*Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia, CANADA, July 6-10, 2008.*

# PROPANE GAS HYDRATE NUCLEATION KINETICS: EXPERIMENTAL INVESTIGATION AND CORRELATION

**Lars Jensen***
**Department of Chemical & Biological Engineering**
**Technical University of Denmark**
**Søltoftsplads, Build. 229, 2800 Kgs. Lyngby**
**DENMARK**

**Kaj Thomsen**
**Department of Chemical & Biological Engineering**
**Technical University of Denmark**
**Søltoftsplads, Build. 229, 2800 Kgs. Lyngby**
**DENMARK**

**Nicolas von Solms****
**Department of Chemical & Biological Engineering**
**Technical University of Denmark**
**Søltoftsplads, Build. 229, 2800 Kgs. Lyngby**
**DENMARK**

## ABSTRACT

In this work the nucleation kinetics of propane gas hydrate has been investigated experimentally using a stirred batch reactor. The experiments have been performed isothermally recording the pressure as a function of time. Experiments were conducted at different stirring rates, but in the same supersaturation region. The experiments showed that the gas dissolution rate rather than the induction time of propane hydrate is influenced by a change in the stirring rate. This was especially valid at high stirring rates when the water surface was severely disturbed.

Addition of polyvinylpyrrolidone to the aqueous phase was found to reduce the gas dissolution rate slightly, however the induction times were prolonged quite substantially.

The induction time data were correlated using a newly developed induction time model based on crystallization theory also capable of taking into account the presence of additives. In most cases reasonable agreement between the data and the model could be obtained. The results revealed that especially the effective surface energy between propane hydrate and water is likely to change when the stirring rate varies from very high to low. The prolongation of induction times according to the model is likely to be due to a change in the nuclei-substrate contact angle.

*Keywords*: gas hydrates, interfacial energy, kinetic inhibitors, nucleation

## NOMENCLATURE

| | | | |
|---|---|---|---|
| c | Shape factor | k | Boltzmans constant [J/K] |
| $C_a$ | Additivconcentration [$m^{-3}$] | K | Kinetic conctant [s] |
| *f* | Fugacity [Pa] | $k_g$ | Adsorption constant [$m^3$] |
| H | Henrys constant [KPa] | $k_n$ | Adsorption constant [$m^3$] |

* Presenting author: Phone: +45 4525 2858 Fax +45 4588 2258 E-mail: lje@kt.dtu.dk
** Corresponding author: Phone: +45 4525 2868 Fax +45 4588 2258 E-mail: nvs@kt.dtu.dk

| | |
|---|---|
| $k^{l}_{L\text{-}V}a_{L\text{-}V}$ | Gas dissolution rate [$s^{-1}$] |
| m | Growth number |
| $n_w$ | Number of water molecules |
| P | Pressure [Pa] |
| S | Supersaturation ratio |
| t | time [s] |
| T | Temperature [K] |
| $v_h$ | Hydrate building unit volume [$m^3$] |
| $v_{hw}$ | Volume of water in hydrate [$m^3$] |
| $x_i$ | Gas solubility, mole fraction |
| $\Delta v_e$ | Volume difference [$m^3$] |
| $\Delta\mu$ | Supersaturation [J] |
| $\sigma$ | Interfacial energy [$mJ/m^2$] |

## INTRODUCTION

Gas hydrates are crystalline compounds formed when water and suitably sized gas molecules are combined at high pressure and low temperature. They consist of polyhedral cavities formed from networks of hydrogen-bonded water molecules in which small gas molecules can enter. Depending on the type of gas molecules present gas hydrates form different structures, known as structure I (sI), structure II (sII) and in special cases structure H (sH) [1].

The gases that form hydrates are normally small molecules, many of which are encountered in natural gas. Examples are methane, ethane, propane, iso-butane, butane, carbon dioxide, nitrogen and hydrogen sulphide [1]. Gas hydrate formation is a problem that the oil and gas industry is most concerned with. Oil- and gas transmission lines, tie-backs and off-shore process equipment are prone to being blocked by hydrates, causing potential hazards or economic loss.

Traditionally the formation of gas hydrates has been prevented by addition of thermodynamic inhibitors such as methanol and glycol. However the amounts needed to avoid hydrate formation may reach 50wt% in the water rich phase [2]. Since water production from fields can be quite severe, especially in cases where water injection has been used to enhance the oil recovery, large amounts of inhibitor are required. For these reasons a particular interest in hydrate formation kinetics has arisen. If the hydrate kinetics are known, and can be controlled, it may then be possible to operate the transmission lines at hydrate formation conditions, while still ensuring that hydrates will not grow sufficiently to cause flow blockage. If the kinetics of gas hydrate formation is very fast, it is possible to slow their formation by the addition of low dosage hydrate inhibitors (LDHI). These are most often water soluble polymers and are effective at concentrations 10-100 times less than conventional thermodynamic inhibitors [3].

From a thermodynamic point of view there is a good understanding of gas hydrate formation conditions and several methods for accurate prediction of these exist [4], [5], [6]. The kinetics of hydrate formation is less well understood, although it is clear that they are a very important property of gas hydrates. Hydrate formation is usually divided into two periods. The first period, the nucleation or induction period, deals with formation of small hydrate nuclei. When these small nuclei have grown to a critical size a second period, the growth period, commences.

Gas hydrate nucleation and growth has been investigated experimentally using different approaches and analytical expressions have been derived to describe the obtained data [7], [8], [9], [10], [11]. It is the general conception that the nucleation process of gas hydrates has a stochastic nature [9] and that induction periods are quite hard to reproduce. One reason for this is that the presence of even very small impurities in the hydrate forming system can have drastic influence on the induction time. This indicates that the nucleation mechanism of hydrates is primarily heterogeneous [12]. However identification of the important factors affecting the nucleation process of gas hydrates is vital in order to gain understanding of the area.

In this work we investigate the effect that the driving force in terms of supersaturation, has on nucleation of sII propane hydrate. The supersaturation is here represented as the difference in the chemical potentials of a hydrate building unit in solution and in the hydrate crystal [13].

We begin by investigating the effect that the magnitude of the driving force has on the induction period of propane hydrate in pure water. The influence of the stirring rate was subsequently investigated. Finally investigation on how the nucleation period is influenced when a kinetic inhibitor, polyvinylpyrrolidone (PVP), is added to the aqueous phase was performed.

The nucleation data will be used to investigate which physical properties of propane hydrate are likely to be influenced when the formation conditions are changed. This is done by using an

induction time model, based on crystallization theory [8].

## THEORY OF HYDRATE NUCLEATION

Nucleation of hydrates is a microscopic stochastic phenomenon where gas-water clusters (nuclei) grow and disperse until the nuclei have grown to a critical size [9]. Primarily hydrate nucleation takes place at the vapor-liquid (V-$L_w$) interface [1], thus the theories dealing with describing this phenomenon have focused on this surface. Two theories dealing with describing the nucleation mechanism have gained acceptance in literature although they are hypothetical. One of these is the cluster nucleation theory which proposes that water molecules form labile clusters around dissolved gas molecules. These clusters combine due to hydrophobic bonding between the apolar molecules inside the clusters, to form hydrate unit cells [1]. The other theory assumes that nucleation is taking place on the vapor side at the V-$L_w$ interface. First gas molecules are transported to the interface and absorbed to the aqueous surface. At suitable adsorption sites water molecules will form first partial and then complete cages around the adsorbed gas molecules. Clusters will join and grow on the vapor side until the critical size is reached [1].

The time taken from when supersaturation is obtained to the appearance of a hydrate crystal is referred to as the induction period. The induction period is considered to be made up by several parts. Time is required for the system to relax to achieve a quasi steady-state distribution of molecular clusters, $t_r$, the formation of stable clusters, $t_n$, and the growth of these to a detectable size, $t_g$. Based on these considerations, the induction time can be expressed as (Mullin, 2004):

$$t_{Ind} = t_r + t_n + t_g \qquad (1)$$

It is not possible to distinguish these separate quantities from each other during the induction period.

From observing the pressure-time relationship for a hydrate-forming system the induction time can be identified. In figure 1 such a relationship is presented.

The initial pressure drop from $P_0$ to $P_{sol}$ is due to absorption of gas in the aqueous phase. After equilibrium is reached the pressure stabilizes until

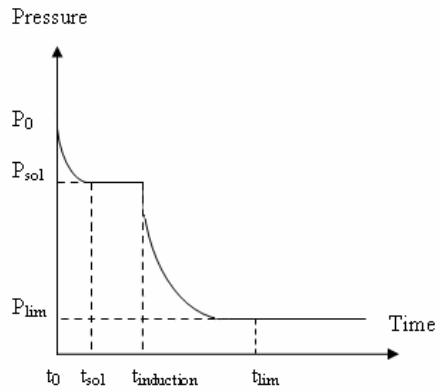


**Figure 1.** Illustration of a typical pressure recording for a hydrate forming system. Important parameters which can be deduced from the recording are indicated with dashed lines. The initial pressure drop is due to gas dissolution followed by an isobaric period where nucleation takes place. The sudden pressure drop during the nucleation period is caused by hydrate formation.

t equals $t_{induction}$ where a sudden pressure drop appears as hydrate starts to form. The pressure keeps decreasing as gas is consumed during the hydrate formation process until it reaches $P_{lim}$ where no more hydrate forms. The induction time should be corrected for the initial time taken for gas to dissolve. The induction time is then found as:

$$t^*_{Ind} = t_{Ind} - t_{Sol} \qquad (2)$$

The curve presented here is slightly idealized and deviation from the shape can appear if $t_{induc}<t_{sol}$ or if the gas solubility in water is sufficiently low.

Heterogeneous nucleation plays an important role in the formation of ice [14] and has been shown also to be thermodynamically favored over homogeneous nucleation of gas hydrates [15]. This causes the induction time to be very sensitive to any heterogeneities in solution i.e. impurities can possibly cause significant deviation among measured induction times.

### Single component driving force

A number of different approaches for calculating the driving force of hydrate nucleation have been described in the literature and summarized by Sloan [1]. We use the definition that the driving force is equal to the difference between the chemical potentials of the old and the new phases upon hydrate formation from an aqueous solution. The expression for the driving force for nucleation of simple hydrates has been described on the basis

of the following phase reaction occurring in the aqueous solution [13]:

$$G + n_w H_2O \Leftrightarrow G \cdot n_w H_2O \qquad (3)$$

Where $n_w$ is the number of water molecules in a hydrate building unit. The resulting expression for the driving force in terms of supersaturation is given below. The derivation of this expression can be found in [13]:

$$\Delta\mu = kT \ln\left(\frac{f(P,T)}{f(P_e,T)}\right) + \Delta v_e (P - P_e) \qquad (4)$$

Where $k$ is Boltzmann's constant, $f$ is the fugacity of the gas in the gas phase and $\Delta v_e$ is the volume difference between a water molecule in solution and a hydrate building unit in the hydrate lattice. For propane hydrate the volume difference has been reported to $-1.370 \cdot 10^{-28}$ $m^3$ [13]. The fugacities of the gas have been calculated using the SRK equation of state. The three-phase equilibrium pressure has been calculated using the program HYDOFF [16]

## EXPERIMENTAL SECTION

The kinetic measurements were performed in a stainless steel hydrate equilibrium cell with a fixed volume of 66.5 $cm^3$ and a maximum working pressure of 150 bar. The cell allows for visual observation of hydrate formation through two sapphire windows. The cell is attached with a gas reservoir and a vacuum pump. The temperature in the cell was controlled by circulating coolant (water-ethanol solution), in a jacket surrounding the cell. The temperature was monitored by using a platinum resistance probe (±0.01 K) placed inside the cell. The pressure of the cell was monitored by a single pressure transducer (BD Sensors, 0-40 bar). The cell was placed on a stir plate which allowed a stirring bar (L = 4 cm) to rotate within the cell. The pressure and temperature in the cell was recorded continuously on a computer. A schematic layout of the experimental equipment used to investigate gas hydrate nucleation is shown in figure 2.

For each experiment the cell was cleaned with distilled water and loaded with distilled water or distilled water containing PVP. A stirring bar was placed in the cell. The cell lid was screwed on and

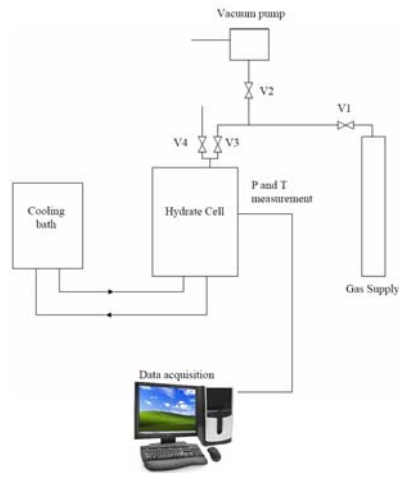


**Figure 2.** Layout of experimental equipment used in the study of gas hydrate nucleation. The hydrate cell is attached to a gas supply unit and a vacuum pump. The temperature is controlled by a cooling bath. Data is collected continuously on a computer.

the cell evacuated using a vacuum pump for approximately 1 hour. The temperature bath was adjusted so the temperature in the cell was 273.75 K. When the temperature in the cell was constant the propane gas was injected through the inlet until the desired pressure at the chosen temperature was obtained. Three experimental series using distilled water were performed. For each series the stirring rate was altered in the range 200-500 rpm in order to investigate the effect of the stirring rate on the nucleation kinetics.

For nucleation experiments involving PVP as a kinetic inhibitor two experimental series at PVP concentrations of 0.05 wt% and 0.025 wt% were performed both at a stirring rate of 500 rpm. In all the experiments the pressure and temperature was recorded in a time interval of 5 s. The data obtained in an experimental run can typically be represented from the pressure-time relationship provided in figure 3.

## RESULTS AND DISCUSSION

Both the induction time and the dissolution rate of the gas have been determined for each experiment. The dissolution rate, $k^l_{L\text{-}V} a_{L\text{-}V}$, at the V-$L_w$ interface has been determined from the two film theory neglecting the resistance on the gas side of the V-$L_w$ interface using the expression:

$$\left(\frac{dx}{dt}\right) = k^l_{L-V} a_{L-V} (x^i_{L-V} - x) \qquad (5)$$

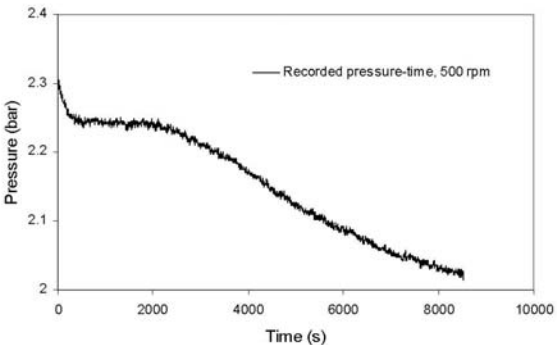


**Figure 3.** Typical pressure-time recording for the propane hydrate forming system. The initial pressure drop is due to gas dissolution followed by an isobaric period where nucleation takes place. The sudden pressure drop during the nucleation period is caused by hydrate formation.

Where $x^i_{L-V}$ is the gas solubility of the hydrate former in the liquid phase at the V-$L_w$ interface at $T_{exp}$ and $P_{exp}$ and $a_{L-V}$ is the vapor-liquid interfacial area per volume of dispersion ($A_{L-V}/V_L$).
All variables in (5) were obtained experimentally except for the dissolution rate which was calculated using a least square analysis. The mole fraction of propane gas dissolved in water was in all cases calculated using the fugacity of the pure component in the vapor phase and the Henry's constant:

$$x_i = \frac{f_i(P_{\exp}, T_{\exp})}{H_{iw}} \qquad (6)$$

Henry's constant was calculated using the empirical expression found by Chapoy et al. [17]:

$$\ln(H_{iw})(KPa) = 552.64799 + 0.078453T - \frac{21334.4}{T} - 85.89736\ln(T) \qquad (7)$$

It was assumed that the addition of PVP did not have any impact on the magnitude of Henry's constant as the concentration was very low.
In table the average dissolution rate of all experiments at the different stirring rates is presented. In the pressure region investigated here 2.1-2.7 bar the dissolution rate was more or less independent of the initial pressure. The measured induction times were taken as the time from when the gas had dissolved into the water until pressure suddenly dropped due to gas hydrate formation.

| RPM | PVP Conc. (wt%) | $k^l_{L\text{-}V} a_{L\text{-}V}$ ($s^{-1}$) |
|---|---|---|
| 500 | 0 | 7.34 |
| 300 | 0 | 2.66 |
| 200 | 0 | 0.94 |
| 500 | 0.005 | 6.12 |
| 500 | 0.025 | 6.94 |

**Table 1.** Gas dissolution rate of propane in distilled water at different stirring rates and polyvinyl- pyrrolidone concentrations. T = 273.75 K.

The induction times have been plotted as a function of the supersaturation for different stirring rates in figure 4 and for different concentrations of PVP in figure 5. The induction periods can be seen to be more or less independent of the stirring rate when this is varied in the range of 300-500 rpm. At lower stirring rates a less regular tendency is observed i.e. there is quite more scattering among the data points. This indicates that in case of low convection, the system will act more randomly which could be due to lower V-$L_w$ interfacial area or a less favorable distribution of gas in the bulk liquid phase.

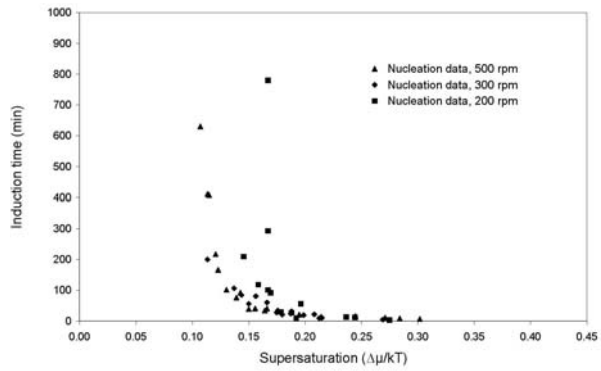


**Figure 4.** Nucleation period vs. driving force at 273.75 K for propane hydrate. The induction times measured at stirring rates of 500 and 300 rpm are very similar. At 200 rpm more scattering among the measured induction times is observed. At this stirring rate the induction times are also seen to be prolonged a little.

When PVP is added in even very small amounts the induction time/supersaturation relationship is shifted to the right as can be observed in figure 5. There seems to be quite steady agreement among the two data sets, i.e. the higher PVP concentration data are shifted to the right with the same Δμ value compared to the data for the lower PVP concentration.

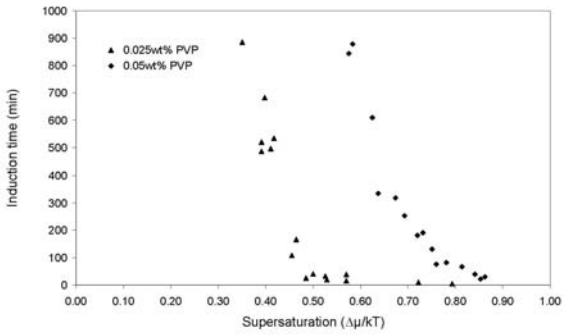


**Figure 5.** Plot of nucleation period vs. driving force at 273.75 K for propane hydrate for two different concentrations of PVP and a stirring rate of 500 rpm. PVP is seen to cause longer induction times compared to nucleation of propane hydrate from a pure aqueous phase.

Based on crystallization theory the following expression describing the relation between nucleation time and the supersaturation ratio, S, has been proposed [8]:

$$t_i = K\left[S(S-1)^{3m}\right]^{-1/(1+3m)} \cdot \exp\left[\frac{B}{(1+3m)\ln^2 S}\right] \quad (8)$$

This expression is appropriate for plotting induction times against supersaturation ratios whereby B and K can be obtained from a regression as the slope and the intercept.
If growth by volume diffusion of dissolved gas, through a stagnant layer formed around the nucleus is assumed then m = 1. Thereby (8) reduces to:

$$\ln\left[S^{1/4}(S-1)^{3/4}t_i\right] = \ln K + \frac{B}{4\ln^2 S} \quad (9)$$

Where K is a kinetic parameter and the supersaturation ratio *S*, and the *B* parameter is given as:

$$S = \left[\frac{f(P,T)}{f(P_e,T)}\right] \cdot \exp\left[\frac{\Delta v_e (P-P_e)}{kT}\right] \quad (10)$$

$$B = \frac{4c^3 v_h^2 \sigma_{ef}^3}{27(kT)^3} \quad (11)$$

where c is a shape factor, $v_h$ is the volume of a hydrate building unit $\sigma_e$ and is the effective surface energy between hydrate and solution. The results using the experimentally obtained induction periods at different supersaturation ratios at a stirring rate of 500 and 200 rpm and the best linear fit is presented in figure 6. The induction time model parameters, K and B and the calculated effective surface energy are all presented in table 2 at the different stirring rates. The numbers in parenthesis are the standard errors. When the stirring rate is decreased K decreases however most pronounced when going from 300 to 200 rpm. The opposite trend is seen for the B-values, thus also for the effective surface energy. The standard error of the model parameters also increases when the stirring rate is lowered thus indicating that the lower stirring rate causes the system to act more stochastic.

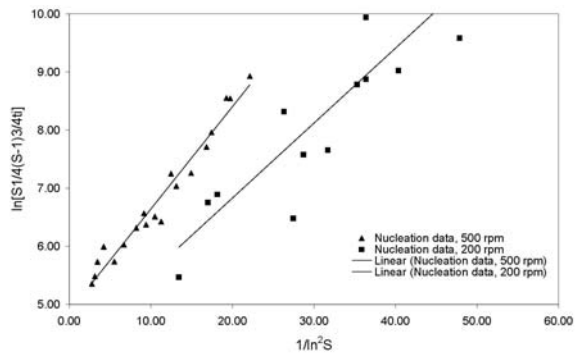


**Figure 6.** Linearized dependence of the induction time on the supersaturation ratio for nucleation of propane hydrate in aqueous solution at T = 273.75, 500 rpm and 200 rpm . Changing the agitation speed causes small changes in nucleation periods.

| RPM | K (s) | B | $\sigma_{ef}$ mJ/m$^2$ |
|---|---|---|---|
| 500 | 130.92 (1.11) | 0.176 (0.008) | 1.11 |
| 300 | 118.73 (1.25) | 0.182 (0.023) | 1.12 |
| 200 | 69.85 (2.32) | 0.516 (0.107) | 1.58 |

**Table 2.** Fitted parameters of the nucleation model. The resulting effective surface energy is not heavily influenced by a change in the stirring rate which explains why similar nucleation periods at different stirring rates are observed. Numbers in parenthesis are standard errors.

The induction time model parameters, K and B and the effective surface energy were also calculated for the system containing PVP. This was done by introducing a term to (8) taking into account adsorption of molecules on nucleation sites and the surface of growing hydrate. Expression (8) thereby becomes:

$$t_i = K\left[\left(1+k_g C_a\right)^{3m}\left(1+k_n C_a\right)^{1/(1+3m)}\right]$$
$$\left[S\left(S-1\right)^{3m}\right]^{-1/(1+3m)} \cdot \exp\left[\frac{B}{(1+3m)\ln^2 S}\right] \quad (12)$$

Where $k_g$ and $k_n$ ($m^3$) are adsorption constants and $C_a$ (molecules/$m^3$) is the concentration of the additive in solution. This expression is valid for additive molecules that 1) do not adsorb on the surface of the hydrate nuclei, but adsorb on the surface of the growing hydrate crystallites, 2) do not provide new nucleation sites in the system, and 3) block existing nucleation sites by adsorbing at the solution/gas interface or onto the surface of the nucleation-active microparticles and solid substrates present in the solution [8]. This expression is likewise rearranged to a form that is suitable for regression:

$$\ln\left[\frac{S^{1/4}(S-1)^{3/4}t_i}{(1+k_g C_a)^3(1+k_n C_a)^{1/4)}}\right] = \ln K + \frac{B}{4\ln^2 S} \quad (13)$$

The result of using the linearized induction time model for the data obtained in the nucleation experiments with PVP are shown in figure 7. Exemplary values of $k_g = k_n = 10^{-18}$ $m^3$, also reported elsewhere in literature [8] have been used. As seen there is a reasonable good linear relationship for the two data sets. The regressed K and B parameters and the calculated effective surface energies are given in table 3 below.

| RPM | [PVP] (wt%) | K (s) | B | $\sigma_{ef}$ mJ/m$^2$ |
|---|---|---|---|---|
| 500 | 0 | 130.92 (1.11) | 0.176 (0.008) | 1.11 |
| 500 | 0.025 | $3.31\cdot10^{-12}$ (1.45) | 3.010 (0.297) | 2.85 |
| 500 | 0.050 | $9.44\cdot10^{-13}$ (1.38) | 6.910 (0.607) | 3.76 |

**Table 3.** Fitted parameters of the nucleation model. The resulting effective surface energy is significant influenced by addition of the polymer.

The addition of PVP to the aqueous phase causes the kinetic constant K to decrease substantially compared to the K value when PVP is absent. When homogeneous nucleation is taking place a K value of 5 ns would be expected however the presence of PVP is here seen to cause even smaller values of K. The B parameter has on the opposite

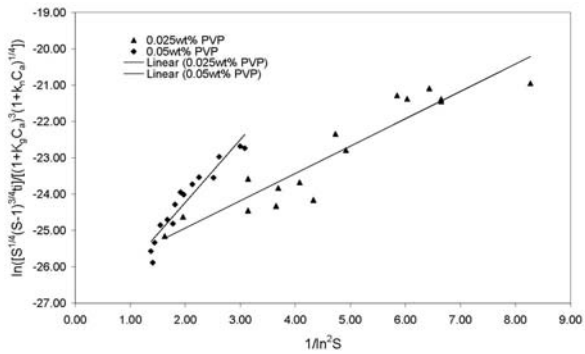


**Figure 7.** Linearized dependence of the induction time on the supersaturation ratio for nucleation of propane hydrate in dilute polymer solutions at 273.75 K and 500 rpm. Small changes in polymer concentration changes nucleation conditions significantly.

increased compared to the B value when no PVP is present. When the PVP concentration is increased the B parameter also increases. This implies that adsorption of PVP on hydrate nuclei does not take place as this would result in a decrease of the surface energy according to the equilibrium adsorption theory. The explanation of why B increases when PVP is added could be various. The definition of the effective surface energy is given as:

$$\sigma_{ef} = \psi\sigma \quad (14)$$

Where the shape factor, ψ, for cap-shaped nuclei can be found from the relation:

$$\psi = \left[(1/4)(2+\cos\theta)(1-\cos\theta)^2\right]^{1/3} \quad (15)$$

Where θ is the contact angle between the hydrate nuclei and the substrate. Thus it follows that B will increase if the contact angle between the hydrate nuclei and substrate increases. This could be the case if for example PVP adsorbs onto the original nucleation sites on the substrate and thereby blocking them. Considering the before listed statements it is seen that this observation is in agreement with 3) thus within the restrictions of the model.

Another reason could be that the additive is a second-type of nucleation site being less active compared to the original heterogeneous nucleation sites. The effective surface energy of the nuclei that forms on this type of substrate could indeed be different from that of nuclei forming on the

original substrate. In fact if the substrate is less active this will result in a higher surface energy [18]. As the model does not account for molecules that themselves acts as nucleation sites this last consideration should be perceived only as a suggestion for the inhibiting mechanism of additives like PVP.

## Conclusions

Nucleation time data have been obtained for propane hydrate at 273.75 K as a function of the driving force in terms of supersaturation. The effect of changing stirring rate and adding a kinetic inhibitor (PVP) were investigated. The main conclusions are:

- The consistency in the measured nucleation data was relatively good at high stirring rates. This could be a result of more unified distribution of the gas in solution.
- At low stirring rates nucleation of propane hydrate becomes more stochastic i.e. more scattering in measured nucleation periods is observed.
- Reasonable agreement between the nucleation model and the measured data can be obtained. Especially at high stirring rates.
- Polymers like PVP effectively prolong the nucleation periods of propane hydrate.
- A likely mechanism by which PVP inhibits the nucleation of propane hydrate is by increasing the contact angle between the hydrate nuclei and the substrate.

**ACKNOWLEDGEMENT**

The authors would like to thank the Danish Research Council for Technology and Production Sciences for financial support through the project "Gas Hydrates – from Threat to Opportunity" and the Technical University of Denmark for financial support through a Ph.D. scholarship.

**REFERENCES**

[1] Sloan, E.D. *Clathrate Hydrates of Natural Gases*. New York: Marcel Dekker, 1998.

[2] Kelland, M. *Studies on New Gas Hydrate Inhibitors*. SPE 1995; 30420: 531-539.

[3] Sloan, E.D., Lederhos, J.P., Long, J.P., Sum, A., Christiansen, R.L. *Effective Kinetic Inhibitors for Natural Gas Hydrates*. Chem. Eng. Sci. 1996; 51: 1221-1229.

[4] Munck, J., Jørgensen, S., Rasmussen, P. *Computations of the Formation of Gas Hydrates*. Chem. Eng. Sci. 1988; 43: 2662-2672.

[5] Ng, H.J., Robinson, D.B. *Measurement and Prediction of Hydrate Formation in Liquid Hydrocarbon-Water Systems*. Ind. Eng. Chem. Fundam. 1976; 15: 293-298.

[6] Parrish, W.R., Prausnitz, J.M. *Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures*. Ind. Eng. Chem. Process Des. Develop. 1972; 11: 26-35.

[7] Englezos, P., Kalogerakis, N., Dholabhai, P.D., Bishnoi, P.R.. *Kinetics of Formation of Methane and Ethane Gas Hydrates*. Chem. Eng. Sci,. 1987; 42: 2647-2658.

[8] Kashchiev, D., Firoozabadi, A. *Induction Time in Crystallization of Gas Hydrates*. Journal of Crystal Growth. 2003; 250: 499-515.

[9] Natarajan, V., Bishnoi, P.R., Kalogerakis, N.. *Induction Phenomena in Gas Hydrate Nucleation*. Chem. Eng. Sci. 1994; 49: 2075-2087.

[10] Skovborg, P., Rasmussen, P., Mohn, U. *Measurement of Induction Times for the Formation of Methane and Ethane Gas Hydrates*, Chem. Eng. Sci. 1993; 48: 445-453.

[11] Vysniaskas, A., Bishnoi, P.R. *A Kinetic Study of Methane Hydrate Formation*. Chem. Eng. Sci. 1983; 38: 1061-1072.

[12] Bishnoi, P.R., Natarajan, V. *Formation and Decomposition of Gas Hydrates*, Fluid Phase Equilibria. 1996; 117: 168-177.

[13] Kashchiev, D., Firoozabadi, A. *Driving Force for Crystallization of Gas Hydrates*. Journal of Crystal Growth. 2002; 241: 220-230.

[14] Mullin, J.W. *Crystallization*. London: Elsevier-Butterworth Heinemann, 2004.

[15] Kashchiev, D., Firoozabadi, A. *Nucleation of Gas Hydrates*, Journal of Crystal Growth. 2002b; 243: 476-489.

[16] Sloan, E.D. *Hydrate Engineering*. Texas: SPE Inc., 2000.

[17] Chapoy, A., Mokroui, S., Valtz, A., Richon, D., Mohammadi, A.H., Tohidi, B. *Solubility Measurement and Modeling for the System Propane–Water from 277.62 to 368.16K*. Fluid Phase Equilibria. 2004; 226; 213-220.

[18] van der Leeden, M.C., Kashchiev, D., van Rosmalen, G.M. *Effect of additives on nucleation rate, Crystal Growth Rate and Induction Time in*

*Precipitation*. Journal of Crystal Growth. 1993; 130; 221-232.