Assessment of Nucleation Kinetic Mechanisms in Gas Hydrate Crystallization Processes

Bahman. ZareNezhad*, Mona Mottahedin, Farshad Varaminian

School of Chemical, Petroleum and Gas Engineering, Semnan University, P.O. Box 35195-363, Semnan, Iran

*Corresponding author's e-mail: prof.b.ZareNezhad@gmail.com

Abstract

Nucleation is one of the most important steps in the process of crystallization of gas hydrates. In the present work the nucleation mechanism of gas hydrate formation process using the propane as a sII gas hydrate former is investigated at isothermal operating conditions. Effects of variations of supersaturation and impeller speed on the kinetics of hydrate nucleation are also presented. Differente expressions for dependence of induction time with degree of supersaturation are employed. The accuracy of the predicted induction times for the case of progressive nucleation are always much higher than those obtained through instantaneous nucleation assumption at all ranges of impeller speeds. It is found that the heterogeneous progressive nucleation is the most probable nucleation mechanism at the early stages of gas hydrate formation processes.

Keywords: gas hydrate, formation, nucleation, mechanism, crystallization, kinetics.

- Nucleation mechanisms of gas hydrate formation processes are investigated.
- Effects of variations of supersaturation and impeller speed on the kinetics of hydrate nucleation are presented.
- It is found that the heterogeneous progressive nucleation is the main nucleation mechanism at the early stages of gas hydrate formation processes.

1. Introduction

Studies on the kinetics of the process of gas hydrate crystallization are at a relatively early stage of development despite notable work of various authors in the last three decades [1-3]. Issues related to the nucleation and growth processes, including the supersaturation, the nucleation and growth rates and the induction time, have not been sufficiently clarified [4-6]. Recently, a mechanistic kinetic model for description of gas hydrate formation processes has also been presented by ZareNezhad et al. [7] and the secondary nucleation mechanisms due to crystal-crystal and crystal-impeller contacts are theoretically described for the first time.

Nucleation is one of the most challenging steps regarding the crystallization of gas hydrates. Depending on where and how nucleation occurs and how is schematic of clusters, there are

different influencing mechanisms such as homogeneous nucleation (HON), heterogeneous nucleation (HEN), and instantaneous nucleation (IN) and progressive nucleation (PN).

In the present study, different mechanisms of hydrate primary nucleation have been investigated at different supersaturations and impeller speeds. The expressions for dependence of induction time with degree of supersaturation are employed and the parameters of model are determined by mathematical optimization.

2. Modeling of gas hydrate nucleation

Kashchiev and Firoozabadi in their thermodynamic analysis of hydrate formation defined that the driving force for the formation of a new phase is the chemical potential difference between the old phase and the new one [8]. This difference is called supersaturation, Δg. Describing hydrate formation from pure gas and its aqueous solution by the general equation:

$$G + n_w H_2 O \Leftrightarrow G.n_w H_2 O \tag{1}$$

These authors expressed the supersaturation for hydrate formation as:

$$\Delta g = \mu_{GS} + n_w \mu_w - \mu_H \tag{2}$$

where μ_{GS} and μ_w are the chemical potentials of gas and water molecules in the aqueous solution, respectively, and μ_H represents the chemical potential of a building unit (one gas molecule and n_w water molecules) in the hydrate crystal.

In a latter work, Kashchiev and Firoozabadi applied the classic nucleation theory to develop the following general expressions for the nucleation rate of one-component gas hydrates at the condition of instantanous nucleation or progressive nucleation by following definitions [9]:

Physically, IN corresponds to the case when all crystallites in the solution are nucleated practically at the initial moment t = 0. An example of such a process is HEN on nucleation-active centers at such a high nucleation rate that just after the solution becomes supersaturated each of these centers generates a hydrate nucleus. Thus, already at t = 0 the solution contains a fixed number N_c of growing crystallites. This means that, mathematically, IN is characterized by a $j(t)$ dependence of the form:

$$j(t) = \left(\frac{N_c}{V_s} \right) \delta_D(t) \tag{3}$$

for volume nucleation and

$$j(t) = \left(\frac{N_c}{A_s} \right) \delta_D(t) \tag{4}$$

for surface nucleation, δ_D being the Dirac deltafunction. Recalling that $\int_0^t \delta_D(t') f(t - t') dt' = f(t)$ for an arbitrary function f yields:

$$\alpha(t) = \left(\frac{b N_c G^{3m}}{V_s} \right) t^{3m} \tag{5}$$

for both volume and surface nucleation. α denotes the fraction of hydrate crystallized until time t and b is a dimensionless shape factor.

But Hydrate crystallization proceeds by PN when the hydrate crystallites are continuously nucleated during the process. The analysis is simple when the nucleation is stationary, then the stationary nucleation rate J $\left(m^{-3}s^{-1}\right)$or $\left(m^{-2}s^{-1}\right)$ being given by [9]:

$$J = A^* e^{\Delta\mu/kT} \exp\left(-4c^3 v_H^2 \sigma_{ef}^3 \Big/ 27kT\Delta\mu^2\right) \tag{6}$$

in which c represents a shape factor ($c = \sqrt[3]{36\pi}$ for spherical clusters) and σ_{ef} is the effective superficial energy for the hydrate–solution interface, whose value, in the case of heterogeneous nucleation, is a function of the contact angle between the hydrate and the pre-existing surface. The kinetic parameter A^* $\left(m^{-3}s^{-1}\right)$or $\left(m^{-2}s^{-1}\right)$ in Eq. (6) depends on the mechanism of attachment of hydrate building units to the nucleus and on the kind of nucleation.

Completing their analysis of hydrate nucleation, Kashchiev and Firoozabadi assumed a power-law crystallite growth to write an equation for the temporal evolution of the gas consumption in the early nucleation stage, which led to the derivation of expressions for the induction time as a function of supersaturation [10]. In the case of instantaneous nucleation, when there is no induction time and all stable crystallites are nucleated practically at the initial moment $t = 0$, one gets:

$$t_{nuc} = K\left[\exp\left(\frac{\Delta\mu}{kT}\right) - 1\right]^{-1} \tag{7}$$

Whereas, for progressive nucleation at a constant rate the induction time becomes:

$$t_{nuc} = K \exp\left(\frac{-\Delta\mu}{kT}\right)\left[1 - \exp\left(\frac{-\Delta\mu}{kT}\right)\right]^{-3m/(1+3m)} \times \exp\left[\frac{4c^3 v_H^2 \sigma_{ef}^3}{27(1+3m)kT(\Delta\mu)^2}\right] \tag{8}$$

Being m the exponent in the power law for crystallite growth. In order to assess the interfacial properties of the hydrate forming system, i.e. the effective surface energy between hydrate and solution, and the hydrate substrate contact angle are linearized. This is done by substituting the following expression into Eq. (8) as follows:

$$B = \frac{4c^3 v_H^2 \sigma_{ef}^3}{27(kT)^3} \tag{9}$$

The supersaturation can be represented as the supersaturation ratio, S:

$$S = \left[\frac{\varphi(P,T)P}{\varphi(P_e,T)P_e}\right].\exp\left[\frac{\Delta v_e (P - P_e)}{kT}\right] \tag{10}$$

Using Eq. (10) as the driving force, Eq. (8) can be expressed on the following form:

$$t_{nuc} = K\left[S(S-1)^{3m}\right]^{-1/(1+3m)}.\exp\left[\frac{B}{(1+3m)\ln^2 S}\right] \tag{11}$$

The above expression is appropriate for plotting induction times against supersaturation ratios whereby B and K can be obtained by mathematical optimization. If growth by volume

diffusion of dissolved gas, through a stagnant layer formed around the nucleus is assumed, hereby Eq. (11) becomes:

$$\ln\left[S^{\frac{1}{4}}(S-1)^{\frac{3}{4}} t_i \right] = \ln K + \frac{B}{4\ln^2 S} \qquad (12)$$

and Eq.(7) describing the instantaneous nucleation can be written in the following form:

$$\ln(t_i) = \ln K - \ln(S-1) \qquad (13)$$

3. Results and Discussion

The predicted induction times using progressive and instantaneous nucleation (PN & IN) mechanisms for the case of propane hydrate formation are compared with measured induction times at different impeller speeds in Figs. 1-3. As shown in Fig 1, at a low impeller speed of 200 RPM, there are significant deviations between measured and predicted induction times regarding both mechanisms. At a higher impeller speed of 300 RPM, the data points are less scattered as shown in Fig 2. This can be attributed to a more uniform supersaturation inside the vessel. This behaviour has been further checked by increasing the impeller speed to 500 RPM.
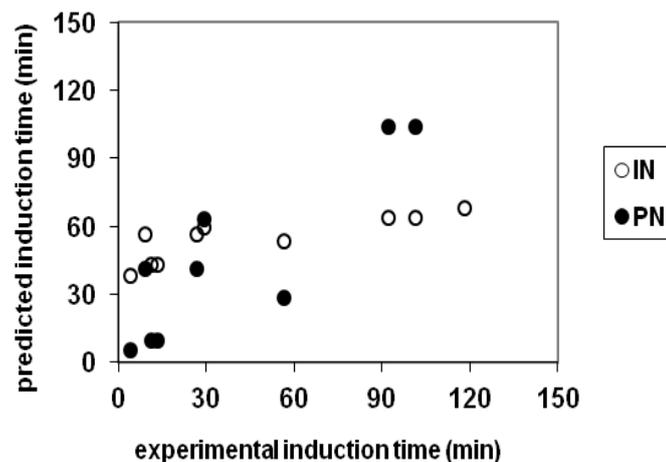

Fig.1. Comparison between predicted and experimental induction time according to the instantaneous (IN) and Progressive nucleation (PN) mechanisms at 200 RPM

As shown in Fig 3, the predicted induction time using the progressive nucleation is in a relative agreement with the measured data. Due to more favorable distribution of gas in the bulk liquid phase and approaching a more uniform supersaturation, the prediction acuuracy at 500 RPM is much more higher as compared to the cases of 200 and 300 RPM according to the progressive nucleation concept (Eq. (12)). According to the results displayed in Figs 1-3, the instantaneous nucleation assumption gives poor results at all agitation intensities especialy at low impeller speeds.
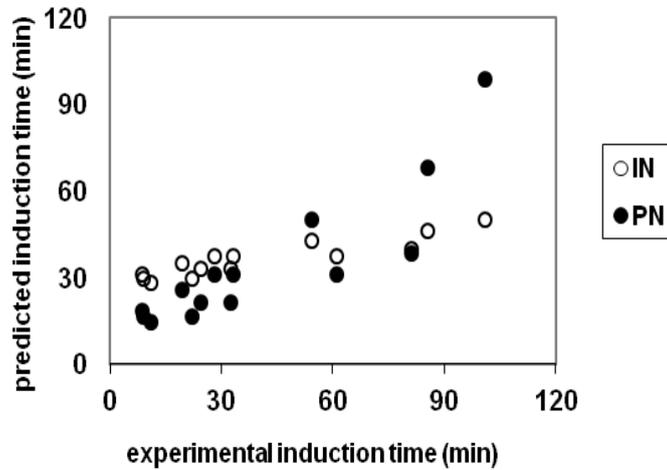
Fig.2. Comparison between predicted and experimental induction time according to the instantaneous (IN) and Progressive nucleation (PN) mechanisms at 300 RPM
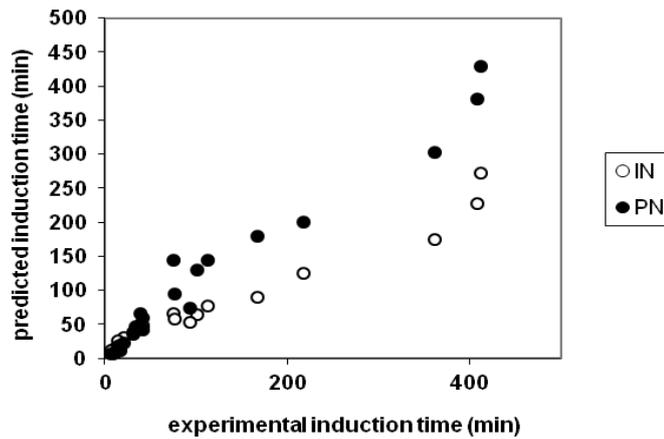

Fig.3. Comparison between predicted and experimental induction time according to the instantaneous (IN) and Progressive nucleation (PN) mechanisms at 500 RPM

The accuracy of induction time prediction using the progressive nucleation mechanism is further evaluated by plotting Eq. (12) in a linear form and calculating the R^2-values at differternt agitation intensities. Fig 4 shows a typical plot at an impeller speed of 500 RPM.
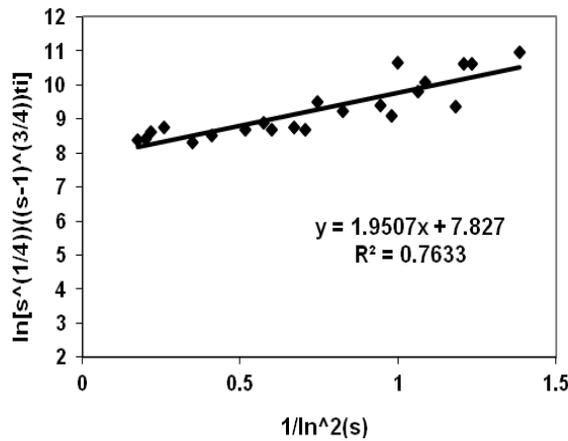
Fig.4. progressive nucleation at 500 RPM

According to Eq. (12), the optimized K and B parameters are about 2507.4 and 7.8 respectively. The magnitude of *K* is rather high for a process to take place on a molecular level indicating that the heterogeneous nucleation is taking place via a polynuclear mechanism. For an operative mononuclear mechanism and homogeneous nucleation very low *K* values would be expected [10].

For both cases of progressiove and instantaneous nucleation, the calculated R^2-values obtained by optimization of Eqs. (12) and (13) are presented in Fig 5. It is clear that at all stirring rates, the progressive nucleation assumption (Eq (12) always give much more accurate results. As shown the calculated correlation coefficients for the case of progressive nucleation are always much higher than those obtained through instantaneous nucleation assumption at all ranges of impeller speeds. It is found that over wide ranges of agitation intensities, the hetergeneous progressive nucleation is the most probable mechanism at the early stage of gas hydrate formation process.
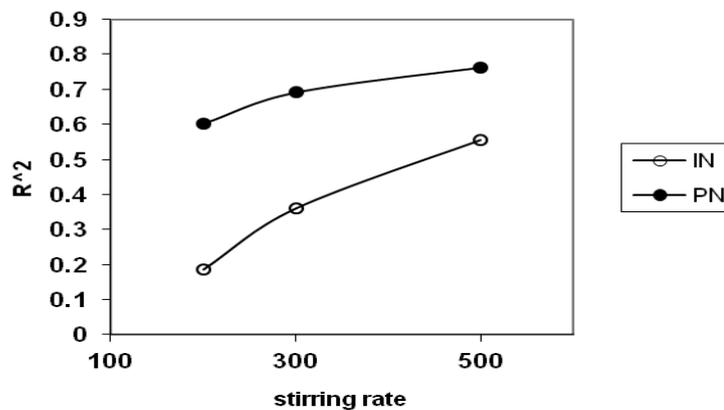

Fig.5. Comparison of progressive and instantaneous nucleation

mechanisms at different impeller speeds (RPM)

4. Conclusions

Nucleation kinetic of gas hydrate formation process using propane as a sII gas hydrate former is investigated in this work. Different mechanisms of gas hydrate nucleation are investigated at the early stage of crystallization process. The governing equations for describing the dependence of induction time with degree of supersaturation are employed. Effects of supersaturation and impeller speed on hydrate nucleation are also presented. Comparison of the predicted and measured induction time data at different operating conditions indicates that the hetergeneous progressive nucleation is the most probable nucleation mechanism at the early stage of gas hydrate formation processes.

References

[1] Vysniauskas, A., Bishnoi, P. R., "*A kinetic study of methane hydrate formation*", Chem. Eng. Sci, Vol. 38, No. 1061, 1983.

[2] Vysniauskas, A., Bishnoi, P. R., "*Kinetics of ethane hydrate formation*", Chem. Eng. Sci, Vol. 40, No. 299, 1985.

[3] Englezos, P., Kalogerakis, N., Dholabhai, P. D., Bishnoi, P. R., "*Kinetics of Formation of Methane and Ethane Gas Hydrates*", Chem. Eng. Sci., Vol. 42, No. 2647, 1987.

[4] Sloan, E.D., Fleyfel, F., "*Molecular mechanism for gas hydrates nucleation from ice*". A.I.Ch.E. Journal, Vol. 37, 1991.

[5] Skovborg, P., Rasmussen, P., "*A mass transport limited model for the growth of methane and ethane gas hydrates*", Chem. Eng. Sci, Vol. 49, No. 1131, 1994.

[6] Natarajan, V., Bishnoi, P. R., Kalogerakis, N., "*Induction Phenomena in Gas Hydrate Nucleation*", Chem. Eng. Sci, Vol. 49, No. 2075, 1994.

[7] ZareNezhad, B. Mottahedin, M., "*A rigorous mechanistic model for predicting gas hydrate formation kinetics: the case of CO2 recovery and sequestration*", Energy Conversion and Management 2012; 53(1): 332-336.

[8] Kashchiev, D., Firoozabadi, A., "*Driving force for crystallization of gas hydrates*", Journal of Crystal Growth, Vol. 241, No. 220, 2002

[9] Kashchiev, D., Firoozabadi, A., "*Nucleation of gas hydrates*", Journal of Crystal Growth, Vol. 243, No. 476, 2002.

[10] Kashchiev, D., Firoozabadi, A., "*Induction time in crystallization of gas hydrates*", J. Crystal Growth, Vol. 250, No. 499, 2003.