the amount of hydrate phase is insignificant when the system is at equilibrium [17].  $\Delta H_{diss}$  value presented in this table of systems without the presence of TEACl is comparable to CH<sub>4</sub> hydrate enthalpy data, 58.88 kJ/mol [17,26]. It has been observed, for system with 1 and 5 wt% of TEACl presence in CH<sub>4</sub> hydrate, the  $\Delta H_{diss}$  is similar as sI hydrates enthalpy value. This evidently shown as at low concentrations TEACl is not inhabiting the hydrate cavity. Increased in TEACl concentrations to 10 wt% shows the increasing of  $\Delta H_{diss}$  as a result of TEACl molecules entering the large water cavity. Nevertheless, the  $\Delta H_{diss}$  values calculated in this work are much less as compared to typical sII hydrate formers such as propane, therefore it indicates sI methane hydrate is competing the hydrate cage occupancy with TEACl.

**Table 2.** Average dissociation enthalpy for CH<sub>4</sub> hydrates with and without the presence of TEACl aqueous solution

TEACl concentrations (wt %)	$\Delta H_d$ (kJ/mol)
0	60.700
1	58.367
5	58.557
10	64.877

## 4. Conclusions

In this work, an experimental investigation for hydrate equilibrium conditions of CH<sub>4</sub> hydrate in the absence and presence of various concentrations of aqueous TEACl has been carried out. In the presence of TEACl in the CH<sub>4</sub> gas, it has been observed that the hydrate formation pressure is increase. The conditions are causing by the disruptions of water activity during hydrate crystalline structure formation by TEACl, thus decreasing hydrate phase equilibrium conditions. The average suppression temperature ( $\Delta T$ ) reduction in the CH<sub>4</sub> systems are up to 0.9 K in the presence of 10 wt% aqueous TEACl, which can be considered useful in ILs perspectives. In addition, Clausius-Clapeyron equation was used to quantify the enthalpy of dissociation for TEACl + CH<sub>4</sub> + H<sub>2</sub>O hydrate system which are found that there is chance of TEACl is occupying large cavities of TypeII hydrate at 10 wt% (higher) TEACl concentration.

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