This is a repository copy of *Nucleation mechanism and kinetics from the analysis of polythermal crystallisation data: Methyl stearate from kerosene solutions*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/83680/

Version: Supplemental Material

# SUPPLEMENTARY MATERIAL FOR DEPOSITION DETERMINATION OF THE NUCLEATION MECHANISM AND KINETICS FROM THE ANALYSIS OF POLYTHERMAL CRYSTALLISATION DATA: METHYL STEARATE FROM KEROSENE SOLUTIONS

Diana M. Camacho Corzo[a], Antonia Borissova[a], Robert B. Hammond[a], Dimo Kashchiev[b], Kevin J. Roberts[a*], Ken Lewtas[c], Iain More[c]


[a] Institute of Particle Science and Engineering and Institute of Process Research and Development, School of Process, Environment and Materials Engineering, University of Leeds, Leeds, LS2 9JT, UK


[b] Institute of Physical Chemistry, Bulgarian Academy of Sciences, ul. Acad. G. Bonchev 11, Sofia 1113, Bulgaria


[c] Infineum UK Ltd, Milton Hill Business and Technology Centre, Abingdon, OX13 6BB, UK

Keywords: Critical Undercooling, Relative Critical Undercooling, Nucleation, Instantaneous Nucleation, Progressive Nucleation.

*Corresponding author

**ABSTRACT**

Additional and more detailed materials are provided as a supplement to the full paper. These are:

1. The full derivation of the *KBHR* approach [1, 2] for the analyses of solutions' crystallisation kinetics.

2. A sensitivity analysis of the experimental methodology for the collection of sufficient and reliable polythermal data.

3. An expression whereby a system´s nucleation mechanism can be determined from the Nyvlt type data analysis is derived.

**1. Detailed derivation of the model equations (10) and (21) presented in the paper from the Kolmogorov-Johnson-Mehl-Avrami ($KJMA$) expression**

A detailed derivation of the set of expressions that conforms the $KBHR$ approach is presented below. Expressions for the dependence of critical undercooling on cooling rate are derived for the cases of progressive $PN$ and instantaneous nucleation $IN$ mechanism from the Kolmogorov-Johnson-Mehl-Avrami $KJMA$ equation using classical nucleation theory.

The $KBHR$ approach makes use of a master equation presented by Kashchiev [11] that describes the first-order transition nucleation process restricted to one component nucleation by either homogeneous or heterogeneous nucleation.

In crystallisation of a single component the phase transformation kinetics can be explained by the Kolmogorov-Johnson-Mehl-Avrami $KJMA$ equation [11]. The central idea of this equation is to focus on the increment in the fraction transformed and to relate it to the current value of the fraction transformed. A conversion fraction of the crystallites´ volume $\alpha$ is typically defined as

$$\alpha = \frac{V_c}{V} \tag{1}$$

where $V_c$ is the volume of crystallites and $V$ the total volume of solution

Estimating the dependence of the volume of crystallites on time $V_c(t)$ from the master equation is a complex mathematical challenge especially at the late stages of crystallisation when multiple contacts between crystallites should be considered. To overcome this

difficulty the $KJMA$ theory assumes that $V_c$ results from nucleation of material points at a rate $J(t)$ which then only expand irreversibly in radial direction with growth rate $G(t)$ [11].Under this assumption $V_c$ can be easily found at the early stage of crystallisation not long after the initial moment $t = 0$ when there is already a certain level of supersaturation, the whole volume of the solution is available for nucleation and there is no contact between the growing crystallites.

The obtained $KJMA$ formula limited to the early stage of nucleation shows that the progression of the fraction of crystallised volume is controlled by two basic parameters of the process of crystallisation: crystallite nucleation and growth rates [1-2, 11].

### 1.1 Progressive nucleation case

In the case of progressive nucleation the $KJMA$ formula can be expressed as [1, 11]

$$\alpha(t) = k_v \int_0^t J(t') \left[ \int_0^{t-t'} G(t'') dt'' \right]^d dt' \quad for\ \alpha < 0.1 \tag{2}$$

where $t$ and $t'$ are time integration variables, $J$ is the time dependent rate of either homogeneous or heterogeneous nucleation, $G$ is the time dependent radial crystallites´ growth rate, $d = 1,2,3$ is the dimensionality of crystallites´ growth i.e. 3 for spheres or cubes, 2 for disk or plates and 1 for needle shaped crystals, $k_v$ $(m^{3-d})$ crystallites´ growth shape factor i.e. $\frac{4\pi}{3}$ for spheres, 8 for cubes, $\pi H_0$ for disks, $4H_0$ for square plates ($H_0$ is the fixed disk or plate thickness), and $2A_0$ for needles ($A_0$ is the fixed needle cross-sectional area)

Starting at $t = 0$ from the equilibrium temperature $T_e$ at steady cooling, relative undercooling is defined as

$$u = \frac{\Delta T}{T_e} = \frac{T - T_e}{T_e}$$ (3)

where $T$ is the solution's temperature

From classical $3D$ nucleation theory the rate of crystallites nucleation can be expressed in terms of relative undercooling as

$$J(t) = K_J e^{\frac{-b}{(1-u)u^2}}$$ (4)

where $K_J$ is the nucleation rate constant and the dimensionless thermodynamic parameter $b$ is given by

$$b = \frac{k_n v_o^2 \gamma_{eff}{}^3}{k T_e \lambda^2}$$ (5)

where $k_n$ is the nuclei numerical shape factor i.e. $16\pi/3$ for spherical nuclei and $32$ for cubic nuclei, $v_o$ is the volume occupied by a solute molecule in the crystal, $\gamma_{eff}$ is the effective interfacial tension of the crystal nucleus, $\lambda$ is the molecular latent heat of crystallisation and $k$ is the Boltzmann constant

In the same way the radial crystallite growth rate $G(t)$ in terms of undercooling can be expressed as

$$G(t) = m\left(\frac{T_e}{q}\right)^{m-1} K_G^m \left[1 - e^{\frac{-au}{(1-u)}}\right]^{nm} u^{m-1} \tag{6}$$

where $K_G$ is the crystal growth rate constant and $n$ and $m > 0$ crystallites' growth exponents. $n = 1$ for growth mediated by diffusion of solute and $n = 2$ growth controlled by the presence of screw dislocations in the crystallite. $m$ ranges between ½ and 1. $m = 1/2$ for growth controlled by undisturbed diffusion of solute and $m = 1$ for growth by diffusion of solute through a stagnant layer around the crystal and normal or spiral growth limited by transfer of solute across the crystal/solution interface. At $m = 1$ the crystallite radius increase linearly with time [1, 11, 18] and the dimensionless latent heat of crystallisation

$$a = \frac{\lambda}{kT_e} \tag{7}$$

Inserting equation (4) and (6) in equation (2) and defining $t' = \left(\frac{T_e}{q}\right)x$ and $t'' = \left(\frac{T_e}{q}\right)z$, $\alpha$ can be expressed in terms of undercooling

$$\alpha(u) = C_{m,d} \int_0^u e^{\frac{-b}{(1-x)x^2}} \left(\int_0^{u-x} z^{m-1} \left[1 - e^{\frac{-az}{(1-z)}}\right]^{nm} dz\right)^d dx \tag{8}$$

where the dimensionless parameter $C_{m,d}$ is given by

$$C_{m,d} = k_v m^d K_J K_G^{md} \left(\frac{T_e}{q}\right)^{md+1} \tag{9}$$

Equation (8) can be solved if the analysis is restricted to small enough values of $u$ satisfying

inequalities

$$u < 0.1, au < 1 \tag{10}$$

then

$$1 - u \approx 1 \text{ and } 1 - e^{\frac{-au}{(1-u)}} \approx au \tag{11}$$

With these simplifications equation (8) then becomes

$$\alpha(u) = C_{m,d} a^{nmd} \int_0^u e^{\frac{-b}{x^2}} \left[ \int_0^{u-x} z^{(n+1)m-1} dz \right]^d dx \tag{12}$$

Likewise, it has been shown [3, 4] that the inner integral in equation (12) can be solved for

small values of $u$, satisfying

$$u < \left( \frac{2b}{3} \right)^{1/2} \tag{13}$$

leading to

$$\alpha(\mu) = K_{m,d} \left( \frac{\mu^3}{2b} \right)^{(n+1)md+1} e^{\frac{-b}{\mu^2}} \tag{14}$$

Additionally, it was observed [1] that the exponential term in the above equation is an approximate of $e^{\frac{-b}{(1-u)u^2}}$ and thus equation (14) becomes

$$\alpha(\mu) = K_{m,d} \left(\frac{\mu^3}{2b}\right)^{(n+1)md+1} e^{\frac{-b}{(1-\mu)\mu^2}} \tag{15}$$

where the dimensionless parameter $K_{m,d}$ is given by

$$K_{m,d} = \frac{\Gamma[(n+1)md+1]}{(n+1)^d} k_v a^{nmd} K_J K_G^{md} \left(\frac{T_e}{q}\right)^{md+1} \tag{16}$$

and $\Gamma$ is the gamma function

Equation (15) can be expressed in terms of the number of crystallites upon replacing $\alpha$ by $N$ and setting $d = 0$

$$N(u) = K_N \left(\frac{u^3}{2b}\right) e^{\left[\frac{-b}{(1-u)u^2}\right]} \tag{17}$$

where $K_N$ is obtained by making $K_N = K_{m,0}$ and is given by

$$K_N = \frac{VK_J T_e}{q} \tag{18}$$

If plots of $\alpha$ and $N$ are constructed as a function of $u$, they show that $\alpha$ and $N$ are monotonically increasing functions of $u$, with a sharp rise at a certain value that corresponds to the relative critical undercooling for crystallisation $u_c$ [1] defined as

$$u_c = \frac{\Delta T_c}{T_e} \tag{19}$$

where

$$\Delta T_c = T_e - T_c \tag{20}$$

Here $T_c$ is the crystallisation temperature

For $u < u_c$ crystallites are so small or few that $\alpha$ and $N$ cannot be detected or are below the detection limit $\alpha_{det}, N_{det}$ . For $u > u_c$ the solution will contain big enough crystallites that $\alpha$ and $N$ will be detected $\alpha > \alpha_{det}$ and $N > N_{det}$. This means $u_c$ is the maximum relative undercooling that a solution can sustain without detectable crystallisation. In other words, $u_c$ represents the solution metastability limit in terms of undercooling [1,2]. This limit, however, depends on a number of parameters among which one of the most featured is the cooling rate ($q$). With the help of the previously presented equations for $\alpha$ and $N$ the $u_c(q)$ dependence can be determined.

Expressing equation (17) it in terms of $u_c$ gives

$$N(u_c) = N_{det} = \frac{VK_J T_e}{q}\left(\frac{u_c{}^3}{2b}\right)e^{\left[\frac{-b}{(1-u_c)u_c{}^2}\right]} \qquad (21)$$

Upon taking logarithms at both sides of equation (21) a model expression that relates relative critical undercooling $u_c$ with cooling rate $q$ is obtained

$$\ln q = \ln\frac{VK_J T_e}{N_{det}\,2b} + 3\ln u_c - \frac{b}{(1-u_c)u_c{}^2} \qquad (22)$$

Likewise if the parameters $q_0$ , $a_1$ and $a_2$ are defined by

$$a_1 = 3 \qquad (23)$$

$$a_2 = b \qquad (24)$$

$$q_0 = \frac{VK_J T_e}{N_{det}\,2b} \qquad (25)$$

Then the latter equation becomes

$$\ln q = \ln q_0 + a_1 \ln u_c - \frac{a_2}{(1-u_c)u_c{}^2} \qquad (26)$$

When equation (26) is derived by means of $\alpha$, the parameters $q_0$ , $a_1$ and $a_2$ are defined by

$$a_1 = 3 + \frac{3nmd}{md+1} \qquad (27)$$

$$a_2 = \frac{b}{md+1} \tag{28}$$

$$q_0 = T_e \left\{ \frac{\Gamma[(n+1)md+1]K_v a^{nmd} K_J K_G^{md}}{(n+1)^d (2b)^{(n+1)md+1} \alpha_{det}} \right\}^{\frac{1}{(md+1)}} \tag{29}$$

The parameters in equation (26) $\ln q_0$, $a_1$ and $a_2$ have a physical meaning. $a_1$ has a relation with the crystallites growth as its values are determined by the growth exponents $n, m$ and $d$. $a_2$ is proportional or equal to the thermodynamic nucleation parameter $b$ and $q_0$ has a relation with parameters of both nucleation and crystallite growth processes.

### 1.2 Instantaneous nucleation case

In the case of instantaneous nucleation $IN$ a similar derivation was done [2] but taking into account that for the case of $IN$ all crystallites nuclei appear at once with a concentration $C_o$ at the moment $t_o$. Thus the change of the volume of crystallites with time will only depend on the crystallites´ growth and can be expressed as

$$\alpha(t) = k_v C_o \left[ \int_{t_0}^{t} G(t') \, dt' \right]^d \tag{30}$$

Where $t'$ time integration variables, $d = 1,2,3$ dimensionality of crystallite´s growth, $k_v$ $(m^{3-d})$ crystallite´s growth shape factor.

Using equation (6) and setting $t^{'} = \frac{T_e}{q}x$ an expression for $\alpha$ in terms of $u$ can be found

$$\alpha(\mu) = C_{m,d} \left( \int_{\mu_0}^{\mu} x^{m-1} \left[ 1 - e^{\frac{-ax}{(1-x)}} \right]^{nm} dx \right)^{d} \tag{31}$$

where the dimensionless parameter $C_{m,d}$ is given by

$$C_{m,d} = k_v m^d C_o \left( \frac{K_G T_e}{q} \right)^{md} \tag{32}$$

For small enough undercooling

$$u < 0.1, au < 1 \tag{33}$$

in which case

$$1 - u \approx 1 \text{ and } 1 - e^{\frac{-au}{(1-u)}} \approx au \tag{34}$$

The integral in equation (31) can be solved leading to

$$\alpha\,(u) = K_{m,d} \left[ u^{(n+1)m} - u_o^{(n+1)m} \right]^{d} \tag{35}$$

In this expression $u_o$ is the relative undercooling at the time $t_o$ and is given by

$$u_o = \frac{\Delta T_o}{T_e} = \frac{qt_0}{T_e} \qquad (36)$$

Here $\Delta T_o$ is defined by

$$\Delta T_0 = T_e - T_0 \qquad (37)$$

where $T_o$ is the solution temperature at the time $t_o$

Likewise $K_{m,d}$ is given by

$$K_{m,d} = \frac{k_v C_o \left(\dfrac{a^n K_G T_e}{q}\right)^{md}}{(n+1)^d} \qquad (38)$$

As in the case of progressive nucleation $\alpha$ is a monotonically increasing function of $u$ [5] with a sharp rise at a certain value that corresponds to the relative critical undercooling $u_c$ .

Therefore defining $\alpha(u_c) = \alpha_{det}$ and taking logarithms at both sides of equation (35), an expression can be obtained for the dependence of relative critical undercooling on cooling rate

$$\ln q = \ln q_0 + \left(\frac{1}{m}\right) \ln\left[\mu_c^{(n+1)m} - \mu_0^{(n+1)m}\right] \qquad (39)$$

In this expression $u_0 \geq 0$, $u_c > u_o$ and the parameter $q_0$ is given by

$$q_o = \left[\frac{k_v C_o}{(n+1)^d \alpha_{det}}\right]^{\frac{1}{md}} a^n K_G T_e \tag{40}$$

If additionally the undercooling at which all nuclei spontaneously appear is small enough so that

$$u_o^{(n+1)m} \ll u_c^{(n+1)m} \tag{41}$$

Equation (39) takes the form of a straight line given by

$$\ln q = \ln q_o + (n+1)\ln u_c \tag{42}$$

It should be noted that a comparison of equation (39) with the one obtained for $PN$ derived by means of $\alpha$ defined as

$$\ln q = \ln q_0 + \left(3 + \frac{3nmd}{md+1}\right)\ln u_c - \frac{a_2}{(1-u_c)u_c^2} \tag{43}$$

shows how the dependence of the relative critical undercooling $u_c$ on the cooling rate $q$ is different depending of the mechanism by which nucleation takes place. In the case of $PN$ the expression contains parameters depending on both crystallites nucleation and growth whereas in the case of $IN$ the parameters in the expression are only related to the crystallite´s growth.

## 1.3 The crystallites growth shape factors

Crystallites growth shape factors $k_v$ refers to the factor that relates an individual crystallite volume ($V_n$) to its effective radius ($R$), so that $V_n = k_v(R)^d$ [11]

From this definition, the shape factors $k_v$ are derived below for ($1D$) one dimensional growth of needles with constant cross sectional area $A_0$, for ($2D$) dimensional growth of disks or square prisms with constant thickness $H_0$ and for ($3D$) three dimensional growth of spheres or cubes [11]

Sphere, $R = R$ with R sphere radius

$$V_{Sph} = \frac{4}{3}\pi R^3 = k_v R^3$$

$$k_v = \frac{4}{3}\pi$$

Cube, $R = \frac{L}{2}$ with $L$ cube side length

$$V_{cube} = L^3 = k_v R^3$$
$$(2R)^3 = k_v R^3$$
$$k_v = 8$$

Needle, $R = \frac{h}{2}$ with cross sectional are $A_0$ and height h

$$V_{need} = A_0 * h = k_v R^1$$
$$A_0 2R = k_v R$$
$$k_v = 2A_0$$

Disk, $R = R$ with fixed thickness $H_0$

$$V_{disk} = A_{circunference} * H_0 = k_v R^2$$
$$\pi R^2 H_0 = k_v R^2$$
$$k_v = \pi H_0$$

Square plate, $R = \frac{L}{2}$ with fixed thickness $H_0$ and $L$ cube side length

$$V_{Sq\ plate} = A_{square} * H_0 = k_v R^2$$
$$L^2 H_0 = k_v R^2$$
$$(2R)^2 H_0 = k_v R^2$$
$$4R^2 H_0 = k_v R^2$$
$$k_v = 4H_0$$

## 2. Sensitivity analysis of the experimental methodology to collect reliable polythermal experimental data for the application of the $KHBR$ approach

A polythermal methodology to collect enough experimental crystallisation temperatures was presented in the paper. Due to the stochastic nature of nucleation, it was suggested the use of eight different cooling rates $q$ at each concentration and ten temperature cycles at each cooling rate, the latter with the aim of reducing the standard deviation $SD$ of the crystallisation temperatures $T_c$. However, the collection of all these data was not an easy task, as it required running 320 temperature cycles, each of which can last an average of three hours. Thus a sensitivity analysis for the applied experimental methodology was carried out. Three additional scenarios were used with the aim of assessing the influence that reducing either the number of cooling rates or/and temperature cycles, will have on the calculated parameters obtained by applying the $KBHR$ approach. The results are presented in Table 1.

In all cases the slopes of the best linear fit of the data are higher than three, still confirming that methyl stearate crystallises from kerosene by means of the progressive nucleation mechanism. However the values of the slopes obtained from the original methodology (fourth scenario) can be up to 40% higher than those of the first scenario as in the case of 250 g/l.

The higher coefficients of determination in all cases are obtained for the second scenario, in which the number of cooling rates were reduced by 50% in comparison to the original methodology (fourth scenario). On the other hand, for three of the concentrations analysed, the lowest coefficients of determination $R^2$ were obtained for those scenarios in which the number of crystallisation temperature collected at each cooling rate have been reduced from ten to three.

**Table 1. Slopes of the best linear fit of experimental data points plotted in $ln\ q$ vs $ln\ u_c$ coordinates and corresponding coefficients of determination, values of the three free parameters $a_1, a_2\ and\ ln\ q_o$ obtained from the data fitting in $ln\ q$ vs $u_c$ coordinates, according to equation (26) and corresponding coefficients of determination. All values provided at four different concentrations 200, 250, 300 and 350 g/l and four different experimental methodologies scenarios**

4 cooling rates 3 temperature cycles at each cooling rate

| Concentration g/l | Slope best fit data straight line of $ln\ u_c\ Vs\ ln\ q$ | $R^2$ linear fitting | $a_1$ | $a_2 = b$ | $ln\ q_0$ | $q_0\left(\frac{K}{s}\right)$ | $\gamma_{eff}\left(\frac{mJ}{m^2}\right)$ | $R^2 fitting$ equation (26) |
|---|---|---|---|---|---|---|---|---|
| 200 | 4.49$\pm$1.28 | 0.86 | 3 | 0.000365$\pm$3.016*10$^{-4}$ | 8.80$\pm$0.83 | 6634.51 | 1.43 | 0.86 |
| 250 | 3.45$\pm$0.82 | 0.90 | 3 | 0.000091$\pm$1.472*10$^{-4}$ | 8.49$\pm$0.57 | 4880.47 | 0.90 | 0.90 |
| 300 | 3.77$\pm$0.36 | 0.98 | 3 | 0.000157$\pm$3.713*10$^{-5}$ | 8.62$\pm$0.14 | 5515.71 | 1.08 | 0.99 |
| 350 | 3.91$\pm$0.95 | 0.89 | 3 | 0.000259$\pm$1.740*10$^{-4}$ | 8.83$\pm$0.57 | 6828.34 | 1.28 | 0.93 |

4 cooling rates 5 temperature cycles at each cooling rate

| Concentration g/l | Slope best fit data straight line of $ln\ u_c\ Vs\ ln\ q$ | $R^2$ linear fitting | $a_1$ | $a_2 = b$ | $ln\ q_0$ | $q_0\left(\frac{K}{s}\right)$ | $\gamma_{eff}\left(\frac{mJ}{m^2}\right)$ | $R^2 fitting$ equation (26) |
|---|---|---|---|---|---|---|---|---|
| 200 | 4.92$\pm$0.81 | 0.95 | 3 | 0.000521$\pm$1.457*10$^{-4}$ | 8.98$\pm$0.37 | 7966.99 | 1.61 | 0.97 |
| 250 | 3.65$\pm$0.66 | 0.94 | 3 | 0.000132$\pm$1.091*10$^{-4}$ | 8.64$\pm$0.42 | 5639.20 | 1.02 | 0.95 |
| 300 | 4.22$\pm$0.36 | 0.99 | 3 | 0.000262$\pm$2.942*10$^{-5}$ | 8.70$\pm$0.093 | 5998.64 | 1.28 | 0.99 |
| 350 | 3.93$\pm$0.66 | 0.95 | 3 | 0.000239$\pm$1.029*10$^{-4}$ | 8.67$\pm$0.33 | 5847.78 | 1.25 | 0.97 |

8 cooling rates 3 temperature cycles at each cooling rate

| Concentration g/l | Slope best fit data straight line of $ln\ u_c\ Vs\ ln\ q$ | $R^2$ linear fitting | $a_1$ | $a_2 = b$ | $ln\ q_0$ | $q_0\left(\frac{K}{s}\right)$ | $\gamma_{eff}\left(\frac{mJ}{m^2}\right)$ | $R^2 fitting$ equation (26) |
|---|---|---|---|---|---|---|---|---|
| 200 | 4.94$\pm$0.66 | 0.90 | 3 | 0.000531$\pm$1.802*10$^{-4}$ | 8.92$\pm$0.33 | 7488.15 | 1.62 | 0.90 |
| 250 | 3.92$\pm$0.52 | 0.91 | 3 | 0.000212$\pm$1.160*10$^{-4}$ | 8.55$\pm$0.27 | 5153.05 | 1.20 | 0.91 |
| 300 | 4.53$\pm$0.33 | 0.97 | 3 | 0.000410$\pm$7.279*10$^{-5}$ | 8.65$\pm$0.14 | 5719.92 | 1.49 | 0.98 |
| 350 | 4.93$\pm$0.57 | 0.93 | 3 | 0.000649$\pm$1.421*10$^{-4}$ | 8.90$\pm$0.24 | 7337.73 | 1.74 | 0.95 |

8 cooling rates 10 temperature cycles at each cooling rate

| Concentration g/l | Slope best fit data straight line of $ln\ u_c\ Vs\ ln\ q$ | $R^2$ linear fitting | $a_1$ | $a_2 = b$ | $ln\ q_0$ | $q_0\left(\frac{K}{s}\right)$ | $\gamma_{eff}\left(\frac{mJ}{m^2}\right)$ | $R^2 fitting$ equation (26) |
|---|---|---|---|---|---|---|---|---|
| 200 | 5.17$\pm$0.57 | 0.93 | 3 | 0.000653$\pm$1.478*10$^{-4}$ | 8.97$\pm$0.26 | 7834.01 | 1.74 | 0.94 |
| 250 | 4.82$\pm$0.59 | 0.92 | 3 | 0.000543$\pm$1.471*10$^{-4}$ | 8.81$\pm$0.26 | 6673.54 | 1.64 | 0.93 |
| 300 | 5.05$\pm$0.47 | 0.95 | 3 | 0.000629$\pm$1.132*10$^{-4}$ | 8.83$\pm$0.19 | 6811.22 | 1.72 | 0.97 |
| 350 | 5.06$\pm$0.51 | 0.94 | 3 | 0.000698$\pm$1.258*10$^{-4}$ | 8.82$\pm$0.20 | 6761.14 | 1.79 | 0.96 |

As for the errors in the parameters, in the case of the linear fitting, the lowest errors in the slopes are obtained for those scenarios where eight cooling rates were used (third and fourth scenario). In the case of the fitting according to equation (26), for the parameter $ln\ q_0$ in general, the lowest errors are reported again for the third and fourth scenarios while for the parameter $a_2$, the lowest errors are for the case of the second and fourth scenario.

It can be inferred therefore that the number of cooling rates has less influence in improving the fitting of the data by either of the two models, than the number of repetitions for crystallisation temperatures at each cooling rate. On the other hand the use of a higher quantity of cooling rates seems to lead to lower errors in the parameters of the models.

In general, the best results in terms of data fitting and parameters' errors were obtained for the second and fourth scenarios. In the former case however, the effort in the collection of experimental data would be significantly reduced. It is also observed that the values of effective interfacial tensions $\gamma_{eff}$ increase with increasing the number of cooling rates and the number of collected crystallisation temperatures at each cooling rate. These values in the fourth scenario can be between 8% to 60% more than those of the second scenario. However, this difference only represents an increase of maximum 0.6 $\left(\frac{mJ}{m^2}\right)$ in the values of the interfacial tensions. Thus the second methodology is recommended.

**3. Analysis of experimental data using the Nyvlt approach and derivation of a correlation equation whereby a system´s nucleation mechanism can be determined from previous Nyvlt type data analysis**

As already mentioned, Nyvlt developed the original approach for the interpretation of metastable zone width data obtained by the polythermal method. The approach is based on the well-known semi-empirical power law [6, 7]

$$J = k_j (\Delta C_{max})^{m_0} \tag{44}$$

where $k_j$ kinetic constant of nucleation, $m_0$ order of nucleation, $\Delta C_{max} = C_{max} - C_e$ maximum supersaturation, $C_{max}$ solution's concentration at the metastability limit and $C_e$ solution's equilibrium concentration

Nyvlt suggested that a plot of cooling rate $q$ vs critical undercooling $\Delta T_c$ in ln-ln coordinates, will deliver the value of the nucleation order $m_0$ according to

$$\log q = (m_0 - 1) \log \frac{dC_e}{dT} + \ln k_j + m_o \ln \Delta T_c \tag{45}$$

where the maximum supersaturation and undercooling are related by

$$\Delta C_{max} = \frac{dC_e}{dT} \Delta T_c \tag{46}$$

Likewise $\Delta T_c$ is defined by

$$\Delta T_c = T_{diss} - T_c \tag{47}$$

where $T_{diss}$ solution's dissolution temperature and $T_c$ crystallisation temperature

Using Nyvlt approach critical undercooling values $\Delta T_c$ were calculated from the experimental data as the difference between the average of dissolution and crystallisation temperatures at each cooling rate as shown in Table 2.

**Table 2. Average dissolution and crystallisation temperatures as a function of cooling rate for methyl stearate in kerosene at 200, 250, 300 and 350 g/l. Corresponding critical undercooling calculated as the difference between dissolution and crystallisation temperatures**

| Rate °C /min | $T_c$ (°C) | $T_{diss}$ (°C) | $\Delta T_c$ |
|---|---|---|---|
| 200 g/l | | | |
| 0.25 | 12.56 | 17.69 | 5.13 |
| 1 | 11.99 | 18.66 | 6.67 |
| 3.2 | 10.26 | 21.92 | 11.66 |
| 5 | 8.77 | 24.07 | 15.30 |
| 7 | 8.10 | 27.29 | 19.20 |
| 9 | 7.68 | 30.16 | 22.48 |
| 11 | 8.53 | 30.85 | 22.32 |
| 13 | 8.09 | 33.46 | 25.38 |
| 250 g/l | | | |
| 0.25 | 14.88 | 19.59 | 4.71 |
| 1 | 14.16 | 20.81 | 6.65 |
| 3.2 | 12.15 | 24.85 | 12.71 |
| 5 | 10.82 | 28.49 | 17.67 |
| 7 | 10.27 | 31.88 | 21.61 |
| 9 | 9.09 | 34.12 | 25.02 |
| 11 | 10.49 | 36.30 | 25.81 |
| 13 | 10.54 | 38.78 | 28.24 |
| 300 g/l | | | |
| 0.25 | 16.54 | 21.03 | 4.49 |
| 1 | 15.29 | 22.46 | 7.17 |
| 3.2 | 13.96 | 26.87 | 12.91 |
| 5 | 12.95 | 29.88 | 16.93 |
| 7 | 11.53 | 33.68 | 22.14 |
| 9 | 10.82 | 35.88 | 25.06 |
| 11 | 11.66 | 37.30 | 25.65 |
| 13 | 11.80 | 40.03 | 28.23 |
| 350 g/l | | | |
| 0.25 | 17.75 | 22.19 | 4.43 |
| 1 | 16.85 | 23.71 | 6.86 |
| 3.2 | 15.12 | 28.29 | 13.17 |
| 5 | 14.33 | 31.44 | 17.11 |
| 7 | 13.31 | 35.36 | 22.06 |
| 9 | 11.69 | 37.52 | 25.84 |
| 11 | 12.86 | 38.96 | 26.11 |
| 13 | 12.91 | 40.12 | 27.21 |

At each concentration, the obtained values for $\Delta T_c$ were plotted as a function of cooling rate in ln-ln coordinates and fitted by the Nyvlt type equation (45); corresponding to a straight line, whose gradient will deliver the nucleation order. Fig. 1 shows an example of the plot for methyl stearate in kerosene at 200 g/l.
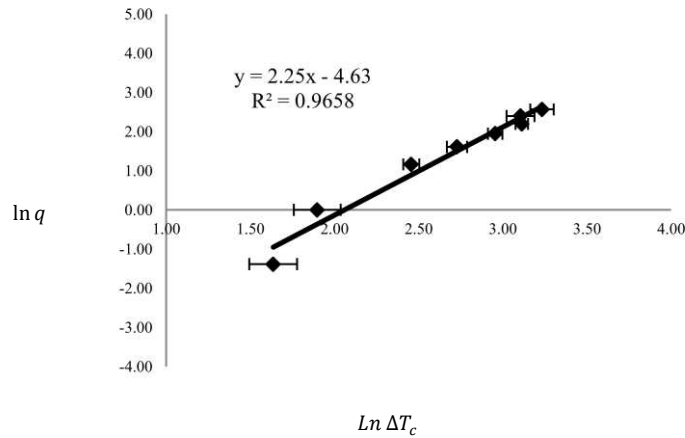


**Fig. 1 Plot of experimental data collected by means of the polythermal methodology in $ln\ q$ vs $ln\ \Delta T_c$ coordinates for methyl stearate in kerosene at a concentration of 200 g solute per litre of solvent. $\Delta T_c = T_{diss} - T_c$**

The obtained nucleation order, coefficients of determination, parameters' standard deviations and covariance at each concentration are also given in Table 3.

**Table 3. Nucleation order as a function of concentration and coefficient of determination of experimental data plotted in $ln\ q$ vs $ln\ \Delta T_c$ coordinates. Standard deviations and covariance of the corresponding linear fitting parameters**

| Concentration g/l | slope /Nucleation order ($m_0$) | $R^2$ | Slope Standard Deviation ($SD$) | Intercept Standard Deviation ($SD$) | Covariance Slope/Intercept |
|---|---|---|---|---|---|
| 200 | 2.2±0.17287 | 0.97 | 0.63 | 1.71 | -1.06 |
| 250 | 2.0±0.12701 | 0.98 | 0.56 | 1.57 | -0.86 |
| 300 | 2.0±0.11204 | 0.99 | 0.56 | 1.58 | -0.87 |
| 350 | 2.0±0.10292 | 0.98 | 0.56 | 1.55 | -0.84 |

The slopes of the lines in all cases show that the nucleation order $m_0$ in equation (44) approximates two. This means that the rate of nucleation of methyl stearate in kerosene is not dependant on solution concentration. As expected the slopes of the best linear fit of the

collected data using the Nyvlt approach [6,7] are lower than those obtained from the best linear fit using the $KBHR$ approach. This is so because in the case of $KBHR$ approach, as derived analytically, critical undercooling $\Delta T_c$ is defined as the difference between the solution equilibrium temperature $T_e$ and the corresponding crystallisation temperature $T_c$.

On the other hand in the case of the Nyvlt approach, as derived from an empirical expression, critical undercooling $\Delta T_c$ is defined as the difference between the dissolution temperatures $T_{diss}$ and the corresponding crystallisation temperature $T_c$. Equilibrium temperatures are always lower than the dissolution ones as they were obtained by extrapolating to 0°C/min a linear fit of increasing dissolution temperatures with cooling rates.

Nonetheless it might be possible to analytically establish a relationship between the slopes obtained by applying the Nyvlt approach and those obtained by applying the $KBHR$ approach. In the case of the former approach, data are plotted on $Ln\ q\ vs\ \ln\Delta T_c$ coordinates with $\Delta T_c = T_{diss} - T_c$ then an approximation of the slope $(s_1)$ of the best linear data fit could be obtained from choosing two experimental data pairs of the dissolution and crystallisation temperatures $(T_{c1}, T_{diss1})$ and $(T_{c2}, T_{diss2})$ to be used in the following expression

$$s_1 = \frac{\ln q_2 - \ln q_1}{\ln \Delta T_{c2} - \ln \Delta T_{c1}} = \frac{\ln q_2 - lnq_1}{\ln(T_{diss2} - T_{c2}) - \ln(T_{diss1} - T_{c1})} \tag{48}$$

This approximation could only holds if the bets linear fit of experimental data according to the Nyvlt approach has a reasonable coefficient of determination $R^2$.

The same principle can be applied to obtain an approximation of the slope $(s_2)$ for the best linear data fit plotted in $\ln q \; Vs \; \ln u_c$ coordinates according to $KBHR$ approach with $u_c = \frac{\Delta T_c}{T_e} = \frac{T_e - T_c}{T_e}$, thus

$$s_2 = \frac{\ln q_2 - \ln q_1}{\ln u_{c2} - \ln u_{c1}} = \frac{\ln q_2 - \ln q_1}{\ln\left(\frac{T_e - T_{c2}}{T_e}\right) - \ln\left(\frac{T_e - T_{c1}}{T_e}\right)} = \frac{\ln q_2 - \ln q_1}{\ln(T_e - T_{c2}) - \ln(T_e - T_{c1})} \qquad (49)$$

As $T_e$ is greater than any of the experimentally collected dissolution temperatures $T_{diss}$ by a known value $\Delta_T$, then equation (49) can be expressed as follow

$$s_2 = \frac{\ln q_2 - \ln q_1}{\ln(T_{diss2} - T_{c2} - \Delta_{T2}) - \ln(T_{diss1} - T_{c1} - \Delta_{T1})} \qquad (50)$$

The numerators of expressions (48) and (50) are equal, therefore

$$s_1[\ln(T_{diss2} - T_{c2}) - \ln(T_{diss1} - T_{c1})] = s_2[\ln(T_{diss2} - T_{c2} - \Delta_{T2}) - \ln(T_{diss1} - T_{c1} - \Delta_{T1})]$$

From this equality the $KBHR$ slope $(s_2)$ could be estimated from the slope $(s_1)$ obtained applying the Nyvlt approach using the following expression

$$s_2 = \frac{s_1[\ln(T_{diss2} - T_{c2}) - \ln(T_{diss1} - T_{c1})]}{[\ln(T_{diss2} - T_{c2} - \Delta_{T2}) - \ln(T_{diss1} - T_{c1} - \Delta_{T1})]} \qquad (51)$$

Again the accuracy with which $(s_2)$ can be predicted from $(s_1)$ using the above expression will greatly depend on the expected coefficient of determination $R^2$ of the best linear fit of experimental data points by applying both the $KBHR$ and the Nyvlt approaches. In general,

from analysis of previously obtained experimental data, the values of $(s_2)$ were observed to be between 1.5 to 2.5 higher than those of $(s_1)$. Using these approximations for the case of methyl stearate crystallising from kerosene the $KBHR$ slope $(s_2)$ will be in the range of 3-5, as $m_0 = s_1 = 2$, indicating that methyl stearate will crystallise from kerosene by the progressive nucleation mechanism which is in agreement with the polythermal analysis presented in the paper.