Chapter 7

Methane Hydrate Formation and Dissociation in Presence of Organic Inhibitors

Fluids commonly found in the oil and gas industries readily form hydrates under favorable conditions of temperature and pressure. Unwanted hydrate formation during processing has motivated researchers to investigate the formation conditions of hydrate in presence of various inhibitors so that occurrence can be avoided. In the present study methane hydrate formation and dissociation has been investigated in presence of ethylene glycol, polyethylene glycol and glycerol. In order to investigate inhibition effects of hydrate formation, depression in hydrate formation temperature in presence of these chemicals at various concentrations have been studied. The phase equilibrium of methane hydrate is also studied in presence of these chemicals to envisage the extent of phase equilibrium shift since phase equilibrium data is useful to evaluate the inhibition of gas hydrates. Once the temperature-pressure condition of hydrate formation is known then how long hydrate formation can be inhibited is also important to know. Therefore induction time of hydrate formation is determined experimentally in presence of the above chemicals.

7.1 Introduction

The formation of gas hydrates is a serious concern in the oil and gas industry since it is identified as a potential cause of blockage of natural gas pipelines, wellbores and natural gas processing units. Gas hydrates are likely to form in subsea flow lines unless the water is removed down to the lowest dew point encountered. It is a substantial problem in deepwater production and underwater pipelines, which transport condensed phase hydrocarbons such as gas condensate or crude oil. The hydrate formation also must be avoided while drilling through hydrate stability zone. The first approach to prevent hydrate formation is dehydration, which can be performed through use of solid desiccants or by normal glycol dehydration. Unfortunately, no process can achieve complete dehydration for economic and/or operative reasons. Another tactic is to keep the system out of the hydrate formation conditions.
method is known as thermodynamic inhibition. Thermodynamic inhibition can be performed by heating the system beyond the hydrate formation temperature, employing insulation, depressurizing the system, or injecting inhibitors such as methanol, glycol or salt solutions. The first three methods are technically impractical or very costly. Therefore the use of thermodynamic inhibitors is the best among thermodynamic inhibition methods. Thermodynamic inhibitors are chemical compounds added to alter the hydrate formation conditions, allowing the new mixtures to form hydrates at lower temperatures or higher pressures. These also alter the chemical potential of the aqueous phase or hydrate phase so that hydrate dissociation curve is displaced to lower temperatures or higher pressures. Although methanol is the most effective thermodynamic inhibitor, its handling is complicated because of its toxicity, volatility and flammability. Furthermore, methanol contamination of the hydrocarbon can compromise the value of the product and give downstream processing problems. Salts solutions might be used for hydrate inhibition but they are corrosive and less effective than organic inhibitors.

The thermodynamic inhibitors depress the freezing point of hydrate formation. The depression of freezing of a liquid due to presence of small amount of solute in it is given by the equation (Eq. 7.1) [Carrol, 2002, Pg. 114]:

$$\Delta T = \frac{x_i R T_m^2}{h_{st}}$$  \hspace{1cm} (7.1)

where $x_i$ is the mole fraction of the solute (inhibitor), $\Delta T$ is the temperature depression in °C, R is the universal gas constant (8.314 J/mol.K), and $T_m$ is the melting point of the pure solvent in K. Rearranging this equation slightly and converting from mole fraction to mass fraction gives

$$\Delta T = \frac{M_s R T_m^2}{h_{st}} \times \frac{W_i}{(100-W_i)M_i} = K_s \frac{W_i}{(100-W_i)M_i}$$  \hspace{1cm} (7.2)

where $M_s$ is the molar mass of the solvent, $W_i$ is the weight per cent solute (inhibitor), and $M_i$ is the molar mass of the inhibitor. For water, $K_s$=1861, when SI Units are used. The leading term in this equation contains only constants, so the freezing point depression is a function of the concentration of the inhibitor and its molar mass. This equation is not applicable to solution containing ionic salt.
To approximate the depression of hydrate formation temperature for several inhibitors in the aqueous phase Hammerschmidt [1934] reported the following equation (Eq. 7.3):

\[ \Delta T = \frac{K_H W}{M(100-W)} \]  

(7.3)

where \( \Delta T \) is the temperature depression in K, \( M \) is the molar mass of the inhibitor in g/mol, \( W \) is the concentration of the inhibitor in weight percent in the aqueous phase, and \( K_H \) is a constant with value of 1297. The Hammerschmidt equation predicts only the deviation from the temperature without an inhibitor present, not the hydrate forming conditions themselves. Originally, the \( K_H \) was constant over the years; some have proposed \( K_H \) a function of the inhibitor to improve the predictive capabilities of the equation. The Hammerschmidt equation is limited to concentration of about 30wt% for methanol and ethylene glycol and only to about 20wt% for other glycols. The freezing point depression method, which is shown to bear a resemblance to the Hammerschmidt method, is only applicable to a few mole per cent of solute.

Nielsen and Bucklin [1983] presented an improved version of the Hammerschmidt equation for estimating hydrate inhibition of methanol solution. Their equation is

\[ \Delta T = -72 \ln (1 - x_M) \]  

(7.4)

where \( \Delta T \) is in °C and \( x_M \) is the mole fraction of methanol. They claim that this equation is accurate up to 0.8 mole fraction (about 88wt %). This equation can be rearranged to estimate the methanol required for a given temperature depression

\[ x_M = 1 - \exp \left[ \frac{-\Delta T}{72} \right] \]  

(7.5)

The Nielsen - Bucklin equation was developed for use with methanol; however, the equation is actually independent of the choice of inhibitor. The equation involves only the properties of water and the concentration of the inhibitor. Therefore, theoretically, it can be used for any inhibitor.

Although Hammerschmidt and Nielsen - Bucklin equations have characteristics of simplicity that make them desirable, they exhibit limiting behavior. As the concentration of inhibitor approaches zero, \( \Delta T \) approaches zero. In other limit, as one approaches pure
inhibitor, the equation predicts infinite $\Delta T$ means no hydrate formation. With this in mind, an advanced equation has been developed. The basis for this equation is same as that for the Nielsen-Bucklin equation. However, an activity coefficient is included for the concentration of the inhibitor. The starting equation is

$$\Delta T = -72 \ln(\gamma_w x_w)$$  \hspace{1cm} (7.6)

where $\gamma_w$ is the activity coefficient of water and $x_w$ is the mole fraction of water. The activity coefficient has been calculated by Margules equation

$$\ln \gamma_w = \frac{a}{RT} x_i^2$$  \hspace{1cm} (7.7)

The term $a/RT$ is independent of the temperature and can be replaced by a more general constant called $A$- the Margules coefficient. Thus, equation (7.7) becomes

$$\Delta T = -72[Ax_i^2 + \ln(1 - x_i)]$$  \hspace{1cm} (7.8)

This equation may be sufficiently accurate over a wide range of inhibitors concentration. The values for the Margules coefficients, $A$, were obtained by fitting experimental data from the literature.

Najibi et al. [2006] used the freezing point depression of aqueous solutions to create the following equation for estimating the safety margin in the presence of salt and/or organic inhibitors:

$$\Delta T = 0.6825 \Delta T_f$$  \hspace{1cm} (7.10)

where $\Delta T$ and $\Delta T_f$ are the hydrate suppression and freezing point depression of aqueous solution in Kelvin respectively.

### 7.2 OBJECTIVE OF THE PRESENT STUDY

Gas hydrate equilibrium data in presence of inhibitors are necessary to develop the models for predicting hydrate phase boundaries of natural gas hydrate. Therefore, the objective of the present study is to identify the hydrate phase equilibrium in presence of organic inhibitors in order to prevent hydrate formation. Hydrate formation conditions of temperature and pressure are examined at different concentrations of inhibitors. The inhibiting effects of chemicals are
investigated by measuring hydrate formation temperature, pressure and induction time of hydrate formation.

### 7.3 EXPERIMENTAL

#### 7.3.1 Materials Used:
Ethylene Glycol, Polyethylene Glycol, and Glycerol were tested as inhibitors in the methane hydrate formation and dissociation. These chemicals were supplied by Merck Specialities Pvt. Ltd., Mumbai, India.

#### 7.3.2 Procedure:

The hydrate cell was filled with 130cc test sample prepared in water and immersed in temperature controlled bath. The cell was evacuated before the introduction of methane gas. Cell temperature was brought to a fixed temperature (293.65K) before charging gas to avoid over pressure. The cell was charged with gas up to the desire pressure (11.77Mpa) and test sample was stirred to saturate the liquid with gas. Cell was again charged with gas to compensate the dissolved gas. After obtaining stability of temperature and pressure, the temperature of the cell was decreased slowly, step wise, to observe hydrate formation. Hydrate formation in the cell was detected by pressure drop. The cell temperature was brought to 271.15K after complete formation of hydrate and kept at this temperature for 8 hours so that hydrate comes to equilibrium state. To observe dissociation condition of hydrate the temperature of cell was increased slowly in steps of 0.5K. At every temperature step, the temperature was kept constant for 3 hour so that equilibrium state of the system is not disturbed.

In the present work the inhibition effect of three chemicals were studied. These are EG, PEG and Glycerol. Three different concentrations (10wt%, 20wt% and 30wt %) of these chemicals in water were used.

### 7.4 RESULTS AND DISCUSSION

#### 7.4.1 Methane hydrate formation in presence of EG, PEG and Glycerol

A typical behavior of methane hydrate formation and dissociation in presence of 10% ethylene glycol (EG) in water is shown in Figure 7.1. The decrease in pressure of methane is noticed with decrease in temperature upon cooling. At temperature 281.07 K, a sharp sudden drop in pressure due to hydrate formation is observed. Dissociation of hydrate is observed
under heating condition. It is found that at 281.98 K, a substantial rise in pressure of the system is noticed indicating the initiation of hydrate dissociation.

![Fig.7.1: Temperature - pressure profile during hydrate formation and dissociation in presence of 10% EG](image)

The effect of different concentrations of EG on methane hydrate formation temperature and pressure is shown in Figure 7.2. The formation temperature of methane hydrate is strongly affected by the presence of glycol. It is noticed that the formation temperature is shifted to lower values of temperature on increasing the concentration of EG in water. Even it has been shifted below the ice point. Hydrate formation pressure is also found to decrease with increase in concentration of EG. The various thermodynamic parameters of hydrate formation and dissociation in presence of EG are presented in Table 7.1. The subcooling of hydrate formation is found to decrease with the concentration of EG. These results suggest that hydrate formation is inhibited more with increase in concentration of EG.
Table 7.1: Formation, dissociation parameters of hydrate in presence of EG

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Formation Pressure (MPa)</th>
<th>Formation Temp.(K)</th>
<th>Dissociation Temp. (K)</th>
<th>Subcooling (K)</th>
<th>ΔP/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>11.19</td>
<td>285.78</td>
<td>286.01</td>
<td>2.87</td>
<td>2.01</td>
</tr>
<tr>
<td>10wt%EG</td>
<td>10.76</td>
<td>281.05</td>
<td>280.98</td>
<td>6.72</td>
<td>1.10</td>
</tr>
<tr>
<td>20wt%EG</td>
<td>10.70</td>
<td>278.06</td>
<td>276.95</td>
<td>6.78</td>
<td>1.14</td>
</tr>
<tr>
<td>30wt%EG</td>
<td>10.03</td>
<td>272.32</td>
<td>273.25</td>
<td>7.33</td>
<td>1.22</td>
</tr>
</tbody>
</table>

The hydrate dissociation temperature is also found to decrease with the concentration of EG in water. It means a lower temperature is required to dissociate hydrate at higher concentrations of EG compared to hydrate dissociation in low concentration of EG in water. It is important to note that there is very small difference in hydrate formation and dissociation temperature. That is a minimum temperature is required to dissociate hydrate. The drop in pressure was observed to increase slightly with increase in concentration of EG but it is small compared to hydrate formation in water at equivalent initial pressure (Table 7.1).

![Temperature-pressure profile during hydrate formation in presence of EG](image)

**Fig.7.2: Temperature-pressure profile during hydrate formation in presence of EG**

To investigate the inhibition effect of EG on hydrate formation, the depression temperature of hydrate formation at different concentrations of EG was measured. The experimental values are summarized in Table 7.2 along with calculated values generated by
freezing point depression of solvent correlation (Equation 7.2), Hammerschmidt Correlation (Equation 7.3) and Naibji et al. correlation (Equation 7.10). It can be seen from Table 7.2 that the experimental depression temperature of hydrate are larger than the calculated values for all the concentrations. The Hammerschmidt equation predicts only the deviation from the temperature without presence of inhibitor, not the hydrate forming conditions themselves. This correlation depends only on the type of chemicals and their amount in the aqueous phase, regardless of hydrate forming condition of temperature and pressure. Similarly the leading term of freezing point depression of solvent correlation contains only constants, so the freezing point depression is a function of the concentration of the inhibitor and its molar mass.

Table 7.2: Depression in hydrate formation temperature in presence of EG

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>$\Delta T^a$/K</th>
<th>$\Delta T^b$/K</th>
<th>$\Delta T^c$/K</th>
<th>$\Delta T^d$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt%EG</td>
<td>4.71</td>
<td>2.32</td>
<td>3.34</td>
<td>2.28</td>
</tr>
<tr>
<td>20wt%EG</td>
<td>7.72</td>
<td>5.23</td>
<td>7.52</td>
<td>5.13</td>
</tr>
<tr>
<td>30wt%EG</td>
<td>13.46</td>
<td>8.96</td>
<td>12.89</td>
<td>8.80</td>
</tr>
</tbody>
</table>

[$\Delta T^a =$ This work (experimental), $\Delta T^b =$ Hammerschmidt Correlation, $\Delta T^c =$ Freezing point depression of solvent correlation, and $\Delta T^d =$ Naibji et al. Correlation]

The effect of PEG of different concentrations on methane hydrate formation temperature and pressure is shown in Figure 7.3 and the thermodynamic parameters of hydrate formation are reported in Table 7.3.
Fig.7.3: Temperature and pressure profile during hydrate formation in presence of PEG

It is observed that the hydrate formation temperature is not affected much on increasing the concentration of PEG from 10% to 20% as it was found in case of EG while on increasing the concentration of PEG further, a shift in hydrate formation temperature is seen. The pressure drop ($\Delta P$) increases as the concentration of PEG is increased from 10% to 20% while further increase in concentration of PEG causes reduction in pressure drop (Table 7.3).

Table 7.3: Formation, dissociation parameters of hydrate in presence of PEG

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Formation Pressure (MPa)</th>
<th>Formation Temp. (K)</th>
<th>Dissociation Temp. (K)</th>
<th>Subcooling (K)</th>
<th>$\Delta P$/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>11.19</td>
<td>285.78</td>
<td>286.01</td>
<td>2.87</td>
<td>2.01</td>
</tr>
<tr>
<td>10wt%PEG</td>
<td>10.66</td>
<td>281.15</td>
<td>283.91</td>
<td>10.50</td>
<td>2.59</td>
</tr>
<tr>
<td>20wt%PEG</td>
<td>10.68</td>
<td>280.25</td>
<td>282.8</td>
<td>10.61</td>
<td>2.92</td>
</tr>
<tr>
<td>30wt%PEG</td>
<td>10.28</td>
<td>276.43</td>
<td>282.0</td>
<td>11.22</td>
<td>2.87</td>
</tr>
</tbody>
</table>

The inhibition effect of PEG on methane hydrate formation is measured experimentally by measuring the depression in freezing point of hydrate at different concentration of PEG and compared with calculated values of hydrate depression temperature using different correlations (Table 7.4). It is found that there is large difference in
experimental and calculated values. This deviation may be arising due to the fact that all the correlations used in the calculation are based on the amount of chemicals regardless of their chemical behavior in hydrate formation.

**Table 7.4: Depression in hydrate formation temperature in presence of PEG**

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>$\Delta T^a$/K</th>
<th>$\Delta T^b$/K</th>
<th>$\Delta T^c$/K</th>
<th>$\Delta T^d$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt%PEG</td>
<td>4.63</td>
<td>0.34</td>
<td>0.49</td>
<td>0.33</td>
</tr>
<tr>
<td>20wt%PEG</td>
<td>5.53</td>
<td>0.77</td>
<td>1.11</td>
<td>0.76</td>
</tr>
<tr>
<td>30wt%PEG</td>
<td>9.45</td>
<td>1.32</td>
<td>1.90</td>
<td>1.29</td>
</tr>
</tbody>
</table>

$[\Delta T^a = \text{This work (experimental)}, \Delta T^b = \text{Hammerschmidit Correlation}, \Delta T^c = \text{Freezing point depression of solvent correlation}, \text{and } \Delta T^d = \text{Naibji et al. Correlation}]$

The inhibition of hydrate in presence of PEG is less effective than that of hydrate formation in presence of EG. EG causes more depression in freezing point temperature of hydrate than PEG of the same concentration.

To investigate the inhibition effect of glycerol on methane hydrate formation, experiment was also carried out. The effect of different concentrations of glycerol on the temperature and pressure conditions of hydrate formation is shown in Figure 7.4. It can be seen (Fig. 7.4) that as the concentration of glycerol increases the formation temperature is shifted to lower values and the hydrate formation pressure is also found to be decreased since it depends on the hydrate formation temperature.
Fig. 7.4: Temperature - pressure profile during hydrate formation in presence of glycerol

All the thermodynamic parameters of methane hydrate formation in presence of different concentrations of glycerol are presented in Table 7.5. The dissociation temperature of hydrate is found to decrease with increase in concentration of glycerol. It can be seen that hydrate start to dissociate at lower temperature in high concentration of glycerol in aqueous medium than hydrate dissociation in lower concentrations of glycerol. It can be also noted that high subcooling is required to form hydrate in presence of glycerol than the hydrate formation in absence of glycerol. These results suggest that hydrate formation is strongly inhibited in presence of glycerol. It is more pronounced when the concentration of glycerol is high (Table 7.5).
Table 7.5: Formation, dissociation parameters of hydrate in presence of Glycerol

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Formation Pressure (MPa)</th>
<th>Formation Temp.(K)</th>
<th>Dissociation Temp. (K)</th>
<th>Subcooling (K)</th>
<th>ΔP/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>11.19</td>
<td>285.78</td>
<td>286.01</td>
<td>2.87</td>
<td>2.01</td>
</tr>
<tr>
<td>10wt% Glycerol</td>
<td>10.55</td>
<td>278.64</td>
<td>282.56</td>
<td>11.75</td>
<td>2.87</td>
</tr>
<tr>
<td>20wt% Glycerol</td>
<td>10.46</td>
<td>276.66</td>
<td>280.79</td>
<td>11.79</td>
<td>2.81</td>
</tr>
<tr>
<td>30wt% Glycerol</td>
<td>9.94</td>
<td>272.21</td>
<td>278.58</td>
<td>11.94</td>
<td>2.35</td>
</tr>
</tbody>
</table>

The amount of gas trapped during hydrate formation in presence of glycerol is more compared to hydrate formation in absence of glycerol. It is found to decrease with increase in concentration of glycerol (Table 7.5).

Inhibition ability of glycerol in hydrate formation is stated in terms of depression in hydrate formation temperature. The experimental depression in temperature of hydrate and calculated depression in temperature are presented in Table 7.6. The hydrate depression temperature seems to be a function of glycerol concentration. As the concentration of Glycerol is increased the hydrate depression temperature also increased in the same way. Glycerol is more effective in depressing the hydrate formation temperature when the concentration is 30%. Calculated values of hydrate depression temperature using different correlations exhibit the same trend but these value are relatively lower than experimental values.

Table 7.6: Depression in hydrate formation temperature in presence of Glycerol

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>ΔTa/K</th>
<th>ΔTb/K</th>
<th>ΔTc/K</th>
<th>ΔTd/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt% Glycerol</td>
<td>7.14</td>
<td>1.55</td>
<td>2.22</td>
<td>1.52</td>
</tr>
<tr>
<td>20wt% Glycerol</td>
<td>9.51</td>
<td>3.48</td>
<td>5.0</td>
<td>3.42</td>
</tr>
<tr>
<td>30wt% Glycerol</td>
<td>13.57</td>
<td>5.97</td>
<td>8.59</td>
<td>5.86</td>
</tr>
</tbody>
</table>

[ΔTa = This work (experimental), ΔTb = Hammerschmidt Correlation, ΔTc = Freezing point depression of solvent correlation, and ΔTd = Naibji et al. Correlation]
There is a large difference between experimental and calculated values of hydrate depression temperatures obtained by Hammerschmidt Correlation and Naibji et al. correlations while this difference is small for freezing point depression of solvent correlation (Table 7.6).

### 7.4.2 Methane hydrate dissociation in presence of EG, PEG and Glycerol

The phase equilibrium of methane hydrate in presence of EG is shown in Figure 7.5. It is clear that phase equilibrium curve of methane hydrate moves to low temperature regions for a given pressure with change in concentration of EG low to high.

![Fig. 7.5: Phase equilibrium of methane hydrate in presence of ethylene glycol (EG)](image)

When the concentration of EG is increased from 10% to 20% the phase equilibrium of methane hydrate is shifted to low temperature region nearly by 3.0K for a given pressure. The phase equilibrium is found to move further to lower temperature region by 5K as the concentration of EG is increased to 30%.

The phase behavior of methane hydrate in presence of PEG is shown in Figure 7.6. PEG affected the phase equilibrium of methane hydrate in a different way as it was observed in presence of EG. PEG causes shift of both phase equilibrium temperature and pressure while EG influenced only the phase equilibrium temperature. Also it is noted that the extent of phase equilibrium curve shift caused by PEG is less than that caused by EG. As the
concentration of PEG is increased from 10% to 20% the phase equilibrium temperature is shifted by 1K and pressure is shifted by 0.65MPa while further increase in concentration of PEG to 30% lead to shift in the phase equilibrium temperature by 0.5K only and pressure by 0.31MPa (Fig. 7.6).

![Graph showing phase equilibrium of methane hydrate in presence of polyethylene glycol (PEG)](image)

**Fig. 7.6: Phase equilibrium of methane hydrate in presence of polyethylene glycol (PEG)**

The phase equilibrium of methane hydrate in presence of glycerol is presented in Figure 7.7. Equilibrium curve is influenced by variation in concentration of glycol. It is seen that glycol affects only the phase equilibrium temperature. It is shifted to lower temperature regions gradually when the concentration of glycol is increased from 10% to 30%. The movement of curve is not found to be symmetric. In high pressure zone the shift of phase equilibrium temperature is more than that in low pressure zone. At a given pressure (10.85MPa) in high pressure region the equilibrium temperature is shifted nearly by 3K towards low temperature zone while for a given pressure (7.65MPa) in low pressure zone it is shifted by 2.23K.
Fig. 7.7: Phase equilibrium of methane hydrate in presence glycerol

Figure 7.8 illustrates the inhibition ability of EG and PEG on phase equilibrium of methane hydrate. It can be seen that EG is more effective than PEG to shift the phase equilibrium of methane hydrate. EG is so effective that its 10% concentration is sufficient to inhibit methane hydrate formation which is not achieved even by 30% PEG.

Fig. 7.8: Phase equilibrium of methane hydrate in presence EG and PEG
The inhibition ability of glycerol is compared with EG on methane hydrate in Figure 7.9. It can be seen that in this case also EG is more effective than glycerol to inhibit methane hydrate. Even 30% glycerol could not inhibit the methane hydrate formation that is achieved by 10% of EG. These results indicate that EG is far more effective for inhibiting the methane hydrate than PEG and glycerol.

![Fig. 7.9: Phase equilibrium of methane hydrate in presence EG and Glycerol](image)

It is also worthwhile to compare the effectiveness of glycerol and PEG to inhibit hydrate. Figure 7.10 illustrates the inhibition ability of glycerol and PEG on methane hydrate. It can be seen that glycerol is more effective to inhibit hydrate formation than PEG (Fig. 7.10).
Fig. 7.10: Phase equilibrium of methane hydrate in presence Glycerol and PEG

The above results obtained during methane hydrate formation and dissociation in presence of inhibitors (EG, PEG and Glycerol) led us to surmise that their interaction with water seems to play a very crucial role in methane hydrate formation and dissociation. When these chemicals are added to water, they interact with water molecules and decrease the chemical potential of water which causes the phase equilibrium P-T curve to shift to inhibition zone. The P-T curves shifted further into the inhibition region when the concentrations of these chemicals are increased.

Among the compounds studied, EG, PEG and Glycerol, EG is found to be the most effective to inhibit methane hydrate formation. The inhibition power of EG is due to the affinity of the EG oxygen atoms for neighboring water molecules. Each oxygen atom has two lone-pair electrons [Bernal and Fowler, 1933], which provides two negative charges. These negative charges attract the positive charge (on the hydrogen) of a neighboring water molecule to form a strong hydrogen bond between the EG and the water molecules. This strong, attractive hydrogen bond between the negative inhibitor oxygen and the positive water hydrogen is also the same force that attracts the oxygen of one water molecule to the hydrogen of another water molecule, in order to form the hydrate cages. The inhibitor hydrogen bond with water may be considered a competitor for the hydrogen bond of water for
itself in hydrates, making it difficult to convert all water to hydrates, relative to the case in which inhibitor is not present.

Thus the physical properties of these inhibitors are thought to affect the inhibition of hydrate-phase equilibrium. The hydroxyl group in PEG and glycerol can also form hydrogen bond with water molecules and prevent water molecules to form hydrogen-bonded cage to capture gaseous guest molecules. But the inhibition of hydrate by EG, PEG and glycerol are not same. EG is found to be the most effective to inhibit hydrate among the tested inhibitors (EG, PEG and Glycerol). Also it is noted that glycerol is more effective than PEG to inhibit hydrate formation. These results indicate that the structure of these compounds might be playing a very important role during formation of hydrate. The structure of EG, PEG and Glycerol is shown in Figure 7.11. It can be seen in Figure (7.11) that the size of EG is smallest while PEG is the largest in size. It may be speculated that the extent to form hydrogen bond with water molecule depend on the size of these chemicals. The hydrogen bonding of inhibitor with water may be hindered with increase in size of inhibitor. Therefore water molecule may not be restricted to by inhibitor of larger size to form hydrate cage. This is a matter for further investigation.

Also it is noticed that the gas consumption is found to increase with increase in size of inhibitor (Table 7.1, 7.2 and 7.5). It suggests that inhibitor with large hydrocarbon may help to form hydrate cage easily for encapsulation of gas.

![Ethylene Glycol](image)

(a) Ethylene Glycol

![Polyethylene Glycol-400 (PEG-400)](image)

(b) Polyethylene Glycol-400 (PEG-400)

![Glycerol](image)

(C) Glycerol

Fig. 7.11: Structure of (a) ethylene glycol, (b) polyethylene glycol, and (c) glycerol
7.4. 3 Induction time of methane hydrate formation in presence of EG, PEG and Glycerol

The response of temperature and pressure during measurement of induction time of hydrate formation in presence of EG is shown in Figures 7.12 and 7.13. It can be noticed that the pressure of the system decreases linearly with decrease in temperature. After some time there is no change in pressure for a short duration even when cooling is continued. The pressure of the system is found to decrease again suddenly but at constant temperature indicates the formation of hydrate.

![Diagram showing induction time and subcooling](image)

**Fig. 7.12: Response of temperature and pressure during measurement of induction time in presence of 10% EG**

**Table 7.7: Hydrate onset temperature, equilibrium temperature, subcooling and induction time in presence of EG**

<table>
<thead>
<tr>
<th>Test Sample (%)</th>
<th>Hydrate Onset Temperature ($T_o$/K)</th>
<th>Equilibrium Temperature ($T_{eq/diss}$/K)</th>
<th>Subcooling (K)</th>
<th>Induction Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt % EG</td>
<td>280.95</td>
<td>287.85</td>
<td>6.9</td>
<td>82</td>
</tr>
<tr>
<td>20 wt % EG</td>
<td>278.25</td>
<td>284.75</td>
<td>6.5</td>
<td>51</td>
</tr>
<tr>
<td>30 wt % EG</td>
<td>272.35</td>
<td>278.95</td>
<td>6.6</td>
<td>72</td>
</tr>
</tbody>
</table>
Fig. 7.13: Response of temperature and pressure during measurement of induction time in presence of 20% EG

Figure 7.14 shows the variation of temperature and pressure during the measurement of induction time of methane hydrate formation in presence of 10% PEG. It is noticed that hydrate formation occurs very rapidly as soon as it gets the favorable conditions of temperature and pressure. It is delayed only by 30 minutes.

Fig. 7.14: Response of temperature and pressure during measurement of induction time in presence of 10% PEG
Induction time is measured in different concentrations of PEG. It is found that there is not much difference of induction time of hydrate formation on variation in concentration of PEG from low to high (Table 7.8).

**Table 7.8: Hydrate onset temperature, equilibrium temperature, subcooling and induction time in presence of PEG**

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Hydrate Onset Temperature ($T_o/\text{K}$)</th>
<th>Equilibrium Temperature ($T_{eq/diss}/\text{K}$)</th>
<th>Subcooling (K) $\Delta T=T_o-T_{eq/diss}$</th>
<th>Induction Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt% PEG</td>
<td>281.45</td>
<td>289.95</td>
<td>8.5</td>
<td>30</td>
</tr>
<tr>
<td>20wt% PEG</td>
<td>280.55</td>
<td>288.65</td>
<td>8.1</td>
<td>35</td>
</tr>
<tr>
<td>30wt% PEG</td>
<td>276.65</td>
<td>285.15</td>
<td>8.4</td>
<td>32</td>
</tr>
</tbody>
</table>

Figure 8.15 shows the variation of temperature and pressure during measurement of induction time in presence of 10% glycerol. The pressure of the system decreases with decrease in temperature and thereafter it becomes almost constant. At constant temperature, sharp drop in pressure indicates hydrate formation. In this particular case hydrate formation is delayed by two hours (Table 7.9).

**Fig. 7.15: The response of temperature and pressure during measurement of induction time in presence of 10% glycerol**
Induction time of hydrate formation observed with further increase in concentration of glycerol. The obtained results are given in Table 7.9. It is found that there is no significant change on induction time with increase in concentration of glycerol.

<table>
<thead>
<tr>
<th>Test Sample</th>
<th>Hydrate Onset Temperature ($T_o$/K)</th>
<th>Equilibrium Temperature ($T_{eq/diss}$/K)</th>
<th>Subcooling (K) $\Delta T = T_o - T_{eq/diss}$</th>
<th>Induction Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt% Glycerol</td>
<td>277.15</td>
<td>288.95</td>
<td>11.80</td>
<td>123</td>
</tr>
<tr>
<td>20wt% Glycerol</td>
<td>276.56</td>
<td>288.35</td>
<td>11.79</td>
<td>128</td>
</tr>
<tr>
<td>30wt% Glycerol</td>
<td>272.15</td>
<td>284.15</td>
<td>11.94</td>
<td>125</td>
</tr>
</tbody>
</table>

It is noted that EG, PEG and glycerol delayed the hydrate formation but have different induction time measured in the same concentration of these chemicals. Glycerol is found to be the most effective to delay the hydrate formation than EG followed by PEG.

### 7.5 CONCLUSIONS

The formation and dissociation condition of methane hydrate has been discussed in the present chapter. Three different chemicals (Ethylene glycol, Polyethylene glycol and Glycerol) have been used to investigate the inhibition effect on methane hydrate formation. It is also examined with different concentrations of the inhibitors. The following conclusions may be drawn based on experimental results and observations:

- The formation of methane hydrate is inhibited thermodynamically in presence of all the chemicals used as inhibitor. Ethylene glycol (EG) is found to be the most effective to inhibit methane hydrate formation while polyethylene ethylene glycol has least impact.
- Measured induction time of hydrate formation reveals that hydrate could not be inhibited kinetically in the presence of these inhibitors since once water and methane gas gets the favorable temperature and pressure conditions, hydrate forms within a few minutes. Glycerol is found to be one of the most effective among all the inhibitors used in delaying the nucleation of hydrate.
- The gas consumption is found to increase with increase in size (chain length) of the inhibitor. It suggests that longer hydrocarbon chain length of inhibitors may help to form hydrate cage that is very crucial for encapsulation of gas inside the cage.