# INFLUENCE OF FORMATION TEMPERATURE AND INHIBITOR CONCENTRATION ON THE DISSOCIATION TEMPERATURE FOR HYDRATES FORMED WITH POLY VINYL CAPROLACTAM

Ann Cecilie Gulbrandsen \* StatoilHydro, Stavanger, NORWAY

# Thor Martin Svartaas Department of Petroleum Engineering, University of Stavanger, NORWAY

### ABSTRACT

Inhibitor containing systems were investigated for hydrate structures I and II. The kinetic inhibitor PVCap was added to the water phase for each hydrate structure. Dissociation temperatures were determined for various formation temperatures and PVCap concentrations. Obtained dissociation temperatures were compared with corresponding values calculated with CSMHYD. Differences between experimental and calculated values were compared for various formation temperatures and inhibitor concentrations. Comparison revealed that these parameters (formation temperature and concentration) had an effect on the dissociation temperature. Dissociation temperatures for hydrates formed at low degrees of subcooling were higher than for hydrates formed at large subcooling. The effect depended on the system pressure; apparently decreasing or vanishing with increasing pressure. Furthermore, the temperature of dissociation increased with the inhibitor dose.

Keywords: gas hydrates, formation temperature, dissociation, kinetic inhibitors, PVCap

### NOMENCLATURE

$\delta T/\delta t$ : Heating rate	[°C/h]
M <sub>w</sub> : Average molecular weight	[Dalton]
$\Delta T$ : Displacement of dissociation temp.	[°C]
T <sub>exp</sub> : measured equilibrium temp.	[°C]
T <sub>CSMHYD</sub> : predicted equilibrium temp.	[°C]

### **INTRODUCTION**

Hydrates consist of molecules from the gas or condensate phase trapped inside a three dimensional framework formed by hydrogen bonded water molecules. This framework constitutes cages, which are stabilized due to the inclusion of guest molecules. They form different structures known as structure I (sI), structure II (sII) and structure H (sH). Structure I and II are cubic structures while sH is a hexagonal structure. The guest molecules may be hydrocarbon molecules, hydrogen sulfide molecules or carbondioxide molecules. A typical natural gas mixture containing components of C1-C4, will typically form structure II hydrates.

Hydrate plugs can form in wells, pipelines as well as processing equipment. This is especially a relevant scenario for shut-in situations since the fluids then have time to cool well into the hydrate region. Low dosage hydrate inhibitors (LDHI) offer a hydrate control technology that can be more cost-effective than traditional methods where thermodynamic inhibitors are applied. Kinetic inhibitors are a class of LDHI and they have already been used in the field for some time. The kinetic inhibitors delay hydrate nucleation and crystal growth providing sufficient time for the transportation of fluids to the process facilities, before any hydrate build-up can occur. The method is already being used in full field applications and have given operators significant savings over alternative hydrate control methods.

# DESCRIPTION

The experimental setup is described in full detail elsewhere [1]. Several mixtures of distilled water and the kinetic inhibitor PVCap were prepared. Different polymerlengths of the kinetic inhibitor PVCap were used; 2.5 k, 6 k and 10 k. Every solution loaded into a cell and flushed and pressurized with a hydrocarbon gas. Pure methane was used as hydrate former for sI hydrates, and a mixture of methane (93%) and propane (7%) was used for the production of sII hydrate. The systems were pressurized and thereafter cooled down, well into the hydrate region. Hydrate formation was not left to happen spontaneously, but was induced by magnetic stirring in the cell. Formation was induced at different temperatures for each of the The cooling/heating systems. unit was programmed to increase the temperature until dissociation took place. As this process took place the hydrate was decomposed into water and free gas as a result of changes in the pressure and temperature conditions. This was done in a similar manner for all the samples, using a low melting gradient to achieve equilibrium conditions in the system. Each of the investigated hydrate structures were examined for several pressures, ranging from 30 bar 90 bar.

Data regarding phase equilibrium were in our experiments obtained using the isochoric temperature cycle method. There are several methods for non-visual hydrate point determination and they are essentially similar, namely the isobaric, isochoric and isothermal method. In the isobaric method, hydrate formation and decomposition are detected by a change in volume, whereas in the isochoric method the volume is constant and a temperature versus pressure plot indicates hydrate formation and decomposition. Hydrate equilibrium temperatures determined by the isochoric method have been found to be lower than the corresponding results obtained with the isobaric method. The differences were however small, approximately 0.1-0.2°C [2].

The dissociation temperature and pressure was determined for the different formation temperatures at each of the applied pressure values. The dissociation temperatures were compared with corresponding values calculated with CSMHYD. The difference ( $\Delta T=Texp-TCSMHYD$ ) between the experimental value and the calculated value was compared for the various formation temperatures.



**Figure1.**Two different procedures for determining the hydrate dissociation point.

Regarding the location of the hydrate dissociation point, there is room for interpretation. Figure1 shows an example of measured data. The location of point (T1,P1) corresponds to an extrapolation method. The location of (T2,P2) corresponds to the point where the pressure versus temperature plot regains the initial slope. The first method compensates to some extent for lack of thermal equilibrium, which is the case when fast melting rates are applied. Whether the latter method can generate reliable data, depends on the melting rate and the mixing efficiency in the cell. In cells which use stirring bars, there is a possibility of encountering a deficient mixing. The hydrates can get isolated and become more stable. This will reduce the mass transfer rate. Hydrate dissociation involves both heat diffusion and mass transfer, and deficient mixing will significantly increase the time required to achieve equilibrium [3]. A slow melting rate and efficient mixing are factors that are decisive for obtaining a high degree of equilibrium. In such a situation the two points in Figure 1 will overlap.

# **RESULTS** Influence of hydrate formation temperature Hydrate Structure I



**Figure 2.** Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of hydrate formation temperature. The solution in the experiment contained 750 ppm PVCap, and the cell was pressurized to 90 bar at 15°C.



**Figure 3.** Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of hydrate formation temperature. The solution in the experiment contained 3000 ppm PVCap, and the cell was pressurized to 90 bar at 20°C.



**Figure 4.** Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of hydrate formation temperature. The solution in the experiment contained 6000 ppm PVCap, and the cell was pressurized to 90 bar at 15°C.

#### **Hydrate Structure II**



**Figure 5**. Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of hydrate formation temperature. The solution in the experiment contained 1500 ppm PVCap6k. Various pressures were applied; 45, 60 and 90 bar.

### Influence of PVCap concentration Structure II hydrate



**Figure 6.** Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of the melting rate. Various PVCap6k doses have been examined; 750 ppm, 1500 ppm and 3000 ppm. The cell was pressurized to 45 bar at 20 °C.



**Figure 7**. Difference between experimentally obtained dissociation temperature and corresponding CSMHYD calculated value is here plotted as a function of the melting rate. Various PVCap6k doses have been examined; 1500 ppm, 3000 ppm and 6000 ppm. The cell was pressurized to 90 bar at 20°C.

### DISCUSSION

Results reveal that the hydrate formation influences the temperature temperature of dissociation. Figures 2-4 and Figure 5 display the results for SI and SII hydrates, respectively. The experimental data reveal that high formation temperatures (low degrees of sub-cooling) result in a larger  $\Delta T$  than formation at low temperatures (high sub-cooling). Experimental data show that the sub-cooling is a parameter decisive for the magnitude of the discrepancy ( $\Delta T$ =TCSMHYD the measured Texp.) between dissociation temperature and the corresponding CSMHYD calculated value. The trend is present for both hydrate structures, namely SI and SII. For SI the differences in  $\Delta T$  seems to be less pronounced at high degrees of subcooling, while the variations have much larger magnitude at intermediate and low sub-coolings. Data for SII show that variations in  $\Delta T$  values corresponding to low and high subcooling are of smaller magnitude, even though each  $\Delta T$  value in absolute has a higher value than for SI. Furthermore, it seems that for SII the impact of pressure is important. The effect of the temperature of formation on the temperature of dissociation seems to vanish as the pressure increases. Results indicate that the degree of subcooling can be influential for the extent to which the inhibitor molecule bonds to the hydrate.

Different PVCap concentrations were compared at two different melting rates. Small inhibitor concentrations (1500 ppm) resulted in lower dissociation temperatures than intermediate (3000 ppm) and high (6000 ppm) concentrations. However, the solutions containing 3000 ppm and 6000 ppm resulted in the exact same dissociation temperatures. Results indicate the existence of a threshold concentration level of the inhibitor, above which the hydrate stabilizing effect of the PVCap was not further influenced. Previous studies where the influence of VC713 concentrations on the temperature of dissociation have been performed on THI hydrates [4]. Concentrations of 5000 ppm resulted in higher dissociation temperatures than and 250 ppm. Increasing the inhibitor concentration to 10000 ppm did not elevate the temperature of dissociation any further.

#### CONCLUSION

Results reveal that the hydrate formation temperature influences the temperature of dissociation. The observed trend is that high formation temperatures (low degrees of subcooling) result in higher dissociation values than hydrate formation at low temperatures (high subcooling). The inhibitor concentration seems to influence the temperature of dissociation. Experiments showed that the dissociation temperature increases with the PVCap concentration, but only up to a certain threshold. Increasing the inhibitor concentration above the threshold value seems to have no effect on the hydrate stability.

# **ACKNOWLEDGEMENTS**

BP and StatoilHydro have provided financial support to the hydrate lab at the University of Stavanger.

# REFERENCES

- [1] 'Influence of the melting rate on the temperature of dissociation of hydrates formed with the kinetic inhibitor PVCap'.Gulbrandsen and A.C. Svartås T.M.International Conference on Gas Hydrates, Vancouver 2008.
- [2] 'Gas hydrates that outcrop the seafloor: stability models' Egorov AV, Crane K, Vog, PR & Rozhkov AN. 1999
- [3] 'Improving the Accuracy of Gas Hydrate Dissociation Point Measurements' Tohidi, Burgass, Danesh, Østergaard and Todd, Annals of the New York Academy of Sciences, 2000.
- [4] 'Hydrate dissociation under the influence of low-dosage kinetic inhibitors' Habetinova, E., A. Lund, and R. Larsen. 4th International Conference on Natural Gas Hydrates. Yokohama, Japan 2002.