

MODELING THE METHANE HYDRATE FORMATION IN AN AQUEOUS FILM SUBMITTED TO STEADY COOLING

Juan Ramón Avendaño-Gómez *
Laboratorio de Ingeniería Química Ambiental
ESIQIE
Instituto Politécnico Nacional
Sección de Estudios de Posgrado
UPALM ed. 8, México D. F. 07738
MEXICO

Fernando García-Sánchez
Laboratorio de Termodinámica
Instituto Mexicano del Petróleo
Eje Central Lázaro Cárdenas, 172
México D. F., 07730
MEXICO

Dynora Vázquez Gurrola
Laboratorio de Diseño de Plantas
UPIBI
Instituto Politécnico Nacional
Acueducto s.n La Laguna Ticoman.
México D. F., 07340
MEXICO

ABSTRACT

The aim of this work is to model the thermal evolution inside a hydrate forming system which is submitted to an imposed steady cooling. The study system is a cylindrical thin film of aqueous solution at 19 Mpa, the methane is the hydrate forming molecule and it is assumed that methane is homogeneously dissolved in the aqueous phase. The model in this work takes into account two factors involved in the hydrate crystallization: 1) the stochastic nature of crystallization that causes sub-cooling and 2) the heat source term due to the exothermic enthalpy of hydrate formation. The model equation is based on the resolution of the continuity equation in terms of a heat balance. The crystallization of the methane hydrate occurs at supercooling conditions ($T_{\text{cryst}} < T_F$), besides, the heat released during crystallization interferes with the imposed condition of steady decrease of temperature around the system. Thus, the inclusion of the heat source term has to be considered in order to take into account the influence of crystallization. The rate of heat released during the crystallization is governed by the probability of nucleation $J(T)$. The results provided by the model equation subjected to boundary conditions allow depict the evolution of temperature in the dispersed phase. The most singular point in the temperature–time curve is the onset time of hydrate crystallization. Three time intervals characterize the temperature evolution during the steady cooling: (1) linear cooling, (2) hydrate formation with a release of heat, (3) a last interval of steady cooling.

Keywords: gas hydrates, undercooling, stochastic nucleation.

* Corresponding author E-mail: juan_avendan@yahoo.com.mx

NOMENCLATURE

A	Coefficient in function $J(T)$
B	Coefficient in function $J(T)$
C_{ps}	Specific heat of the dissolved methane at solid phase
C_{pl}	Specific heat of the dissolved methane at liquid phase.
ΔG	Gibbs free energy
E	Coefficient in function $J(T)$
i	Radial position in discretized terms
J	Probability of nucleation
k	Boltzman constant
k	Global heat transfer coefficient
L	Apparent latent heat of the dissolved phase
m	Time in discretized terms
M	Final time of the cooling experiment in discretized terms
N	Total number of liquid micro-domains
n	Number of crystallized micro-domains
$\dot{q}$	Rate of heat released by the crystallization of micro-domains
r	Radial position
R	Width of the annulus cylinder
t	Time
t_{end}	Final time of the cooling experiment
T_F	Melting temperature of the dispersed phase
T_{end}	Lower limit of temperature of the cooling experiment
β	Cooling rate
λ_s	Thermal conductivity of the dissolved phase in liquid state
λ_l	Thermal conductivity of the dissolved phase in solid state
ϕ	Fraction of solidified micro-domains
Φ	Mass fraction of dissolved phase
Θ	Temperature in discretized terms
μ	Chemical potential
ρ	Density of the dissolved phase

INTRODUCTION

Gas hydrates or clathrate hydrates are one class of inclusion compounds. The gas hydrate is an ice-like compound; it results from kinetic process of crystallization of an aqueous solution supersaturated with a dissolved gas.

From the thermodynamics point of view, the prediction of hydrate formation is performed out knowing the gas and water composition and the

temperature (or pressure) of the gas-water system. In this way, the series of equilibrium points allows to construct the phase diagram of the hydrate system. The state of the art in equilibrium thermodynamics of methane hydrates has evolved since the pioneering works of Parrish and Prausnitz (1972), Ng and Robinson (1976), Vyasuskas and Bishnoi (1983), Englezos et al (1987).

However, when the hydrate former solution is subject to dynamic conditions of pressure and temperature, the onset point of methane hydrate formation differs from that stipulated by equilibrium thermodynamics. Such a dynamic scenario characterized by low temperatures and high pressures is commonly met during the transportation of hydrocarbon fluid in submarine pipelines. First, the water content of the hydrocarbon fluid condensates and then high pressure enhances the solubility of methane gas in the liquid aqueous phase. The concentration of methane in the aqueous solution gradually increases until the system reaches the saturation concentration. From this moment or super saturation condition, the environment required to begin the nucleation and crystallization is fulfilled. Nucleation and growth of the crystal occur predominantly on the gas-water interface, where the super saturation is higher than in bulk water. Nevertheless, in several cases the solution reaches a uniform super saturation before the appearance of the nuclei, and as a result, the nucleation process occurs everywhere in the liquid phase.

Unfortunately, the actual temperature of hydrate formation in undersea pipelines usually differs from that stipulated by equilibrium considerations. Such a difference between theoretical equilibrium temperature T_e , and the actual temperature of hydrate crystallization is due to the stochastic nature of nucleation. The difference $\Delta T = T_e - T$ is also known as sub-cooling. In addition, the non-equilibrium occurrence of hydrate formation is emphasized by the amount of heat released during the crystallization. Most of the hydrate work focuses on the equilibrium conditions of hydrate formation [13–18]. It has been confirmed since the nineteenth century that hydrate formation follows a complicated process of crystallization. In this sense, there are still few works that deals with the kinetic aspects of hydrate formation. Two of the pioneering works that deals with the induction

time concept are due to Englezos et al. [9] and the work of Natarajan et al. [19]. It is worthwhile to mention the experimental works of Jakobsen et al. [20], Lekvam and Ruoff [3], Munck et al. [21] and Zatssepina and Buffet [22]. The works aforementioned make evident the influence of the supercooling on hydrate formation kinetics. As those fine writers have shown, the gas hydrate is formed through a kinetic process which requires three necessary steps: (1) The first one is supercooling, (2) The second step is nucleation, (3) The third step is the growth of the crystal.

The objective of this work is to develop a simplified model to determine the onset time of hydrate nucleation within a hydrate forming system subject to an imposed steady cooling. The model includes a function that allows to consider the stochastic nature of the nucleation.

The model in this work necessarily takes into account both factors stated before: 1) the stochastic nature of crystallization that causes sub-cooling and 2) the heat source term due to the exothermic enthalpy of crystallization. The steady temperature decrease β acting on the hydrate former system is a known parameter in the model. Thus, once the onset point of hydrate crystallization is determined, it is possible to transform the sub-cooling ΔT into an induction time.

STATEMENT OF THE PROBLEM

Methane hydrate is formed through a kinetic process of nucleation and crystallization. The need to predict the onset time of nucleation with a model necessarily requires to consider the induction time. In this work, the model is based on the resolution of the continuity equation in terms of the heat balance which includes the source term and the probability of nucleation $J(T)$. The boundary volume of the aqueous solution is a cylindrical annulus of a few μm of width as shown in figure 1. The internal radius R of the crucible is small in comparison to its length L ($R < L$). In order to simulate the steady cooling of the emulsion we imposed a constant cooling rate around the external surface of the boundary volume.

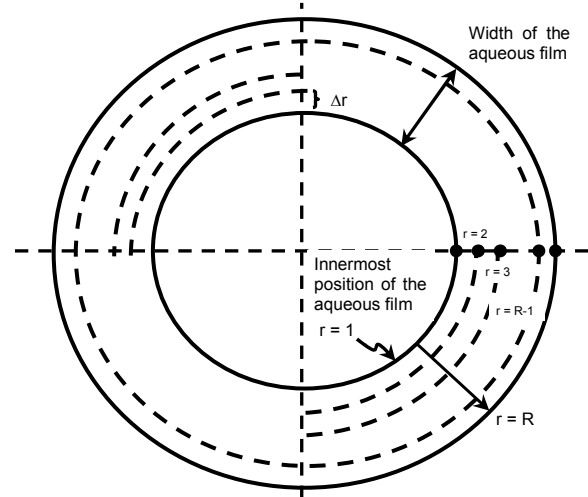


Figure 1. The study system is an annulus cylinder of width R . The system may be assimilated to an aqueous film at the saturation concentration in methane. The aqueous thin film is partitioned in a grid of 40 points.

The interest of this work to the real industrial needs lies in the fact that it enables to link the thermodynamic aspects of hydrate formation with the kinetic aspects through the function probability of nucleation $J(T)$.

Ehmimed et al. [4] measured the influence of the global heat transfer coefficient k on the rate of thermal transfer between a wall and a dispersed system by differential scanning calorimetry. In that work [4] the authors concluded that thermal transfer is influenced by the heat transfer coefficient only for values of k lower than $100 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. The modeling conditions in this particular work are similar to that reported by Zeraouli [5]. The coefficient of heat transfer greater than $500 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, so, it is possible to neglect the influence of the global heat transfer coefficient k on the rate of thermal transfer. In addition, the viscosity of the aqueous solution allows to consider the liquid as a Newtonian fluid. Therefore, we can assume that the thermal transfer between the cooling boundary and the solution is not ruled by the global heat transfer coefficient k , neither by the viscosity of the emulsion. In contrast, the thermal transfer is strongly influenced by an important amount of heat released during the formation of the solid hydrate. In consequence, the temperature distribution in the time interval of

hydrate formation in the emulsion is determined by two effects:

- (1) The external effect of the imposed steady cooling (Temperature decrease from the bulk liquid phase towards the boundary wall).
- (2) The internal effect due to the exothermic heat released by the crystallization of the droplets.

For long, thin cylinders having negligible axial variations in heat flux, the gradient of heat transfer in the radial direction dominates over the axial. Since the geometry of the boundary volume fulfills this condition of $R > L$ we can focus the analysis on the heat transfer in radial direction. Additionally, since the methane is homogeneously dissolved in the solution volume, we can assume that the temperatures varies in the radial direction, such a variation of temperature is axisymmetrical [6,7]. The metastability of the solution is broken when the nucleation begins. In this manner, the problem is to determine the temperature of solution $T(r, t)$, at any time, t during the steady cooling, and for all position r between the wall of the annulus cylinder and the radius R (interface of the aqueous film in contact with the methane gas). The initial and final temperatures of the cooling interval are free parameters that must be specified. In this work, the steady cooling begins at 298 K and the lower limit of temperature is 240 K. The cooling rate denoted as β is $10 \text{ K} \cdot \text{hr}^{-1}$.

Therefore, the numerical modeling of the thermal history is expressed as a heat transfer balance. A heat source term is taken into consideration within the energy balance of the dispersed phase. During the thermal history of the aqueous solution, the onset time of crystallization initiates the release of heat inside the aqueous solution. The source term depends on the probability of nucleation. Not all the aqueous volume crystallizes simultaneously due to the steady cooling. Actually, a progressive crystallization occurs and the rupture of the metastable state in the liquid phase begins when the rate of nucleation $J(T) > 0$ [8].

Hereafter ϕ shall denote the mass fraction of the dissolved methane phase in the solution. This parameter is the ratio of the mass of methane to the total mass of aqueous solution. It is assumed that the thermal conductivity λ and the specific heat C_p do not vary in the range of cooling temperatures. Nevertheless, λ and C_p are considered dependent functions of the fraction of

crystallized mass ϕ in the solution. The fraction of solid state within the solution at position r and time t shall be denoted by $\phi(r, t)$ and it varies between $0 < \phi(r, t) < 1$. Therefore, from the work of Fouconnier et al. [10] a linear law of variation allows to write the following equations:

$$\lambda(\phi) = \lambda_l + (\lambda_s - \lambda_l)\phi \quad (1)$$

$$C_p(\phi) = C_{p_l} + (C_{p_s} - C_{p_l})\phi \quad (2)$$

The thermal transfer during the cooling process of the aqueous solution is modeled with the continuity equation of heat conduction:

$$\rho \cdot C_p \frac{\partial T}{\partial t} = \nabla(\lambda \nabla T) + \dot{q} \quad (3)$$

The heat source term $\dot{q}$ is different from zero at the onset time of nucleation. The occurrence of such event at undercooling conditions is governed by a probabilistic law of nucleation [9,11,12]. A fraction of the undercooled aqueous volume crystallizes $\phi(r, t) \neq 0$ only when the probability of nucleation $J(T) > 0$. The latent heat of solidification of the fraction $\phi(r, t)$ represents the

heat source term $\dot{q}$. The solution of equation (3) enables the determination of the space-time distribution of temperature across the radial position in the annulus cylinder $T(r, t)$. Before enterprising the solution of equation (3) it is important to point out the connection between the

heat source term $\dot{q}$ and the probability of nucleation $J(T)$. In order to precise such a connection, it is convenient to remind the mechanisms of nucleation and crystallization that allow to derive an expression of the type

$\dot{q} = J(T)$. Then, the continuity equation (3) can be expressed in terms of the dependent variable $T(r, t)$ and known functions.

The probability of nucleation .

The supercooling phenomenon is characterized by the persistence in the liquid state of a material below its melting point T_F . However, the rupture of the metastable equilibrium of the supercooled liquid occurs at the beginning time of hydrate formation. One of the main parameters that has

influence on the supercooling is the volume of the liquid. For example, a bulk volume of water of a few cm³ is characterized by a supercooling degree of $\Delta T = -14$ K, while micro-droplets of water dispersed in a w/o emulsion (volumes of a fraction of μm^3) the crystallization occurs at 233 K or lower temperatures [5, 6, 25].

The steady cooling of an aqueous solution shows the stochastic nature of crystallization [4].

During the induction time the nuclei growth in size, once the nuclei attain a stable size the metastable equilibrium of the aqueous solution no longer exists. The occurrence of such instant in time is a phenomenon of random and probabilistic nature if the conditions of supercooling, pressure and composition are fulfilled [11, 27]. At conditions of nucleation, it is not possible to determine the place where the nuclei are formed inside the aqueous volume. Nevertheless, a probability $P = VJt$ of appearance of solid phase within the aqueous volume can be predicted because it is possible to calculate the nucleation rate J [5, 22].

The appearance of a nucleus is essentially a random phenomenon for which a probability can be predicted. If we consider a population of N aqueous micro-domains whose volumes are V , the nucleation will not occur in all those micro-domains at the same time as temperature decreases. Instead, the birth of nuclei occurs randomly. Let $n(r, t)$ be a fraction of N that represents the number of solidified micro-domains at position r and time t , then the proportion of solidified micro-domains in the total population of N at position r and time t is:

$$\varphi(r, t) = \frac{n(r, t)}{N} \quad (4)$$

and the number of micro-domains remaining in liquid state at time t is $N - n(r, t)$. Assuming that each solidified micro-domain of n corresponds to the appearance of a nucleus, there is an equal probability of forming a nucleus in each of them. The probability of nucleation in a micro-domain of volume V in a time increment dt is $1/VJdt$.

Let us consider not only one aqueous micro-domain but a large population composed of N micro-domains per unit volume of aqueous solution. The aqueous solution is submitted to a steady cooling from a starting temperature of 298 K until an imposed temperature lower than T_F . At the beginning of the cooling all the aqueous micro-domains N are in liquid state, as the cooling progresses the metastable equilibrium will be broken at instant time t . In consequence, at time $t > 0$ there are $n(r, t)$ micro-domains in solid state per unit volume aqueous solution.

The rate of crystallization is proportional to the number of micro-domains remaining in liquid state, $N - n(r, t)$, and proportional also to the probability of crystallization by unit of time and volume $J(T)$. The rate of crystallization of those remaining micro-domains in a time increment dt is expressed as: $dn(r, t)$

$$\frac{dn(r, t)}{dt} = [N - n(r, t)] \cdot J(T) \quad (5)$$

We can also express equation (5) in terms of the proportion of crystallized micro-domains $\varphi(r, t)$, then:

$$\frac{d\varphi(r, t)}{dt} = [1 - \varphi(r, t)] \cdot J(T) \quad (6)$$

Equation (6) expresses the kinetics of crystallization of the dispersed micro-domains inside the total volume of aqueous solution subject to steady cooling.

4. Estimation of the rate of nucleation $J(T)$

In classical nucleation theories the rate of homogeneous nucleation J represents the number of nuclei formed per unit time and unit volume, the expression of $J(T)$ is given by:

$$J(T) = A \cdot \exp\left(-E + \frac{\Delta G}{kT}\right) \quad (7)$$

$J(T)$ is a nonlinear function of temperature T . For temperatures above the melting temperature the function $J(T)$ is close to zero. On the contrary, as

supercooling increases $J(T)$ also increases exponentially and very quickly [8,28].

The coefficient E is a function of the viscosity of the liquid whereas ΔG is the energy barrier that nuclei must overcome in order to reach a stable critical size. The energy barrier is basically imposed by the interfacial tension between the nuclei and the liquid phase [12,29,30].

Moreover, if the viscosity of the liquid is too large in comparison to ΔG , then the value of E must be taken into consideration. A large value of E implies that the rate of nucleation is limited by viscosity. In this work, the viscosity of the aqueous solution behaves as a Newtonian liquid, hence, it has a weak influence on the crystallization behavior of the dispersed phase [1]. It is assumed the following form of Eq. (7):

$$J(T) = A \cdot \exp\left(\frac{\Delta G}{kT}\right) \quad (8)$$

Quantifying the rate of hydrate nucleation is a difficult experimental problem. First, we must be able to detect the appearance of hydrate nuclei. Second, we need to observe a large number of nucleation events in order to obtain a meaningful statistical average for the nucleation rate.

The rate of nucleation can be determined by means of the differential scanning calorimetry technique (DSC) [6, 31]. An experimental function described in the form of equation (9) can be fitted from measurements by means of differential scanning calorimetry [5, 8].

$$J(T) = A \cdot \exp\left(\frac{-B}{T \cdot (T - T_F)^2}\right) \quad (9)$$

To carry out the experimental procedure may turn most difficult than the determination of A and B . Several temperatures must be recorded at different positions inside the sample container, this implies the use of thermocouple in contact with the liquid. In this work such method was not followed since it requires very coercive experimental conditions inside the crucible. A complete description of the method may be found in references [5,27,32,33].

The main condition to validate the quantification of $J(T)$ by means of the cooling-heating thermogram is to use a cooling rate lower than $15 \text{ K} \cdot \text{hr}^{-1}$. In this manner we can assume that the same temperature is maintained between the first layer of liquid inside the crucible and the surrounding resistance of the calorimeter [5].

In this work the coefficients A and B of equation (9) are fitted from kinetic data of a previous experimental work developed by Sloan et al [1]. The fitted values are $A = 1.6755 \times 10^{34} \text{ nuclei} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ and $B = 4 \times 10^6 \text{ K}^3$.

MATHEMATICAL MODEL AND BOUNDARY CONDITIONS

Assumptions and derivation of the model.

The nonlinear heat conduction of a cylindrical annulus of aqueous solution is defined by the model equation (3). Equation (3) can be expressed in terms of the dependent variable $T(r, t)$, the rate of crystallization $J(T)$ and the fraction of crystallized micro-domains $\varphi(r, t)$. The precedent assumption of $R < L$ enables to consider a one-dimensional heat conduction in radial direction [34]. The analog form of equation (3) in cylindrical coordinates is:

$$\rho \cdot C_p \cdot \frac{\partial T(r, t)}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left[r \cdot \lambda(r, t) \cdot \frac{\partial T(r, t)}{\partial r} \right] + \dot{q}(r, t) \quad (10)$$

The thermal properties of the dissolved methane in Eqs. (1) and (2) are linear functions of $\varphi(r, t)$. In this sense, during the steady cooling $\varphi(r, t) = 0$ for the time interval where the dissolved methane in the form of subcooled liquid. Nevertheless, from the moment of hydrate formation $\varphi(r, t) > 0$ and increases until $\varphi(r, t) = 1$. In consequence the thermal properties λ and C_p change in time. In this sense, the rupture of the metastable equilibrium of the liquid micro-domains points out the beginning of hydrate formation.

The source term is no longer $\dot{q} = 0$ in reason of the exothermic character of the phase transition. The heat flow per unit volume of dispersed phase (in

$J \cdot m^{-3} \cdot s^{-1}$) is proportional to the kinetics of crystallization. The relation between $\dot{q}(r, t)$ and the kinetics of crystallization can be expressed as follows:

$$\dot{q} = \rho \cdot L \frac{d\phi(r, t)}{dt} \quad (11)$$

where L is the apparent latent heat of the dissolved methane.

The boundary conditions.

The temperature of the cooling fluid decreases at a constant rate, at $t = 0$, $T_\infty(0) > 0$ where T_F is the melting temperature of the dissolved methane. At any time $t > 0$ the external surface of the cylindrical annulus is always in contact with the cooling fluid at $T_\infty(t)$, therefore:

$$T(r, t) = T_\infty(t) \quad \text{at} \quad r = R \text{ and } t > 0$$

The condition of axisymmetrical temperatures in relation to r imposes:

$$\frac{\partial T(r, t)}{\partial r} = 0 \quad \text{at} \quad r = 0 \text{ and } t > 0$$

The initial conditions

$$\begin{aligned} T(r, t) &= T_\infty(0) > T_F & \text{for} & \quad 0 < r < R, t = 0 \\ \phi(r, t) &= 0 & \text{for} & \quad 0 < r < R, t = 0 \end{aligned}$$

Numerical solution of the model equation

The equation (10) of heat conduction can be solved by means of a numerical algorithm for $T(r, t)$. Here we choose an explicit forward finite difference method for the solution of the partial differential equation (10). In order to determine $T(r, t)$ in the radial direction during the cooling, the position coordinate r and the time t are represented by discrete set points m and i respectively,

$$\begin{aligned} i &= 1, 2, 3, \dots, I & \text{for} & \quad t_1 = 0, \quad t_2 = t_1 + \Delta t, \quad t_3 = t_1 + \\ & & & \quad 2 \Delta t, \dots, t_{\text{end}} \end{aligned}$$

$$m = 1, 2, 3, \dots, M \quad \text{for} \quad r_1 = 1, \quad r_2 = r_1 + \Delta r, \quad r_3 = r_1 + 2 \Delta r, \dots, R$$

Thus, the coordinate r in radial direction is represented by a dimensional grid shown in Fig. 1. The innermost position of the aqueous film corresponds to the radius $r = 1$ is assigned with the node $m = 1$, each node spans the radius with a fixed radial length Δr . At radius R the corresponding node is M . The duration of time of the cooling experiment is also discretized by constant time steps Δt . The cooling experiments begin at $t = 0$ that corresponds in the time grid to $i = 1$, the final instant of the experiment t_{end} in the finite difference representation corresponds to $i = I$. Hereafter we denote the temperature and the crystallized fraction in node m and time i as Θ_{im} and ϕ_{im} respectively. The explicit forward scheme means that $\Theta_{i+1, m}$ for each m can be calculated explicitly from the quantities that are already known. The requirement of stability to maintain convergence is:

$$\frac{\Delta t}{\Delta(r)^2} \leq \frac{\rho \cdot \min(C_{pl}, C_{ps})}{4 \max(\lambda_l, \lambda_s)} \quad (12)$$

The solution of the nonlinear second order partial differential equation (10) is carried out by means of the explicit finite difference approach. The resultant equations are as follows:

$$\Delta r = \frac{2 \cdot R}{2 \cdot M - 1} \quad (13)$$

$$\Delta t = \frac{T}{I - 1} \quad (14)$$

$$\Theta_m^{i+1} = \Theta_m^i + L \cdot \Delta t \cdot \frac{1}{C_{p1}^i} \cdot (1 - \phi_1^i) \cdot J(\Theta_1^i) + 4 \cdot \frac{\Delta t}{\rho \cdot (\Delta r)^2} \cdot \frac{\lambda_1^i}{C_{p1}^i} \cdot (\Theta_2^i - \Theta_1^i) \quad (15)$$

$$\begin{aligned} \Theta_m^{i+1} &= \Theta_m^i + L \cdot \Delta t \cdot \frac{1}{C_{p1}^i} \cdot (1 - \phi_1^i) \cdot J(\Theta_1^i) + \frac{\Delta t}{\rho \cdot (\Delta r)^2} \cdot \frac{\lambda_m^i}{C_{p1}^i} \cdot (\Theta_{m+1}^i - 2\Theta_m^i + \Theta_{m-1}^i) \\ &+ \frac{\Delta t}{\rho \cdot (\Delta r)^2} \cdot \frac{1}{2 \cdot m - 2} \cdot \frac{\lambda_m^i}{C_{p1}^i} \cdot (\Theta_{m+1}^i - \Theta_{m-1}^i) \end{aligned} \quad (16)$$

$$\Theta_{M+1}^i = \Theta_\infty^{i+1} \quad (17)$$

$$\Theta_m^i = \Theta_\infty^i + (1 - \Theta_m^i) \cdot J(\Theta_{M+1}^i) \cdot \Delta t \quad (18)$$

The numerical calculations were performed using a Fortran programming. The step size in time is $\Delta t = 0.0125$ s and 40 radial positions are considered for $\Delta r = 0.0005125$ m.

RESULTS OF THE SIMULATION

The evolution of the temperature $T(r, t)$ of the cylindrical annulus of aqueous solution is obtained from the numerical solution of equations (15) and (16). The parameters used in the modeling are listed in Table 1. The thermo-physical properties of the dissolved methane are listed in Table 2. The aqueous solution contains $\Phi = 0.00305$ mol fraction of dissolved methane ($P = 19.0$ MPa). The melting temperature of the aqueous hydrate solution is $T_m < 293$ K.

Symbol	Value	Units
β	10	K / hr
$T_\infty(0)$	298	K
T_{end}	236	K
Δt	0.0125	s
Δr	0.0005125	m
M	40	Number of radial positions
R	0.0205	m

Table 1. Parameters used in the modeling of the cooling of the aqueous film of methane solution.

Symbol	Value	Units
Φ	62.4	wt %
ρ	194.6748	Kg / m ³
A	1.6755×10^{34}	s ⁻¹
B	4×10^6	K ³
λ_s	2.6973	W / m K
λ_l	0.46022	W / m K
C_{p_s}	1.6628	KJ / Kg K
C_{p_l}	4.029855	KJ / Kg K
L	129.32	KJ / Kg
T_F	293	K

Table2. Thermochemical properties of the dissolved methane in the aqueous solution.

Before starting the cooling experiments, the temperature of the sample is homogeneous inside the boundary volume and equal to $T_\infty(0) = 298$ K. Then, from $t = 0$ a constant steady cooling process is imposed on the external surface of the boundary volume. The temperature of the cooling fluid decreases linearly at a constant cooling rate of $\beta = 10$ K·hr⁻¹. The lower limit of temperature reached in the cooling simulation is $T_{end} = T(r, t) = 236$ K.

The result of a simulation of the cooling process for the radial position $r = 1$ is shown in Fig. 2.

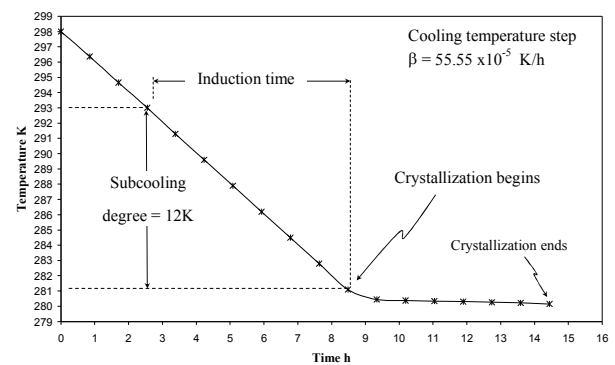


Figure 2. Thermal evolution of the innermost position of the aqueous film.

The evolution of the curve $T(r, t)$ reveals two different behaviours. The first one in the time interval $0 < t < 8$ hr presents the profile of a continuous cooling. During this first stage the

fraction of solidified droplets is zero, $\varphi(r, t) = 0$. The second time interval between 8 hr $< t < 14$ hr presents a different slope of the curve $T(r, t)$. The sudden change of slope at $t = 8.5$ hr indicates the onset time of hydrate crystallization. From the beginning of the second stage $t = 8$ hr the fraction of solidified micro-domains starts to increase $\varphi(r, t) > 0$. This implies that formation of solid hydrate is occurring in the aqueous solution. The fraction $\varphi(r, t)$ shall vary until it reaches the magnitude $\varphi = 1$. Correspondingly, an amount of heat is released as hydrate crystallization progresses in the large population of liquid micro-domains. The heat balance between the imposed steady cooling and the exothermic heat of crystallization results in the change of slope of $T(r, t)$ which is almost horizontal.

From Fig. 2 it can be seen that for the innermost position $r = 1$ the stabilizing effect disappears at $t > 14.5$ hr. From this moment the cooling tendency becomes once again more important than the heat released. The behaviour of $T(r, t)$ for the external position $r = R$ is nearly constant due to the proximity with the cooling fluid. We can also identify the onset time of hydrate crystallization at $t = 8.5$ hr. The constant coefficients A and B in the function $J(T)$ define the influence of the volume of crystal and the interfacial tension liquid–crystal on the process of hydrate crystallization respectively.

REFERENCING OTHER WORKS

[1] D. Clausse, B. Fouconnier, J. Avendaño-Gomez, *Ripening phenomena in emulsions—a calorimetry investigation.*, J. Dispersion Sci. Technol. 23 (2003) 379–391.

[2] E.D. Sloan, F. Fleyfel, *Hydrate dissociation enthalpy and guest size*, Fluid Phase Equilibria 76 (1992) 123–140.

[3] K. Lekvam, P. Ruoff, *A reaction kinetic mechanism for methane hydrate formation in liquid water*. J. Amer. Chem. Soc. 115 (1993) 8565–8569.

[4] J.A. Ehmimed, Y. Zeraouli, J.P. Dumas, A. Mimet, *Heat transfers model during the crystallization of a dispersed binary solution.*, Int. J. Thermal Sci. 42 (2003) 33–46.

[5] Y. Zeraouli, *Étude thermique des transformations des emulsions concentrées: application à la calorimétrie à balayage*. PhD thesis, Université de Pau et Pays de l'Adour, France, 1981.

[6] D. Clausse, *Research Techniques Utilizing Emulsions*. Encyclopedia of Emulsion Technology, vol. 2, Marcel Dekker, New York, 1985.

[7] D. Clausse, *Thermal behavior of emulsions studied by differential scanning calorimetry*. J. Thermal Anal. 51 (1998) 191–201.

[8] S. Gibout, M. Strub, J.P. Dumas, *Estimation of the nucleation probability in emulsions*. Int. J. Heat Mass Transfer 47 (2004) 63–74.

[9] P. Englezos, N. Kalogerakis, P.D. Dholobhai, P.R. Bishnoi, *Kinetics of formation of methane and ethane gas hydrates*. Chem. Engrg. Sci. 42 (11) (1987) 2647–2658.

[10] B. Fouconnier, Y. Manissol, D. Dalmazzone, D. Clausse, *Study of trichlorofluoromethane hydrate formation in w/o emulsions: dissociation energy and equilibria with salt + water solutions.*, Entropie 239/240 (2002) 72–77.

[11] G.F. Frank, J.Z. Chao, B.R. Andrew, D.C. Xiao, J.C. John, R. Lindsay, *Simulation and experiment of the unsteady heat transport in the onset time of nucleation and crystallization of ice from the subcooled solution*. Int. J. Heat Mass Transfer 46 (2003) 3221–3231.

[12] D. Frenkel, *Old and new phases in complex liquids*. Revue de l'Institut Francais du Pétrole 51 (1) (1996).

[13] A. Chapoy, C. Coquelet, D. Richon, *Solubility measurement and modeling of water in the gas phase of the methane/water binary system at temperatures from 283.08 to 318.12 K and pressures up to 34.5 Mpa*. Fluid Phase Equilibria 214 (2003) 101–117.

[14] P. Englezos, N. Kalogerakis, P.R. Bishnoi, *Simultaneous regression of binary VLE and VLLE data*. Fluid Phase Equilibria 61 (1990) 1–15.

- [15] P. Englezos, N. Kalogerakis, M.A. Trebble, P.R. Bishnoi, *Estimation of multiple binary interaction parameters in equations of state using VLE data. Application to the Trebble–Bishnoi equation of state*. Fluid Phase Equilibria 58 (1990) 117–132.
- [16] P. Englezos, P.R. Bishnoi, *Gibbs free energy analysis for the supersaturation limits of methane in liquid water and the hydrate–gas–liquid water phase behavior*. Fluid Phase Equilibria 42 (1988) 129–140.
- [17] G.D. Holder, P.M. Lakshmi, R.P. Warzinski, *Formation of gas hydrates from single phase aqueous solutions*, Chem. Engrg. Sci. 56 (2001) 6897–6903.
- [18] J.B. Klauda, S.I. Sandler, *A fugacity model for gas hydrate phase equilibria*. Ind. Engrg. Chem. Res. 39 (2000) 3377–3386.
- [19] V. Natarajan, P.R. Bishnoi, N. Kalogerakis, *Induction phenomena in gas hydrate nucleation*. Chem. Engrg. Sci. 49 (13) (1994) 2075–2087.
- [20] T. Jakobsen, J. Sjöblom, P. Ruoff, *Kinetics of gas hydrate formation in w/o emulsions. The model system trichlorofluoromethane/water/nonionic surfactant by means of dielectric spectroscopy*. Colloids and Surfaces, A: Physicochemical and Engineering Aspects 112 (1996) 73–84.
- [21] J. Munck, S. Skjold-Jorgensen, P. Rasmussen, *Computations of the formation of gas hydrates*. Chem. Engrg. Sci. 43 (10) (1988) 2661–2672.
- [22] O.Y. Zatsepina, B.A. Buffet, *Nucleation of CO₂ hydrate in porous medium*. Fluid Phase Equilibria 200 (2002) 263–275.
- [23] C.A. Koh, R.P. Wisbey, W. Xiaoping, R.E. Westacott, *Water ordering around methane during hydrate formation*. J. Chem. Phys. 113 (2000) 6390–6397.
- [24] B. Fouconnier, V. Legrand, L. Komunger, D. Clausse, L. Bergfoldt, J. Sjöblom, *Formation of trichlorofluoromethane hydrate in w/o emulsions studied by differential scanning calorimetry*. Progr. Colloid Polym. Sci. 112 (1999) 105–108.
- [25] B. Fouconnier, J. Avendano-Gomez, K. Ballerat-Busserolles, D. Clausse, *Thermal Behaviour of Dispersed Systems*. Marcel Dekker, New York, 2000.
- [26] E.D. Sloan, *Clathrate hydrate measurements: microscopic, mesoscopic, and macroscopic*. J. Chem. Thermodyn. 35 (2003) 41–53.
- [27] J.P. Cordiez, *Contribution à l'étude des phenomenes de nucleation en bain surfondu. Étude de l'acide stearique en emulsion dans l'eau*. PhD thesis, Universite Aix Marseille, France, 1981.
- [28] R.A. Lambert, R.H. Rangel, *Solidification of a supercooled liquid in stagnation-point flow*. Int. J. Heat Mass Transfer 46 (2003) 4013–4021.
- [29] M. Sugaya, Y.H. Mori, *Behavior of clathrate hydrate formation at the boundary of liquid water and a fluorocarbon in liquid or vapor state*. Chem. Engrg. Sci. 51 (1996) 3505–3517.
- [30] H.T. Nguyen, N. Kommareddi, V.T. John, *A thermodynamic model to predict clathrate hydrate formation in water-in-oil microemulsion systems*. J. Colloid Int. Sci. 155 (1993) 482–487.
- [31] H. Suga, *Calorimetric studies of some energy related materials*. Termochim. Acta 328 (1999) 9–17.
- [32] C. Dalmazzone, *Differential scanning calorimetry: a new technique to characterize hydrate formation in drilling muds*. SPE 62962 (2000).
- [33] F. Danes, B. Garnier, *Estimating heat transfer bias of kinetic measurement for polymers by differential scanning calorimetry with isothermal mode*. Int. J. Thermal Sci. 42 (2003) 583–590.
- [34] M.H. Hussain, I. Dincer, *Two-dimensional heat and moisture transfer analysis of a cylindrical moist object subject to drying: a finite difference approach*. Int. J. Heat Mass Transfer 46 (2003) 4033–4039.