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Heat transfer inside emulsions. Determination of the DSC thermograms.
Part 1. Crystallization of the undercooled droplets

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Abstract

A general study of the heat transfers inside the cell of a differential scanning calorimeter is presented. In Part 1 of this study, the crystallization of undercooled droplets of an emulsion is analysed. It is demonstrated that the classical assumption of a uniform temperature in the cell cannot explain the shape of the thermogram. The model, which considers the local heating due to the exothermic transformations of the droplets and the erratic character of the crystallizations, shows, despite the small size of the cell, important temperature gradients and explains the shape of the thermogram upon cooling. The analysis indicates that the undercooling is well characterized by the beginning of the peak and not by the peak minimum as suggested before.

LIST OF SYMBOLS

c	specific heat of the emulsion in J K^{-1} kg^{-1}
h_{sl}	specific latent heat of fusion (>0) in J kg^{-1}
h^{ext}, h'^{ext}	external exchange coefficient for the cell in W m^{-2} s^{-1}
$\mathcal{J}(T)$	probability of crystallization of one droplet per unit time in s^{-1}
k	heat conductivity of the emulsion in W m^{-1} K^{-1}
$n(r, t)$	number of crystallized droplets per unit volume in m^{-3}
n_t	total number of droplets per unit volume in m^{-3}
P	mass fraction of the dispersed substance
$\dot{q}$	heat source in J m^{-3} s^{-1}
r	radius in m
R_0	inner radius of the cylinder in m
t	time
$T(r, z, t)$	temperature at r, z and t in °C
T_F	melting temperature in °C

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$T_\infty(t)$	programmed temperature of the bath in °C
T_0	initial temperature in °C
∇	gradient or divergence operator

Greek letters

α	diffusivity of the emulsion in $\mathrm{m^2\,s^{-1}}$
β	cooling rate (<0) in $\mathrm{^\circ C\,h^{-1}}$
$\varphi(r, t)$	local proportion of the crystallized droplets
ρ	mass density of the emulsion in $\mathrm{kg\,m^{-3}}$

INTRODUCTION

Many years ago, we presented [1] a study of the thermograms obtained through differential scanning calorimetry (DSC) for the steady cooling of an emulsion of a supercooled liquid. We used the classical assumptions to analyse these DSC curves, particularly the hypothesis of the uniformity of the temperature inside the cell. But recent experimental and theoretical studies [2, 3] have described in detail the kinetics of heat transfer inside an emulsion when the droplets crystallize or melt. These results predict significant temperature gradients, even with a small cell.

In the present study, we describe models for the heat transfer in an emulsion where the droplets transform inside the DSC cells, and the consequences of these models for the interpretation of the thermograms. In fact, the models for cooling and heating are completely different because of the non-symmetry of the crystallization and melting due to the undercooling phenomenon. Therefore, the cooling experiments are presented in Part 1, whereas the heating experiments are presented in Part 2.

UNDERCOOLING

It is well known that on cooling liquids do not crystallize at the melting temperature T_F but at a lower temperature T. The undercooling, defined as $\Delta T = T_F - T$, depends on different parameters [4], the most important of which being the volume of the investigated sample. The smaller the volume the larger ΔT.

A good way to obtain the highest value of ΔT is to disperse the liquid within an appropriate emulsifying medium. The droplets obtained have a volume $\leq 1\ \mu\mathrm{m}^3$ and the ΔT can be very large, for example, 38 K for water, more than 100 K for certain organic compounds, and more than 200 K for certain metals [4].

However, the main feature of undercooling is its erratic character, i.e. apparently identical samples do not crystallize at the same time or temperature. Thus, it is only possible to determine, for a droplet, its probability of

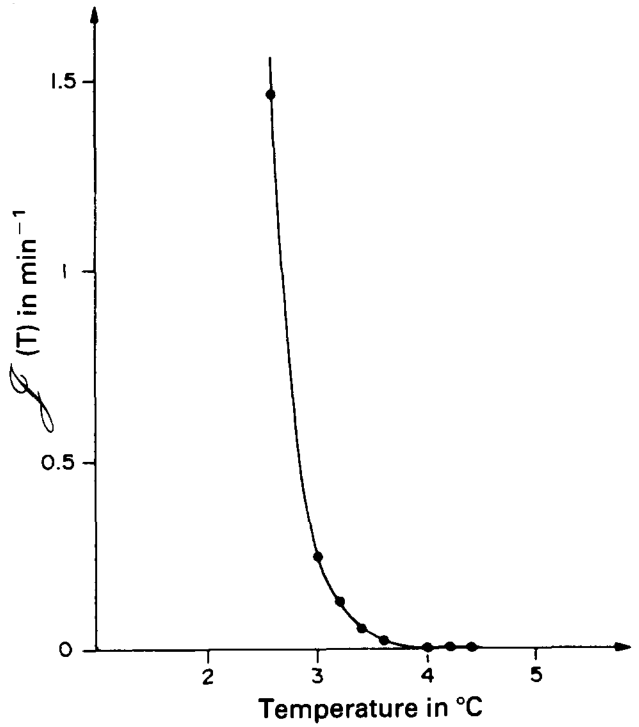


Fig. 1. Experimental curve of the crystallization probability per unit time $\mathcal{J}(T)$ versus temperature for hexadecane ($T_F = 18°C$).

crystallization per unit time, $\mathcal{J}(T)$. As indicated by the theories of nucleation, e.g. ref. 5, $\mathcal{J}(T)$ can be practically zero over a large temperature range below T_F and then increases sharply. This function can be determined experimentally [2]. Figure 1 shows an example for hexadecane ($T_F = 18°C$).

Most of the earlier papers concerning the crystallization of dispersed droplets of emulsions present the results of DSC experiments during steady coolings. A typical thermogram is given schematically in Fig. 2. Its considerable breadth is explained by the erratic nature of the undercooling of the droplets. They do not crystallize at the same time: the crystallizations occur successively in the temperature range defined by the width of the peak. A "most probable temperature" [1] has been defined, given approximately by T_{min} the peak minimum temperature. Crystallizations at this temperature are most numerous.

But, as we will demonstrate later, when the kinetics of heat transfer inside the DSC cell are considered, the interpretation of the thermograms is quite different. However, first we must review the classical theory of differential scanning calorimetry in order to criticize its deficiencies.

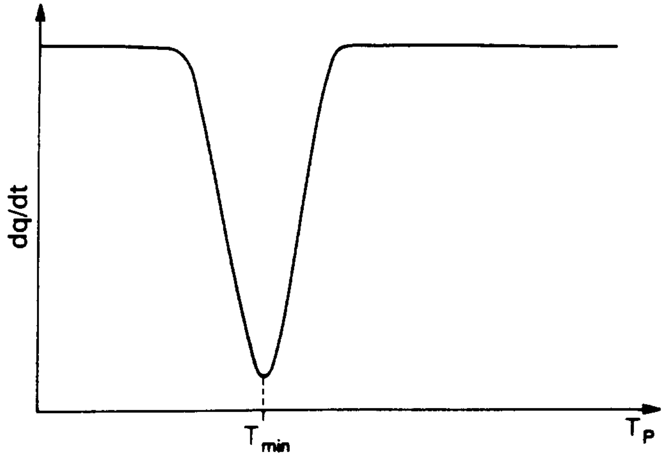


Fig. 2. Schematic thermogram obtained for crystallization of the droplets of an emulsion being cooled steadily.

CLASSICAL THEORY OF DIFFERENTIAL SCANNING CALORIMETRY

The calorimeter concerned in this study is a Perkin-Elmer apparatus but the models can easily be applied to other calorimeters.

The holder of the calorimeter (Fig. 3) consists of two plates: one supporting the cell containing the emulsion (active cell) and the other containing a reference cell (generally an empty cell). At each time, the apparatus imposes the same temperature at the two plates. Both sample holders are in permanent contact with a cold source and with the heaters which supply the required energy to control the temperature T_P. An

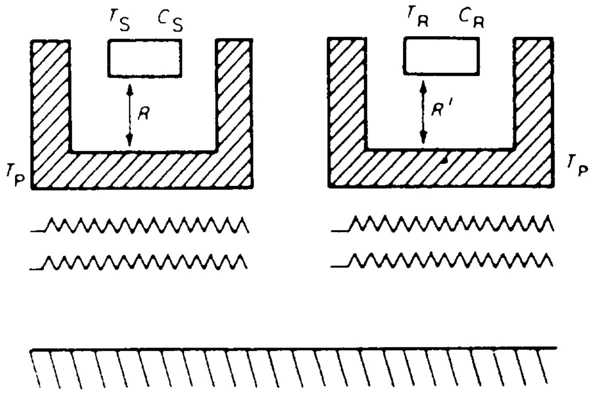


Fig. 3. Scheme of the apparatus: C_S, total heat capacity of the sample; C_R, total heat capacity of the reference (container empty); T_S, uniform temperature of the sample; T_R, temperature of the reference; T_P, temperature of both sample holders; R and R', thermal resistances through which the thermal energy flows to or from the sample, or to or from the reference, respectively.

electronic control system imposes the equality of the temperature T_P of both holders. However the heaters work independently of each other; when there is a thermal phenomenon in the sample, the heaters provide different powers in order to maintain this equality in the temperatures of the holders.

The thermogram is given by the power difference

$$\frac{dq}{dt} = \left(\frac{dq}{dt}\right)_{cell} - \left(\frac{dq}{dt}\right)_{ref} \tag{1}$$

According to the classical assumption that the temperature T_S inside the active cell is uniform, we can predict the thermogram for the crystallizations of the undercooled droplets dispersed within an emulsion as it is steadily cooled.

If dh/dt is the amount of energy released per unit time by the emulsion, it is directly proportional to the latent heat of crystallization per unit mass, h_{sl} (>0) and to the number of droplets crystallizing per unit time dN/dt

$$\frac{dh}{dt} = \rho_0 V h_{sl} \frac{dN}{dt} \tag{2}$$

where ρ_0 is the density of the droplet and V its volume (we assume that all droplets have the same volume).

The number of droplets which crystallize per unit time is proportional to the probability of crystallization per unit time $\mathcal{J}(T_S)$ and to the number of droplets which remain unfrozen $(N_t - N)$

$$\frac{dN}{dt} = \mathcal{J}(T_S)(N_t - N) \tag{3}$$

where the total number of droplets is $N_t = \rho P \mathcal{V}/\rho_0 V$, ρ being the density of the emulsion, P its mass fraction (the ratio between the mass of the dispersed liquid and the total mass of the emulsion), and $\mathcal{V}$ its volume.

If we define $\varphi_S = N/N_t$ as the fraction of crystallized droplets, we have

$$\frac{d\varphi_S}{dt} = \mathcal{J}(T_S)(1 - \varphi_S) \tag{4}$$

$$\frac{dh}{dt} = \rho P h_{sl} \mathcal{V} \mathcal{J}(T_S)(1 - \varphi_S) \tag{5}$$

Knowing that the two plates are steadily cooled at a cooling rate β (<0), we have

$$T_P = \beta t + T_0 \tag{6}$$

The conservation of the energy of the sample plate shows that the rate of the temperature change in the sample cell with respect to time is (see the legend of Fig. 3)

$$\frac{\mathrm{d}T_S}{\mathrm{d}t}=\frac{1}{C_S}\frac{\mathrm{d}h}{\mathrm{d}t}+\frac{1}{RC_S}(T_P-T_S) \tag{7}$$

We can also demonstrate [1–6] that the power exchanged at the reference plate is practically constant and equal to $(\mathrm{d}q/\mathrm{d}t)_{\mathrm{ref}}=\beta C_R$. So, to simplify the model we will omit this term from the calculation of $\mathrm{d}q/\mathrm{d}t$ (equivalent to a shift of the baseline) which is reduced to

$$\frac{\mathrm{d}q}{\mathrm{d}t}=\frac{T_P-T_S}{R} \tag{8}$$

At $t=0$ we have

$$T_P=T_S=T_0 \tag{9}$$

$$\frac{\mathrm{d}h}{\mathrm{d}t}=0 \tag{10}$$

$$\varphi_S=0 \tag{11}$$

From the initial conditions given by eqn. (9) and the boundary condition eqn. (6), φ_S is determined by eqn. (4), $\mathrm{d}h/\mathrm{d}t$ by eqn. (5), T_S by eqn. (7) and finally the thermogram $\mathrm{d}q/\mathrm{d}t$ is given by eqn. (8).

But, as indicated in Fig. 4 for an emulsion of hexadecane, the model is not adequate because whatever the value of R (the thermal resistance between the active cell and the corresponding plate) the calculated thermogram does not have a shape similar to the experimental one. Thus, we now present a model that considers the heat transfers inside the active cell.

A MODEL FOR COOLING TAKING INTO ACCOUNT THE HEAT TRANSFERS

The model is based on the classical equation for the conduction of heat with a heat source $\dot{q}$

$$\frac{\partial T}{\partial t}=\alpha\nabla^2T+\frac{\dot{q}}{\rho c} \tag{12}$$

where T is the local temperature, $\alpha=k/\rho c$ is the diffusivity, k the thermal conductivity of the emulsion, ρ its mass density and c its specific heat. The heat source $\dot{q}$ is the energy released by the crystallizations of the droplets, assumed instantaneous, per unit time and unit volume of emulsion. Similar to eqn. (5) we have

$$\dot{q}=\rho Ph_{\mathrm{sl}}\mathscr{J}(T)(1-\varphi) \tag{13}$$

where φ is the local fraction of crystallized droplets given by $\varphi=n/n_{\mathrm{t}}$, n is the number of crystallized droplets per unit volume and n_{t} is the total number of droplets per unit time. Similar to eqn. (4), we also have

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t}=\mathscr{J}(T)(1-\varphi) \tag{14}$$

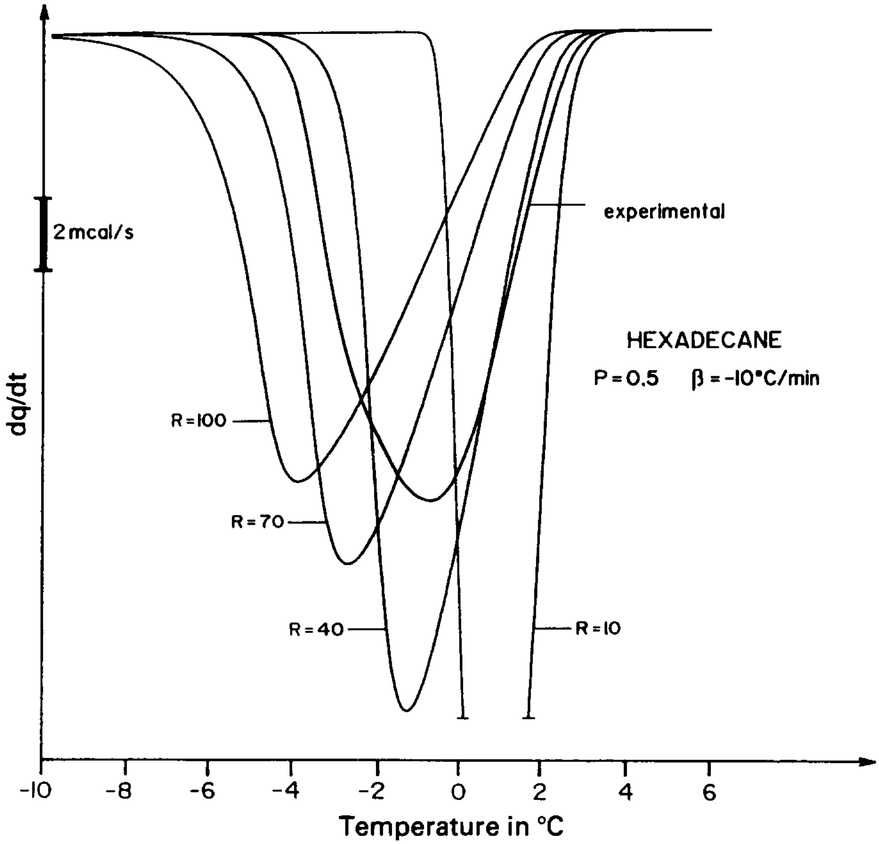


Fig. 4. Calculated thermograms for different values of R in the uniform temperature model and comparison with the experimental curve (R in °C W^{-1}).

We have represented the active cell by a cylinder whose dimensions are: $2R_0 = 4.25$ mm for the diameter, and $Z = 0.82$ mm for the height of the emulsion (Fig. 5). T and φ depend on the two space variables r and z and on the time t. The system to be solved is

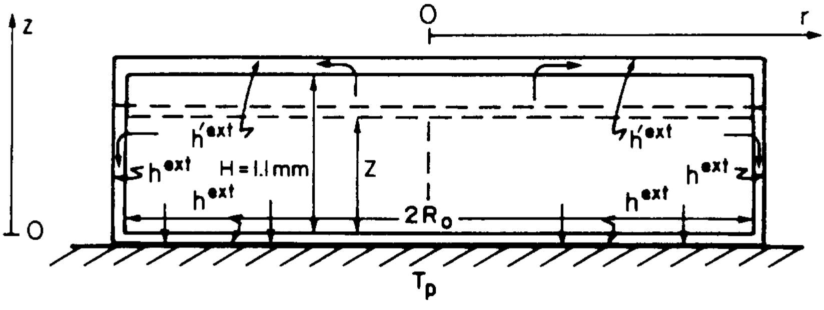


Fig. 5. Scheme of the cell.

$$\frac{\partial T}{\partial t}=\alpha\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial z^2}\right)+\frac{Ph_{\mathrm{sl}}(1-\varphi)}{c}\mathscr{J}(T) \tag{15}$$

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t}=(1-\varphi)\mathscr{J}(T) \tag{16}$$

This is a non-linear system of partial differential equations as a result of the non-linearity of the function $\mathscr{J}(T)$.

To take into account the air between the emulsion and the cover of the cell, we consider two different heat exchange coefficients h^{ext} and h'^{ext} (see Fig. 5). The boundary conditions take into account the cylindrical symmetry

$$\left(\frac{\partial T}{\partial r}\right)_0=0 \tag{17}$$

$$-k\left(\frac{\partial T}{\partial r}\right)_{r=R_0}=h^{\mathrm{ext}}(T-T_{\mathrm{P}}) \tag{18}$$

$$-k\left(\frac{\partial T}{\partial z}\right)_{z=0}=h^{\mathrm{ext}}(T-T_{\mathrm{P}}) \tag{19}$$

$$-k\left(\frac{\partial T}{\partial z}\right)_{z=Z}=h'^{\mathrm{ext}}(T-T_{\mathrm{P}}) \tag{20}$$

The initial conditions are

$$T(r,z,0)=T_{\mathrm{P}}(0)=T_0 \qquad \varphi(r,z,0)=0 \tag{21}$$

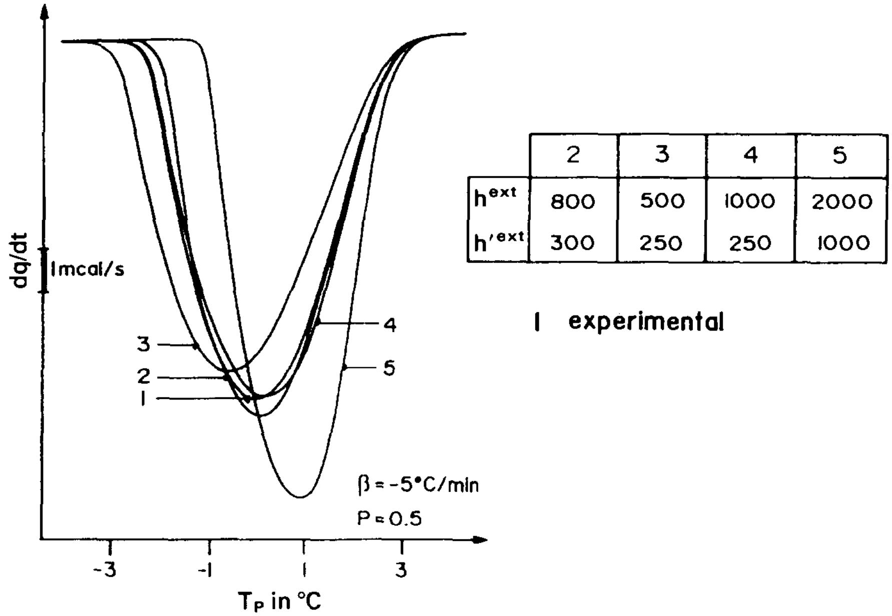
Because the thermal conductivity of the air is much smaller than that of the metal of the cell, we assume that all the energy is transmitted to the plate by the lower boundary of the cell. Moreover, we assume that all the parts of the cell are at the temperature of the plate T_{P}, given by eqn. (6); $\mathrm{d}q/\mathrm{d}t$ is the sum of the thermal fluxes through the walls of the metallic cell

$$\frac{\mathrm{d}q}{\mathrm{d}t}=-\sum_i h_i(T-T_{\mathrm{P}})\Delta S_i \tag{22}$$

where $h_i=h^{\mathrm{ext}}$ or h'^{ext}, and ΔS_i is the area of the different boundaries of the cell.

RESULTS

In the model, h^{ext} and h'^{ext} are adjustable parameters. The study of the influence of these two parameters has provided two values of h^{ext} and h'^{ext} that conform to the experimental thermogram (see Fig. 6). These values, found at -5°C min^{-1}, also yield good agreement between the experimental and theoretical thermograms for all cooling rates β. The height and width are reproduced: this is impossible with the assumption of a uniform temperature inside the cell.



	2	3	4	5
h^{ext}	800	500	1000	2000
h'^{ext}	300	250	250	1000

Fig. 6. Calculated thermograms at different values of h^{ext} and h'^{ext}.

In Fig. 7 we present the values of $T(r, z, t)$ and $\varphi(r, z, t)$ during a steady cooling for different points inside the cell. The figure is given versus T_P, i.e. versus time (eqn. (6)). We also represent on the same scale the thermogram and the curve giving $\mathrm{d}h/\mathrm{d}t = \int \dot{q}\, \mathrm{d}\mathscr{V}$ (the summation is for the whole volume $\mathscr{V}$ of the emulsion).

From these curves, we can observe important temperature gradients in the cell that depend on the radius r or the height z. Despite the smallness of the cell, we can observe up to 5°C difference ($\beta = -10°\mathrm{C\,min}^{-1}$) between the central region of the cell and the metallic boundary. There is a temperature plateau, more marked in the central region, which is a self regulation of the temperature due to local heating by the crystallizations of the droplets; this induces a decrease in the probability of crystallization of the other droplets [2, 3].

The actual temperatures of the inflection points of the curves $\varphi(r, z, t)$ giving the local fraction of crystallized droplets, defined as the most probable temperatures, corresponding to the temperature of the beginning of the peak where the probability $\mathscr{J}(T)$ increases sharply, and not to the temperature $T_{\min}$ of the minimum of the thermogram, which is lower. If we consider that, physically, the nucleation phenomenon is characterized by the temperature range where the probability $\mathscr{J}(T)$ sharply increases, this temperature range is better located by the beginning of the peak (for example, the onset temperature) than by the minimum of the thermogram as suggested before [1].

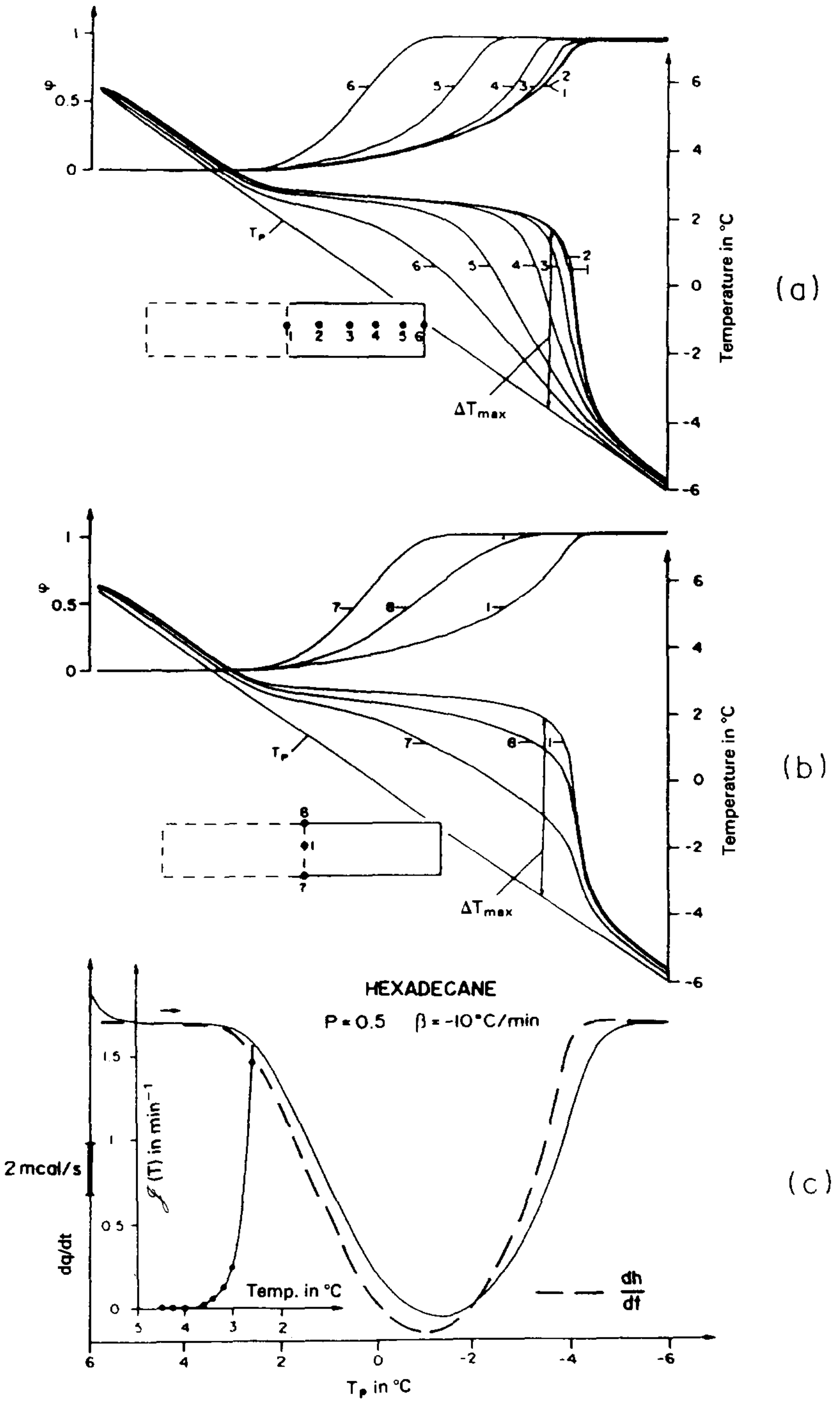


Fig. 7. Calculated values of $T(r, z, t)$ and $\varphi(r, z, t)$ versus the programmed temperature T_P for different points: (a) in a median horizontal plane; (b) on the axis; in comparison with (c) the thermogram, the curve giving $\mathrm{d}h/\mathrm{d}t$ and the probability $\mathcal{J}(T)$.

However, in agreement with ref. 1, the curve dh/dt indicates that about 50% of the droplets are crystallized when the minimum of the thermogram occurs, but if 100% of the droplets are crystallized in the periphery of the cell, only 25% are crystallized in the central region. The other droplets will only crystallize when the local temperature becomes sufficiently low.

CONCLUSION

In this paper, we have shown that the classical assumption of a uniform temperature inside the cell cannot explain the shape of the DSC thermogram obtained during a steady cooling for the crystallization of the undercooled droplets of an emulsion. This shape is better described with our model which takes into account the heat transfers through the emulsion.

The analysis indicates the existence of large temperature gradients and that the crystallizations of the droplets locally stabilize the temperature at a value corresponding to that at which the probability of crystallization $\mathcal{J}(T)$ increases rapidly. This is close to the onset temperature. Therefore, this temperature is more characteristic of the undercooling breakdown than the minimum of the thermogram, as indicated in the past.

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