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Asymptotic Modelling of Crystallisation in Two Layers Systems. Application to Methane Hydrate Formation in Batch Reactor.

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This paper proposes to re-visit the problem of gas-liquid crystallization in the framework of a two-layer model and with the help of data coming from experiments on methane hydrate crystallization in a semi-batch reactor. Preliminary quantitative discussion of the order of magnitude of different effects makes possible realistic simplifications in the theoretical models. In particular, the role of the interfacial film is clearly defined. As previous authors did, we use a formulation in terms of moments of the crystal size distribution, however we are not interested in the numerical solution to the corresponding differential system, but we propose a general procedure to express analytically the asymptotic behaviour of the physical system. Thanks to this formulation, influence of different parameters can be easily identified and validated on available experimental data.

1 Introduction

Gas-liquid crystallization can be described by the overall reaction:

$A_{1(gas)} + pA_{2aq} \rightarrow qA_{3(solid)}$ [R1]

in which $A_{2\ aq}$ is a compound dissolved in an aqueous solution and p and q are stoichiometric coefficients, are frequently met in industrial or natural systems. This is for instance the case of carbonatation of lime water. The latter case has been extensively studied by (Wachi and Jones, 1991 a,b; Jones *et al.*, 1992) and has given rise to comprehensive interpretations.

Gas hydrate crystallization can be also represented by a [R1]-type reaction in which A_{2aq} would denote simply water and A_3 the gas hydrate phase (Englezos *et al.* 1987 a,b; Skovborg and Rasmussen, 1994; Herri *et al.*, 1999).

Models are generally based on the assumption of a two-layer configuration which consists of :

i) the superficial film at the gas-liquid interface in which absorption and diffusion of the gas into the liquid phase take place (possibly accompanied by reactions between dissolved species); this zone, of both high supersaturation and high concentration gradient values in dissolved gas, is favourable to primary nucleation of crystals;

ii) the bulk zone in which crystals develop mainly by growth; this is a region of lower concentration values and nearly zero gradients all the more so since the medium is generally stirred.

Classical models take into account:

1. basic equations for the gas-liquid mass transfer (film theory) accompanied with kinetic models of chemical reactions;
2. equations for the distributed crystal population and dissolved gas mass balances;
3. crystallization kinetic laws.

The associated mathematical problem is a partial derivative equation (PDE) problem when simplification cannot be introduced (Wachi and Jones, 1991) or an ordinary differential equation problem when simplifying procedures or assumptions (steady state ; use of the crystal population moments) can be applied. (Englezos *et al.* 1987 a,b; Herri *et al.*, 1999)

In this paper we would like to revisit several aspects of gas-liquid precipitation in the framework of the two-layer model. Particularly, the different assumptions concerning gas transfer through the interfacial film, crystal growth, nucleation and transport in this film will be examined. Then, we will propose a general model of crystallization and discuss some possible simplifications particularly at later stages of the process. The main originality of this paper, however, is to propose analytical laws for the system asymptotic behaviour ; these predictions can be easily compared to experimental results and give in several cases quantitative estimation of the model parameters. This approach, although general, will be supported (and possibly validated) by the experimental context of methane hydrate crystallization (Herri *et al.*, 1999) for which we have many results.

2 Models

System configuration. We consider a vertical cylindrical stirred reactor filled with water. The liquid height, volume and cross-section section area are respectively denoted by H, V, and A. z is the vertical co-ordinate (the gas-liquid interface is located at $z = 0$) ;

t is the time. Two zones are considered (Figure 1).

- ***interface layer***: the interface layer, of thickness d is characterised by a concentration profile $c'(z, t)$ in dissolved gas. The boundary conditions are: $c'(0, t) = C_{ext}$ and $c'(d, t) = c_b(t)$; C_{ext} is the gas solubility; $c_b(t)$ is the bulk concentration. The crystal diameter density function should be considered in its local, z-dependent form, $n'(D, z, t)$ expressed per unit volume. As the agitation state of the interface layer is probably weak, we consider it at rest as other authors did.

- ***bulk zone***: due to the effect of stirring, the concentration in dissolved gas $c_b(t)$ and the crystal diameter density function per unit volume, $n_b(D, t)$ are considered as independent of z. The agitation state, imposed by the stirrer, is assumed to be uniform and completely characterised by the stirring rate.

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In what follows, superscript ' will be used to denote variables or parameters relative to the surface layer whereas bulk variables or parameters will be written with subscript *b*. Variables without particular indication are relative to the system or to both zones.

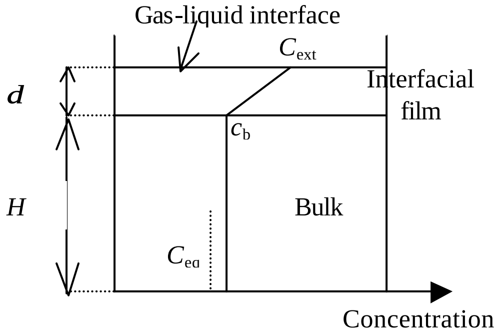

Figure 1. The two-film system.

Processes

-gas absorption

The gas absorption rate per unit volume $r(t)$ is expressed by the well-known relation (Mehta and Sharma, 1971):

$$r(t)=k_{\text{L}}a\,(C_{\text{ext}}-c_b(t)) \qquad (1)$$

a is the mass transfer surface area per volume of liquid and k_{L} the mass-transfer coefficient. In the experiments reported here, $k_{\text{L}}a$ ranges between 0.001 and 0.005 s^{-1}.

-mass transport in the interfacial layer

In the two-film theory, the interfacial layer thickness is obtained from the relation :

$$\boldsymbol{d}=\frac{D_G a}{k_L a} \qquad (2)$$

in which D_{G} is the dissolved gas diffusivity. For instance, $\boldsymbol{d}$ ranges between 10 and 50 µm in (Herri *et al.*, 1999). Thus, the interfacial layer is very thick compared to the usual height of the reactor(0.2 m).

Concentration is maintained at value C_{ext} by the gas-liquid equilibrium at the external interface. Crystallization occurs because C_{ext} is greater than C_{eq}, the equilibrium concentration in presence of crystals. Concentration in the bulk, c, is proved to be close to C_{eq}, at least, at late stages of the crystallization process. This means that supersaturation sharply decreases throughout the film layer. In gas-liquid precipitation experiments, visual observations clearly show that nucleation mainly takes place in the interfacial film from which the nucleated crystals are then transferred to the bulk where they go on growing. According to the authors this transfer process is differently described. Wachi and Jones (1991 a) attribute it to Stokes-Einstein diffusion whereas Englezos *et al.* (1987 a,b) consider that nuclei appear in the film and are instantaneously transferred to the bulk as soon as supersaturation conditions are created. We propose here a discussion on the inter-layer transfer process by taking into account Stokes diffusion, floating and crystal growth.

The Stokes-Einstein diffusion coefficient D_{P} of a spherical particle of diameter *D'* is given by :

$$D_P=\frac{kT}{3\boldsymbol{p}\boldsymbol{h}_L D'} \qquad (3)$$

in which T is the temperature, $\boldsymbol{h}_L$, the dynamic viscosity of the liquid medium and k the Boltzmann constant.

Methane hydrate particles immersed in water move upwards (floating) because they are lighter than the fluid medium. Their limit velocity w is given by :

$$w=\frac{D'^2\,g\left|\Delta \boldsymbol{r}\right|}{18\,\boldsymbol{h}_L} \qquad (4)$$

g denotes the gravity and $|\Delta \boldsymbol{r}|$ the absolute value of the density difference between solid and liquid.

Relative importance of Stokes-Einstein diffusion and settling floating can be judged from the corresponding particle flux, *i.e.* respectively :

$$J_P=-D_P\frac{\partial n'}{\partial z} \qquad (5)$$

and $J_{\text{F}}=n'.w$ (6)

From dimensional analysis follows: $\frac{J_P}{J_F}\cong\frac{6kT}{\boldsymbol{p}g}\frac{1}{D'^3\left|\Delta \boldsymbol{r}\right|}\frac{1}{\boldsymbol{d}}$

For the methane hydrate-water system (Herri *et al*, 1999), the parameter typical values $\{T, \boldsymbol{d}, |\Delta \boldsymbol{r}|\}$ are respectively: {275 K, 30 *m*m, 912 $kg.m^{-3}$}. Stokes-Einstein diffusion is preponderant for $D' < 0.65$ µm. This crystal size is reached in about 19s (growth rate $G \approx 2$ $µm.min^{-1}$). The floating time : t_{F} ($t_{\text{F}} = \boldsymbol{d}w^{-1}$) is equal to 143 s . From the order of magnitude of these values, it appears that, once a crystal is nucleated in the interfacial film, it rapidly reaches a size for which diffusion is negligible ; this means that its motion is essentially ruled by flotation. Most crystals of methane hydrate are nucleated at the gas-solid boundary, where supersaturation is maximum. As they are lighter than water, they tend to move upwards to the gas-liquid interface where they go on growing. Their transfer to the bulk zone is due to entrainment by the bulk flow, however should occur only beyond a minimum size. (2)

-crystallization processes

The crystallization processes are presented independently of the reactor zone in which they occur.

Classical assumptions are taken for the kinetic laws of the different crystallization processes :

i) linear growth rate G:

$$G=k_g\,\boldsymbol{s}^{\,p}, \quad \left(\boldsymbol{s}=\frac{c}{C_{eq}}-1\right) \qquad (8)$$

in the considered medium ; C_{eq} is the equilibrium concentration in presence of the solid phase ; constant k_{g} is assumed to be independent of crystal diameter *D* (Mac Cabe simplification), however possibly dependent on stirring ; *p* is a constant, of typical values 1 or 2 (Garside, 1985 ; Dirksen and Ring, 1991).

ii) primary nucleation rate B_1 :

The production rate of primary nuclei per unit volume is expressed according the classical expression (Nielsen, 1964):

$$B_1 \propto \exp\left(-\boldsymbol{b}/\left[\ln(1+\boldsymbol{s})\right]^2\right) \qquad (9)$$

or more simply by $B_1=k_1\,\boldsymbol{s}^{n}$ (10)

in which k_1 is a constant and n, positive exponent; can commonly take relatively high values (5 to 10). The nuclei are supposed to be created at a zero initial size.

iii) secondary nucleation rate B_2:

The production rate of secondary nuclei per unit volume is expressed by (Garside, 1985):

$$B_2 = k_2 \sigma^{m} m_2 \qquad (11)$$

in which k_2 is a constant, generally dependent on agitation, m is a positive exponent ranging from zero (purely mechanical origin of the nuclei) to relatively low values (typically 2 to 3 ; case of "true" secondary nucleation). (Garside, 1985); m_2 denotes the second order moment of the diameter distribution (proportional to the crystal surface area per unit volume of the medium). As before for primary nucleation, the initial size of the secondary nuclei is assumed to be zero.

iv) agglomeration :

The agglomeration kernels depend both on agitation and supersaturation (Hounslow *et al.*, 1988). The role of agglomeration in the different crystal population balances will be represented by an additive term A_{ag} which will be expressed later on.

Model dynamic equations. In this section we present the general dynamic equations which describe the time evolution of the system, particularly of the concentration in dissolved gas and of the crystal density function and the simplification which can be assumed in each zone.

- mass balance

In any point of the two zones, the mass balance in dissolved gas is expressed by the general partial derivative equation :

$$\frac{\partial c}{\partial t} = -\frac{k_v m_2}{v_{mol}} G - \frac{\partial J_D}{\partial z} \qquad (12)$$

J_D is the molar flux of the dissolved gas, m_2 the second-order moment of the crystal distribution, v_{mol} the solid molar volume, and k_v a crystal shape constant ($k_v = \pi/2$ for spherical particles).

bulk zone :

As the bulk zone is supposed perfectly mixed, Equation (12) is not relevant, at least in the present form, it should be replaced by the following global balance using relation (1) :

$$\frac{dc_b}{dt} = k_L a\left(C_{ext} - c_b\right) - \frac{k_v m_{2b}}{v_{mol}} G_b \qquad (13)$$

interfacial layer:

As commonly in the framework of the film model (Welty *et al.*, 1969 ; Beek *et al.* 1975), comparison between the gas absorption flow-rate and the gas amount actually consumed in the interfacial layer can suggest simplifications.

Ratio γ between the two flow-rates is given by :

$$\gamma = k_L a\left(C_{ext} - c_b\right) H \Big/ \frac{k_v m_2'}{v_{mol}} G' \delta \qquad (14)$$

Denoting φ the volume fraction of solid and $\overline{D'}$ the crystal mean diameter in the film, assuming $C_{ext} >> c_b$, and $a \approx 1/H$ and using relation (2), we obtain an approximate expression of α:

$$\gamma = \frac{D_G}{3 \varphi G'} D' \frac{1}{\delta^2} C_{ext} v_{mol} \qquad (15)$$

The parameter typical values $\{D', \delta, G', C_{ext}.v_{mol}\}$ are : {5μm, 30μm, 2μm.min^{-1}, 7.2 x 10^{-3}} for methane hydrate in water. D_G = 5 x 10^{-9} m^2.s^{-1} and φ is estimated to 0.01.

The corresponding calculated value of γ is 200 for methane hydrate in water. Due to the uncertainty of the different parameters, this value is questionable, however probably realistic. This proves that crystallization weakly affects mass transfer in the interfacial layer ; consequently, from Equation (12), it follows that a linear profile of concentration ranging between C_{ext} and C_b can be assumed in the interfacial layer at the steady state.

- crystal population balances

The crystal population balance is expressed by the general partial derivative equation:

$$\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial D} - B_1 - B_2 + \frac{\partial J}{\partial z} - A_{ag} = 0 \qquad (16)$$

where the population density function n depends on diameter D, time t and height z. Flux J refers to the circulation of the particles in the system (J_F, J_P, as mentioned before or convection flux).

interfacial layer:

We propose several simplifying assumptions for the interfacial layer.

- steady state : this is justified by the small extension of this layer and its constant exchange with the gaseous atmosphere and the liquid bulk;

- linear profile of concentration in dissolved gas and negligible crystallization processes (*i.e.* growth, agglomeration and secondary nucleation) except of course primary nucleation: this is justified by the calculated α;

Taking into account too that particles nucleated in the film are rapidly transferred to the bulk by flow entrainment), their starting size in the bulk is probably little dispersed and small. This is the reason why we give up calculating it accurately and we restrict the role of the interfacial film to an external source of nuclei which feeds the bulk of the reactor.

Averaged nucleation rate $\overline{B'_1}$ can be calculated from integration of Equation (10) over the film to give :

$$\overline{B'_1} = \frac{k_1}{n+1} \frac{\sigma_{ext}^{n+1} - \sigma_b^{\,n+1}}{\sigma_{ext} - \sigma_b} \qquad (17)$$

σ_{ext} and σ_b are the supersaturation level respectively at the gas-liquid and at the two-layer interface.

bulk zone

Population balance is deduced from general equation (16), however taking into account the bulk homogeneity and the feed in nuclei from the interfacial film ; it follows :

$$\frac{\partial n_b}{\partial t} + G_b \frac{\partial n_b}{\partial D} - \frac{\delta}{H} \overline{B'_1} - B_{1b} - B_{2b} - A_{agg\,b} = 0 \qquad (18)$$

In the classical crystal population balance equations (Randolph and Larson, 1988), particularly in the framework of the MSMPR model, nuclei are generally assumed to be generated at initial zero size. This simplification is certainly valid for nuclei created by primary nucleation (B_{1b}) or "true" secondary nucleation (B_{2b} ; Equation (11) with m 0). However, according to previous discussions in this text, it is certainly questionable in the case of the nuclei which are produced in the interfacial film and then transferred to the bulk (term $\overline{B'_1}$). We propose to consider a non necessarily zero initial size (D'_{b0}) for these nuclei.

moment equations

The first three moments of the crystal size distribution by number are :

$$m_{0b}=\int n_b(D).dD \tag{19}$$

$$m_{1b}=\int n_b(D).D.dD \tag{20}$$

$$m_{2b}=\int n_b(D)D^2.dD \tag{21}$$

The partial derivative equation (18) results in the following moment equations :

$$\frac{\mathrm{d}m_{0b}}{\mathrm{d}t}=\frac{\boldsymbol{d}}{H}\overline{B'_1}+B_{1b}+B_{2b}-\frac{K_{agg}}{2}m_{0b}^2 \tag{22}$$

$$\frac{\mathrm{d}m_{1b}}{\mathrm{d}t}=G_b m_{0b}+\frac{\boldsymbol{d}}{H}\overline{B'_1}D'_{b0}-\boldsymbol{b}_1 K_{agg}m_{0b}m_{1b} \tag{23}$$

$$\frac{\mathrm{d}m_{2b}}{\mathrm{d}t}=2G_b m_{1b}+\frac{\boldsymbol{d}}{H}\overline{B'_1}D'^2_{0b}-\boldsymbol{b}_2 K_{agg}m_{0b}m_{2b} \tag{24}$$

Presence of terms in $\overline{B'_1}$ in Equations (23) and (24) results from the possibility of nuclei of non zero size as aforesaid. Last terms of left-hand side of these equations are due to the contribution of agglomeration (K_{agg}, $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ are positive constants).These are approximate expressions which assume constant agglomeration kernel and take into account the experimental shape of the crystal size distribution. This simplification has been introduced and validated in (Herri *et al.*, 1999) in the case of crystallization of methane hydrate.

Asymptotic solution to the problem. Solving Equations (13), (22-24) requires numerical integration which presents no particular difficulty, however is not straightforward (Englezos *et al.* 1987 ; Wachi and Jones, 1991, a,b ; Herri *et al.*,1999). Sensitivity to the system parameters clearly appears in these results, however cannot be described in simple words. We will prove here that the asymptotic solution of the problem can be found in an analytical form the parameters of which are the characteristics of the system and the processes.

-mathematical procedure

The calculation procedure starts with the mass balance equation :

$$\frac{dc_b}{dt}=k_L a\left(C_{ext}-c_b\right)-\frac{k_v m_{2b}}{v_{mol}}G_b \tag{13}$$

In presence of crystals, the variance of the present solid-liquid-gas system is equal to 1. This means that, at given temperature, equilibrium conditions are determined, particularly pressure and temperature. If, like here, external pressure is fixed at a value P_{ext} higher than the equilibrium value P_{eq} (or equivalently $C_{ext} > C_{eq}$), the system continuously absorbs gas to create new crystals. Thus, m_{2b} continuously increases and is assumed to be asymptotycally proportional to : t^{α} where $\boldsymbol{a}$ is a positive exponent.

Remark : in presence of agglomeration, the situation is more complex and will be examined in a next paper (Cournil and Herri, 2002). For the moment, we assume that K_{agg} is zero.

As, in Equation (13), product $G_b m_{2b}$ should keep finite values, G_b necessarily tends to zero, thus is of the form :

$$G=Kt^{-a} \tag{25}$$

Thus, from (8), c_b tends asymptotycally to C_{eq}.

Putting these asymptotic values into (13) gives :

$$m_{2b}=\frac{A}{K}t^a \tag{26}$$

$$\text{with : } A=\frac{k_L a C_{eq}\boldsymbol{s}_{ext}v_{mol}}{k_v} \tag{27}$$

Asymptotic value of the nucleation rate in the film is :

$$\overline{B'_1}=\frac{k_1}{n+1}\boldsymbol{s}^n_{ext} \tag{28}$$

The following steps of the procedure consist of :

i) putting m_{2b} and G_b into Eqn(24) and deriving m_{1b}

ii) putting m_{1b} and G_b into Eqn (23)and deriving m_{0b}

iii) putting m_{0b} into Eqn (22) and identifying $\boldsymbol{a}$ and K

iv) expressing the different moments and characteristics of the crystal population (particle number and mean diameter).

-typical cases

The previous procedure can be applied to different situations of determining crystallization processes.

-film nucleation and bulk growth

In this case, the basic assumption is that nucleation only occurs in the film and is negligible in the bulk (due to too low supersaturation in the bulk).

Equations (24), (23), (22) can be respectively simplified in :

$$\frac{\mathrm{d}m_{2b}}{\mathrm{d}t}=2G_b m_{1b}+\frac{\boldsymbol{d}}{H}\overline{B'_1}D'^2_{b0}$$

$$\frac{\mathrm{d}m_{1b}}{\mathrm{d}t}=G_b m_{0b}+\frac{\boldsymbol{d}}{H}\overline{B'_1}D'_{b0}$$

$$\frac{\mathrm{d}m_{0b}}{\mathrm{d}t}=\frac{\boldsymbol{d}}{H}\overline{B'_1}$$

Applying the previous procedure successively gives :

$$m_{1b}=\frac{A}{2K^2}\boldsymbol{a}t^{2a-1}-\frac{\boldsymbol{d}}{HK}\overline{B'_1}D'^2_{b0}t^a \tag{29}$$

$$m_{0b}=\frac{A}{2K^3}\boldsymbol{a}(2\boldsymbol{a}-1)t^{3a-2}-\frac{\boldsymbol{d}}{HK^2}\overline{B'_1}D'^2_{b0}t^{2a-1}-\frac{\boldsymbol{d}}{H}\overline{B'_1}D'_{b0}t^a \tag{30}$$

$$\begin{aligned}1=&\frac{AH}{2dK^3}\frac{n+1}{k_1 s^n_{ext}}a(2a-1)(3a-2)t^{3a-3}\ldots\\&\ldots-\frac{1}{K^2}(2a-1)D'^2_{b0}t^{2a-2}-\frac{1}{K}D'_{b0}a\,t^{a-1}\end{aligned} \tag{31}$$

The values of $\boldsymbol{a}$ and K are obtained from identification according to the powers of t in Equation (31) :

$\boldsymbol{a} = 1$ and K is a root of the equation:

$$1=\frac{AH}{2\boldsymbol{d}K^3}\frac{n+1}{k_1\boldsymbol{s}^n_{ext}}-\frac{1}{K^2}D'^2_{b0}-\frac{1}{K}D'_{b0}$$

If the initial size of the nuclei transferred to the bulk can be neglected, then using also (2) and (27), we can express respectively K, N_b, the asymptotic number of crystals in the bulk and $\overline{D}_b$ their mean size :

$$N_b=\frac{D_G a k_1 S\boldsymbol{s}^n_{ext}}{(k_L a)(n+1)}t \tag{32}$$

$$\overline{D}_b=\left(\frac{(k_L a)^2 C_{eq}v_{mol}H}{2D_G a k_v}\frac{n+1}{k_1\boldsymbol{s}^{n-1}_{ext}}\right)^{\frac{1}{3}} \tag{33}$$

Consequently, in this case, the number of crystals increases linearly and their mean size keeps constant.

- film nucleation, bulk growth, and bulk secondary nucleation

In this case, we still consider film nucleation and bulk growth as determining, however we take also into account secondary nucleation which could play a part because of the continuously increasing surface area of the crystals. As previously we consider that $D'_{b0}=0$.

Equations (24), (23), (22) can be respectively simplified in :

$$m_{1b}=\frac{A}{2K^2}\alpha t^{2\alpha-1} \qquad (34)$$

$$m_{0b}=\frac{A}{2K^3}\alpha(2\alpha-1)t^{3\alpha-2} \qquad (35)$$

$$\frac{k_1\sigma_{ext}^n}{n+1}\frac{\delta}{H}+B_{2b}=\frac{A}{2K^3}\alpha(2\alpha-1)(3\alpha-2)t^{3\alpha-3} \qquad (36)$$

From (8) and (11) follows :

$$B_{2b}=k_2\left(G/k_G\right)^{\frac{m}{p}}\cdot m_{2b} \qquad (37)$$

Using (8) and the expressions (25) and (26) of the asymptotic variation of G and m_{2b} with time, we transform (37) in (38):

$$\frac{k_1\sigma_{ext}^n}{n+1}\frac{\delta}{H}+A\frac{k_2}{k_G^{\frac{m}{p}}}K^{\frac{m}{p}-1}t^{\left(1-\frac{m}{p}\right)\alpha}=\frac{A}{2K^3}\alpha(2\alpha-1)(3\alpha-2)t^{3\alpha-3}$$

Identification according to the powers of t is a little more complicated than previously. Two cases should be considered :

a) $3\alpha-3 = 0$, i.e., $\alpha = 1$, however with : $m > p$; this latter condition expresses that secondary nucleation rate should depend more on supersaturation than growth rate. This behaviour is rather common for “true” secondary nucleation. If these conditions are fulfilled, case a) is asymptotically similar to the situation of film nucleation-growth bulk which was discussed just before (Equations (32)-(34)). This means that asymptotycally bulk “true” secondary nucleation is less active than film primary nucleation.

b) $\left(1-\frac{m}{p}\right)\alpha = 3\alpha-3$, *i.e.*, $\alpha=\frac{3}{\left(2+\frac{m}{p}\right)}$

however, with $m < p$; as explained in the previous section, this latter condition is not frequently met for “true” secondary nucleation ; however, it is observed of course in the case of purely mechanical nuclei generation ($m=0$).

The respective expressions of asymptotic N_b, and $\overline{D}_b$ are :

$$N_b=\frac{k_L a C_{eq}\sigma_{ext}\nu_{mol}HS}{2k_v\left[\alpha(2\alpha-1)\right]^{\alpha-1}\left[\frac{k_G^{\frac{m}{p}}}{2k_2}(3\alpha-2)\right]^{\alpha}}t^{3\alpha-2}$$

$$\overline{D}_b=\frac{\left[\frac{k_G^{\frac{m}{p}}}{2k_2}\alpha(3\alpha-2)\right]^{\frac{\alpha}{3}}}{(2\alpha-1)^{1-\frac{\alpha}{3}}}t^{1-\alpha}$$

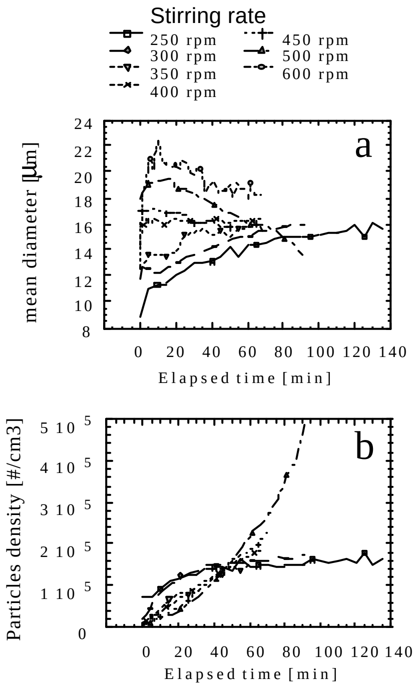

Figure 2 Time evolution of crystal mean diameter (a) and number per unit volume (b) at different stirring rates during methane hydrate crystallization at 30 bars and 1°C

In the case of secondary nucleation of purely mechanical origin ($m=0$; $\alpha = 3/2$), these expressions become:

$$N_b=\frac{3k_L a C_{eq}\sigma_{ext}\nu_{mol}HS}{2k_v^{\frac{1}{2}}\left[\frac{15}{4k_2}\right]^{\frac{3}{2}}}t^{\frac{5}{2}} \quad (39) \qquad \overline{D}_b=\frac{\left[\frac{15}{16k_2}\right]^{\frac{1}{2}}}{t^{\frac{1}{2}}} \qquad (40)$$

3 Comparison with experimental data

The theoretical results are now examined in the framework of the already mentioned experimental study of (Herri *et al.*, 1999) on methane hydrate crystallization. This work is very rich in data because of the instrumentation of the reactor with an optical sensor for in situ particle size determinations.

Agreement between theory and experiment will be discussed in several aspects :

Time evolution of crystal number and mean diameter at different stirring rates. In Figure 2, we recall experimental results obtained by us (Herri *et al.*, 1999) on methane hydrate crystallization. According to the stirring rate, the time evolution of the crystal density and mean diameter is quite different.

Concerning the asymptotic law of variation with time of the crystal mean diameter and crystal number, if we represent them using respectively a law in t^{β} and a law in t^{ε}, we obtain the following results :

$\beta < 0$ and $\varepsilon > 1$ at high stirring rate (500 rpm)

$\beta = 0$ and $\varepsilon = 1$ at medium values (400 rpm)

$\beta > 0$ and $\varepsilon < 1$ at low stirring rate (250 rpm)

These results are quite consistent with the different theoretical possibilities we considered before, i.e., respectively :

i) case of film nucleation, bulk crystal growth and secondary nucleation (with m/p = 1/2 at 500 rpm); this latter assumption is particularly plausible, because high stirring rate can result in crystal erosion or attrition;

ii) case of film nucleation and bulk crystal growth (at these moderate stirring rates, agglomeration and fragmentation have opposite somewhat balanced effects);

iii) case of film nucleation, bulk crystal growth and agglomeration ; at the lowest stirring rate agglomeration overcomes fragmentation

Influence of stirring rate on the crystal mean diameter. We consider only experiments in which primary nucleation and crystal growth are preponderant, that is to say with constant asymptotic mean diameter $\overline{D}_b$.

From Figure 2, it appears that $\overline{D}_b$ increases with the stirring rate in the range [350 rpm - 450 rpm] for which $\overline{D}_b$ is nearly independent of time. The previous model predicts the following asymptotic value for this diameter:

$$\overline{D_b} = \left(\frac{(k_L a)^2 C_{eq} v_{mol} H}{2 D_G a k_v} \frac{n+1}{k_1 s_{ext}^{n-1}} \right)^{\frac{1}{3}} \qquad (33)$$

In this expression, the most dependent factor on stirring rate is k_L which is known to be an increasing function (Wachi and Jones, 1991b, Herri *et al.*, 1999). This is quite consistent with the experimental results.

4. Conclusion

In this paper we propose a new discussion on gas-liquid crystallization in the framework of two-film models. Assumptions and interpretations are systematically placed in the context of the experimental system methane hydrate-water. This leads us to propose a simplified, however realistic, expression of the process dynamics in the form of a system of differential equation in dissolved gas concentration and crystal distribution moments. Instead of solving numerically this system as several authors did, we propose a general and easy procedure to obtain the asymptotic solution. According to the relevant crystallization processes (primary nucleation, secondary nucleation, crystal growth, agglomeration), the different asymptotic laws of crystal number and mean diameter versus time are calculated and found in an analytical form in which the influence of different parameters (stirring rate, supersaturation) is quantitatively expressed. Using these predictions, we can interpret data coming from methane hydrate crystallization. In particular, we prove the strong influence of stirring rate through its action on agglomeration and fragmentation.

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