Pergamon

Int. J. Heat Mass Transfer. Vol. 37, No. 5, pp. 747–752, 1994

0017-9310/94 $6.00+0.00

Models for the heat transfers during the transformations inside an emulsion—II. Melting of the crystallized droplets

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(*Received* 24 *March* 1993 *and in final form* 6 *October* 1993)

Abstract—The heat transfers during the melting of the crystallized droplets inside an emulsion are investigated. Contrary to the crystallization case (see Part 1), in the case of pure substances, the melting of the crystallized droplets occurs, upon heating, at a fixed temperature T_F which corresponds to the phase equilibrium and the kinetics of melting depends on the heat transfer between the droplet and the emulsifying medium. So, the model, for melting, is quite different from the model for crystallization. As for cooling, the space–time evolution of the temperature inside a metallic cylinder filled with the emulsion is investigated. The dispersed substances are hexadecane, octadecane and water. The effect of different parameters such as the heating rate, the mass fraction or the final temperature is analyzed. A comparison will be made with experimental results.

1. INTRODUCTION

In Part I, we have presented experimental results and a model [1, 2] for the heat transfers due to the crystallizations of the undercooled droplets dispersed within an emulsion. The transformations occurred in a temperature range below the melting temperature T_F because of the undercooling phenomenon. The erratic character of the crystallizations was evidenced and we considered that the release of heat was instantaneous and proportional to the number of droplets which crystallize per unit time, this number being proportional to the probability of the phase transformations.

In this paper, we present a model for the determination of the heat transfers and the kinetics of the transformations, upon heating, during the melting of the crystallized droplets of the emulsion. This model is quite different from the model for cooling because, at the crystallization the release of energy, for a droplet, is practically instantaneous because it occurs far from the thermodynamic equilibrium but, at the melting, the absorption of energy is at the fixed melting temperature and its kinetics depends on the exchange with the surrounding medium.

2. EXPERIMENTAL

Hexadecane ($T_F = 18.0°C$) and octadecane ($T_F = 27.5°C$) are dispersed by a high speed stirrer within an emulsifying medium made of a mixture of water, glycerol and Tween 80® as surfactant. Water is dispersed within a mixture of paraffin oil and natural lanolin. Although, with a particular choice of the concentration of the emulsifying medium, it is possible, for hexadecane, to obtain a microemulsion [3], we will denominate the dispersed systems as emulsions.

We have already presented the experimental cell in Part I [1] which consists of a metallic cylinder with a inner radius radius $R_0 = 30$ mm and a height of 130 mm steadily heated by a bath.

3. ANALYSIS

As for the cooling, we present the model in the case of an emulsion in a cylinder with a height much larger than its diameter. So, only the radius of the cylinder r and the time t are the variables taken into account.

For the same reasons mentioned in Part I (smallness of the droplets, high viscosity and variation of the density negligible), no movement of the emulsion as a whole is possible; so, only the conduction is taken into account.

Hence, we use the energy equation:

$$\rho c \frac{\partial T(r,t)}{\partial t} = \nabla(k \nabla T(r,t)) + \dot{q} \qquad (1)$$

where k is the thermal conductivity of the emulsion, ρ its density and c its specific heat. The heat source $\dot{q}$ is different from zero when the melting occurs.

As for the cooling, we should consider the temperatures of the emulsifying medium and of the droplet as the same. It is the measured temperature. But theoretically, there exists a small temperature difference between the inside and the outside of the droplets depending on the thermal resistance of the droplet-emulsifying medium interface. In fact, this difference is very small (a few hundredths of a degree). We will neglect this difference except when the temperature

NOMENCLATURE

a	diffusivity of the emulsion $[\mathrm{m^2\,s^{-1}}]$
Bi^{ext}	Biot number of the cell
Bi	Biot number of the droplet
c	specific heat of the emulsion $[\mathrm{J\,K^{-1}\,kg^{-1}}]$
c_L or c_S	specific heat when the droplets of the emulsion are liquid or solid $[\mathrm{J\,K^{-1}\,kg^{-1}}]$
h	exchange coefficient between the droplet and the emulsifying medium $[\mathrm{W\,m^{-2}}]$
h_{SL}	specific latent heat of fusion (>0) $[\mathrm{J\,kg^{-1}}]$
h^{ext}	external exchange coefficient for the cell $[\mathrm{W\,m^{-2}\,s^{-1}}]$
k	heat conductivity of the emulsion $[\mathrm{W\,m^{-1}\,K^{-1}}]$
k_0	heat conductivity of the dispersed substance $[\mathrm{W\,m^{-1}\,K^{-1}}]$
k_L or k_S	heat conductivity when the droplets of the emulsion are liquid or solid $[\mathrm{W\,m^{-1}\,K^{-1}}]$
M	number of intervals in the grid
n_t	total number of droplets per unit volume $[\mathrm{m^{-3}}]$
P	mass fraction of the dispersed substance
$\dot{q}$	heat source $[\mathrm{J\,m^{-3}\,s^{-1}}]$
r	radius [m]
$\bar{r}$	dimensionless radius
R_0	inner radius of the cylinder [m]
S	mean area of a droplet $[\mathrm{m^2}]$
Ste	Stefan number of the emulsion
t	time [h]
$\bar{t}$	dimensionless time
$T(r, t)$	temperature at r and t [°C]
T_F	melting temperature [°C]
$T_{\max}$	final temperature after the steady heating [°C]
$T_\infty(t)$	programmed temperature of the bath [°C]
T_0	initial temperature [°C]
T_m^i	temperature of the node m at time i [°C]
V	mean volume of a droplet $[\mathrm{m^3}]$
$X(r, t)$	local melted fraction of droplet
X_m^i	local melted fraction of droplet for the node m at time i.

Greek symbols

β	heating rate (>0) $[\mathrm{°C\,h^{-1}}]$
β'	dimensionless cooling rate
γ	ratio of the heat conductivities of the emulsion and of the dispersed substance
Γ	scale factor
θ	dimensionless temperature
$\theta_{\max}$	final dimensionless temperature
$\theta_\infty(\bar{t})$	dimensionless temperature of the bath
μ	ratio between the mass densities of the emulsion and of the dispersed substance
ρ	mass density of the emulsion $[\mathrm{kg\,m^{-3}}]$
ρ_0	mass density of the dispersed phase $[\mathrm{kg\,m^{-3}}]$
τ'	duration of the plateau for the axis [h]
∇	gradient or divergence operator.

inside the droplet is exactly T_F when the droplet is melting because this difference commands the kinetics of the fusion. So, at the melting, we consider that the temperature of the melting droplet is T_F whereas the temperature of the emulsifying medium $T(r, t)$ varies.

At the melting there is no delay for the transformation and as soon as the temperature of the droplet is T_F, the droplet acts as a heat source (in fact a heat sink) during the lapse of time where the melted fraction of the droplet $X(r, t)$ is such as $0 < X(r, t) < 1$.

The heat source is proportional to the number of droplets whose temperature is T_F and to the fraction of the droplet $\mathrm{d}X/\mathrm{d}t$ which melts per unit time. The melted fraction of the droplet $X(r, t)$ is such as $0 < X(r, t) < 1$ and the heat sink operates only when these inequalities are true.

During the melting the energy balance of one droplet is given by:

$$\rho_0 V h_{SL} \frac{\mathrm{d}X}{\mathrm{d}t} = -h(T_F - T(r, t))S$$

where ρ_0 is the density of the liquid of the droplet, V its volume, S its external area and h an exchange coefficient between the droplet and the surrounding emulsifying medium. h is characteristic of the thermal resistance due to the absorbed surfactant which surrounds the droplet and separates the droplet from the emulsifying medium.

If R is the mean radius of the droplets, we have:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -\frac{3h}{\rho_0 R h_{SL}}(T_F - T(r, t)). \tag{2}$$

The energy absorbed per unit time by one droplet is $-\rho_0 V h_{SL}(\mathrm{d}X)/(\mathrm{d}t)$.

P is the mass fraction of the dispersed phase (ratio between the mass of the dispersed substance and the total mass of the emulsion), the number of droplets per unit volume is $(\rho P)/(\rho_0 V)$. Because all the droplets reach the temperature T_F together and because there is no delay for the melting, all the droplets (unlike the case of crystallizations [1]) participate in the heat source (sink). So:

$$\dot{q} = -\rho h_{\mathrm{SL}} P \frac{\mathrm{d}X}{\mathrm{d}t} = \frac{3hP}{R}\frac{\rho}{\rho_0}(T_{\mathrm{F}} - T(r,t)).$$

When $0 < X(r, t) < 1$, the system to be solved is:

$$\rho c \frac{\partial T}{\partial t} = \nabla(k\nabla T) + \frac{3hP}{R}\frac{\rho}{\rho_0}(T_{\mathrm{F}} - T(r,t)) \quad (3)$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -\frac{3h}{\rho_0 R h_{\mathrm{SL}}}(T_{\mathrm{F}} - T(r,t)). \quad (4)$$

When $T(r, t) < T_{\mathrm{F}}$ $(X = 0)$ or when the melting is complete $(X(r, t) = 1)$ the only conduction equation which has to be solved is:

$$\rho c \frac{\partial T}{\partial t} = \nabla(k\nabla T). \quad (5)$$

The resolution of these equations is made by an explicit finite differences method. The numerical calculations begin for $t = 0$ at a temperature lower than T_{F} solving first equation (5) as long as $T < T_{\mathrm{F}}$. But as soon as T is equal to T_{F}, the system of equations (3) and (4) is solved as long as X is such as $0 < X(r, t) < 1$. As soon as the calculated $X(r, t)$ is 1, we solve again equation (5).

In the case of the cylinder heated by a bath whose temperature T_∞ is a linear function, we have:

$$T_\infty(t) = \beta t + T_0 \quad (6)$$

where T_0 is the temperature at the beginning of the heating (indeed $T_0 < T_{\mathrm{F}}$) at the rate β $(\beta > 0)$. We have:

$$\left(\frac{\partial T}{\partial r}\right)_{r=0} = 0 \quad (7)$$

$$-k\left(\frac{\partial T}{\partial r}\right)_{r=R_0} = h^{\mathrm{ext}}[T(R_0, t) - T_\infty(t)] \quad (8)$$

where h^{ext} is the exchange coefficient between the emulsion and the bath [1] and k the heat conductivity of the emulsion.

Moreover we can examine either the case of full heating or heating limited at a temperature $T_{\max}$.

For the initial conditions we can choose:

$$T(r, 0) = T_0. \quad (9)$$

If the values of k and c were constant, equation (3) would become:

$$\frac{\partial T(r,t)}{\partial t} = a\left(\frac{\partial^2 T(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial T(r,t)}{\partial r}\right) + \frac{3hP}{cR\rho_0}(T_{\mathrm{F}} - T(r,t)) \quad (10)$$

and equation (5) would be

$$\frac{\partial T(r,t)}{\partial t} = a\left(\frac{\partial^2 T(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial T(r,t)}{\partial r}\right) \quad (11)$$

where $a = k/\rho c$ is the diffusivity.

In this case, it would be possible to give dimensionless equations defining the dimensionless variables:

$$\bar{t} = \frac{a}{R_0^2}t, \quad \bar{r} = \frac{r}{R_0}, \quad \theta = \frac{T - T_{\mathrm{F}}}{T_{\mathrm{F}} - T_0}. \quad (12)$$

Before the melting, when $\theta(\bar{r}, \bar{t}) < 0$, and after the complete melting when $X(\bar{r}, \bar{t}) = 1$ equation (5) becomes:

$$\frac{\partial \theta}{\partial \bar{t}} = \frac{\partial^2 \theta}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial \theta}{\partial \bar{r}}. \quad (13)$$

As soon as $\theta(\bar{r}, \bar{t}) = 0$ and as long as $0 < X(\bar{r}, \bar{t}) < 1$ the system of equations (10) and (4) becomes:

$$\frac{\partial \theta}{\partial \bar{t}} = \frac{\partial^2 \theta}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial \theta}{\partial \bar{r}} - \frac{P}{Ste}\frac{\mathrm{d}X}{\mathrm{d}\bar{t}} \quad (14)$$

$$\frac{\mathrm{d}X}{\mathrm{d}\bar{t}} = 3\,Ste\,\mu\,Bi\,\gamma\Gamma^2\theta. \quad (15)$$

The boundary conditions would be:

$$\left(\frac{\partial \theta}{\partial \bar{r}}\right)_{\bar{r}=0} = 0 \quad (16)$$

$$\left(\frac{\partial \theta}{\partial \bar{r}}\right)_{\bar{r}=1} = Bi^{\mathrm{ext}}[\theta_\infty - \theta(1, \bar{t})] \quad (17)$$

with

$$\theta_\infty = \beta'\bar{t} - 1 \quad (18)$$

where

$$\beta' = \frac{\beta}{T_{\mathrm{m}} - T_0}\frac{R_0^2}{a}$$

is the dimensionless heating rate.

We can have full heating or heating limited at a temperature:

$$\theta_{\max} = \frac{T_{\max} - T_{\mathrm{F}}}{T_{\mathrm{F}} - T_0}.$$

The initial conditions are:

$$\text{for } \bar{t} = 0 \quad \theta = -1.$$

The dimensionless parameters are:

$$Ste = \frac{c(T_{\mathrm{F}} - T_0)}{h_{\mathrm{SL}}}$$

the Stefan number,

$$Bi = \frac{hR}{k_0}$$

the Biot number of the droplet,

$$\gamma = k/k_0$$

the ratio of the heat conductivities of the emulsion and of the dispersed liquid

$$Bi^{\text{ext}} = \frac{h^{\text{ext}} R_0}{k}$$

the external Biot number of the cylinder,

$$\Gamma = \frac{R_0}{R}$$

a scale factor,

$$\mu = \frac{\rho}{\rho_0}$$

the ratio between the mass densities of the emulsion and of the dispersed phase.

In this study of melting we obtain universal equations referenced to the melting point. But we have the same problem as for the cooling because k and c are different when the dispersed phase is either liquid or solid. For this reason, and to be coherent with the results upon cooling, we have kept the equations with their dimension. A good approximation [4] for the values of k and c is given by the linear equations:

$$k = k_L + (k_S - k_L) X(r, t) \qquad (19)$$

and

$$c = c_L + (c_S - c_L) X(r, t) \qquad (20)$$

where k_L and c_L are the heat conductivity and the specific heat of the emulsion when the dispersed phase is liquid and k_S and c_S the corresponding values when the dispersed phase is solid.

So, we have directly solved the system of equations (4) and (3) or equation (5) taking for k and c the values calculated by equations (19) and (20).

Although, the mathematical problem posed by this model is not classical [5], it can be simply solved by a numerical explicit finite differences method. The radius r of the cylinder being the only spatial variable, we divide the radius R_0 into M intervals with a length $\Delta r = R_0/M$, the location of the node m being at $r = (m-1)\Delta r$. For each interval of time Δt labelled by i, equations (4), (3) or (5) become for $1 < m < M$:

$$\rho c(X^i_m) \frac{T^{i+1}_m - T^i_m}{\Delta t} = -\frac{k(X^i_m)}{(\Delta r)^2} \times \left[\left(1 - \frac{1}{2(m-1)}\right)(T^i_{m-1} - T^i_m) + \left(1 - \frac{1}{2(m-1)}\right)(T^i_{m+1} - T^i_m) \right] + \frac{3hP\rho}{R\rho_0}(T_F - T^i_m) g \qquad (21)$$

$$\frac{X^{i+1}_m - X^i_m}{\Delta t} = \frac{3hP\rho}{R\rho_0}(T_F - T^i_m) \qquad (22)$$

where the coefficient $g = 0$ before the melting when $T^i_m < T_F$ ($X^i_m = 0$) or after the complete melting when $T^i_m > T_F$ and $X^i_m = 1$ (equation (5)) and where $g = 1$ during the melting as soon as $T^i_m \geqslant T_F$ and as long as $0 < X^i_m < 1$ (equation (3)).

To express the limit conditions we use the following equations: for $m = 1$ ($r = 0$) we have

$$\rho c(X^i_1) \frac{T^{i+1}_1 - T^i_1}{\Delta t} = 4 \frac{k(X^i_1)}{(\Delta r)^2}(T^i_2 - T^i_1) + \frac{3hP\rho}{R\rho_0}(T_F - T^i_1) g \qquad (23)$$

for $m = M$ ($r = R_0$) we have:

$$\rho c(X^i_M) \frac{T^{i+1}_M - T^i_M}{\Delta t} = \frac{2k(X^i_M)}{(\Delta r)^2}\left(1 - \frac{1}{2(M-1)}\right) \times (T^i_{M-1} - T^i_M) + \frac{2h^{\text{ext}}}{\Delta r}(T^i_\infty - T^i_M) + \frac{3hP\rho}{R\rho_0}(T_F - T^i_M) g \qquad (24)$$

where $T^i_\infty = \beta i \Delta t + T_0$ after equation (6).

4. RESULTS

In Figs. 1–3 we present the experimental curves of the temperatures vs time for different values of the radius r for water, octadecane and hexadecane, respectively. The heating is limited at $T_{\max} = 24.0$°C, $T_{\max} = 44.1$°C and $T_{\max} = 29.8$°C because full heating would necessitate a very high temperature where the emulsions would be destroyed.

We observe the curves present a quasi plateau whose temperature at its end is T_F, the melting temperature. The length of this plateau is all the greater as r is nearer 0.

For the axis we define this length of the plateau τ' as indicated on Figs. 1–3. τ' will be characteristic of the melting of the dispersed phase in the cylinder.

In Fig. 4(a) we have the corresponding calculated curves for hexadecane where all the physical parameters k_L, k_S, c_L, c_S and ρ have been determined [1]. The parameter h^{ext} has been determined by the experiments on cooling. For h, the exchange coefficient between the inside and the outside of the

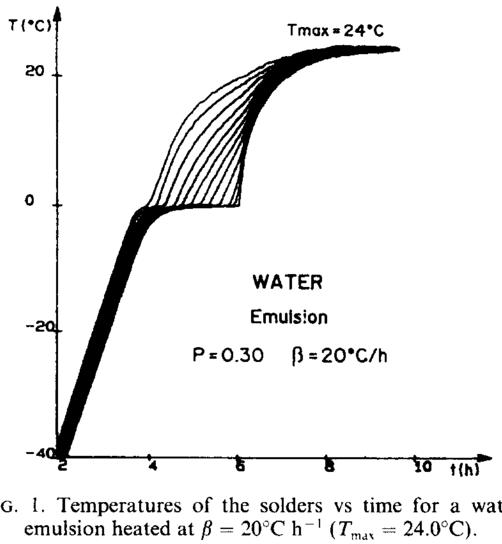

FIG. 1. Temperatures of the solders vs time for a water emulsion heated at $\beta = 20$°C h^{-1} ($T_{\max} = 24.0$°C).

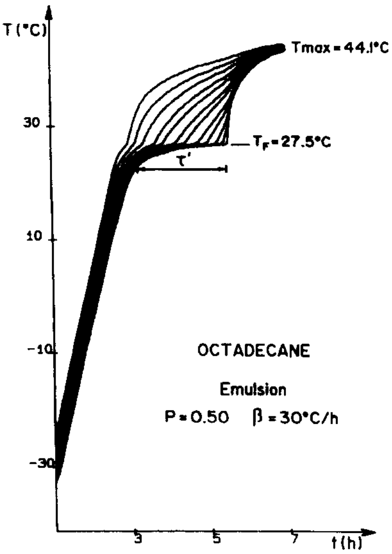

FIG. 2. Temperatures of the solders vs time for an octadecane emulsion heated at $\beta = 30°\mathrm{C\ h^{-1}}$ ($T_{\max} = 44.1°\mathrm{C}$).

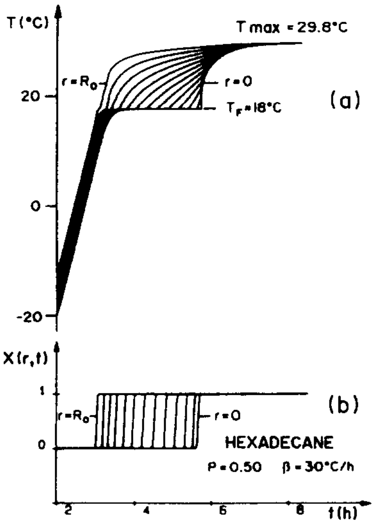

FIG. 4. (a) Calculated temperatures $T(r, t)$ at different radii from $r = 0$ to $r = R_0$ (step of 2.5 mm), vs time for an hexadecane emulsion heated at $\beta = 30°\mathrm{C\ h^{-1}}$ up to $T_{\max} = 29.8°\mathrm{C}$ and (b) the corresponding calculated proportions of crystallized droplets $\phi(r, t)$.

droplet, we have chosen the value of 0.1 $\mathrm{W\ m^{-2}\ K^{-1}}$ because for lower values the general shape of the curves is different (we would not have a plateau) but with $h = 0.1\ \mathrm{W\ m^{-2}\ K^{-1}}$ or higher values we have a similar shape and the value of τ' is practically independent of h [6]. In this case, not only do we find the same shape for the curves but also the length of the plateau defined in the same way as for the experimental results is in good accordance.

For the melting, it seems more logical to have a plateau of temperature because the transformations of the dispersed phase occurs at a fixed temperature T_F which corresponds to the thermodynamical equilibrium if we assume that the droplets are all melting during the lapse of time τ'. But, in Fig. 4(b) giving $X(r, t)$, the fraction of the droplet which is melted, we see that, in fact, the melting of the droplets actually occurs at the end of the plateau. Analysing the curves more accurately, we observe that before the end of the plateau, the temperature is close to T_F but always slightly lower except at the end. As for the cooling, we have a narrow front of fusion which moves from the cylinder to the axis and not the progressive melting of all droplets together.

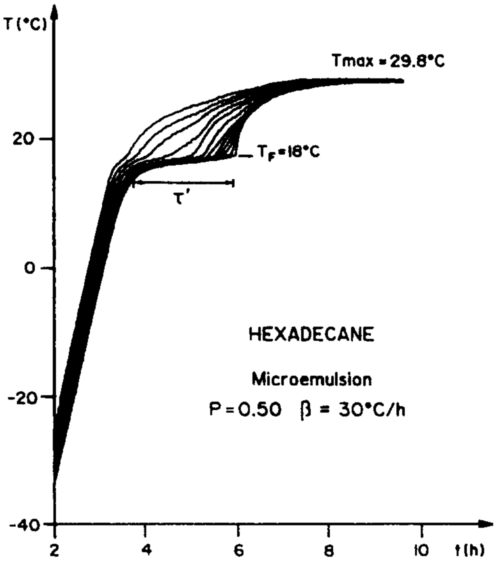

FIG. 3. Temperatures of the solders vs time for a hexadecane emulsion heated at $\beta = 30°\mathrm{C\ h^{-1}}$ ($T_{\max} = 29.8°\mathrm{C}$).

As for cooling, changing the different parameters we observe the same shape for the curves. So, it is sufficient to analyse the variation of τ', the duration of the axis temperature plateau.

Influence of the heating rate β

As indicated above, to avoid the destruction of the emulsions, it was impossible to heat sufficiently high to have full heating. Hence, Fig. 5 gives only calculated values of τ' for different values of the heating rate β.

We observe that τ' decreases when β increases but τ' is not a linear function of β.

Influence of the mass fraction P

As explained for the experiments upon cooling [1], it has been possible to study only emulsions of hexadecane where P is 0.50 or 0.25. In Table 1, we com-

Table 1. Values of τ' vs P

τ' (h)	$P = 0.50$	$P = 0.25$
Experimental	5.5	3.0
Model	5.3	2.8

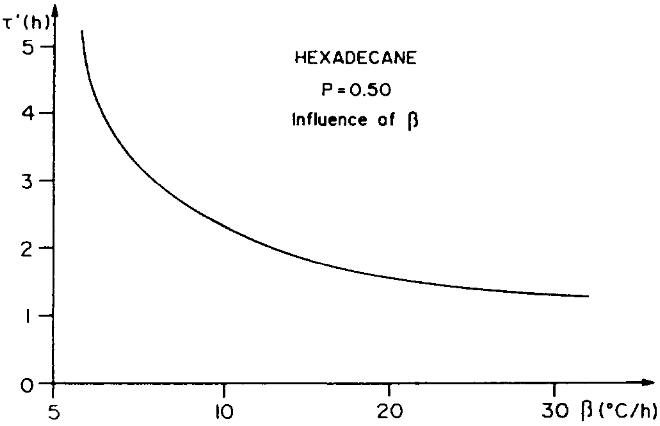

FIG. 5. Calculated values of τ' for different heating rates.

pare the experimental and theoretical results for τ' ($T_{max} = 23.0°C$).

The values are in good accordance.

Influence of the higher temperature T_{max}

In Fig. 6 we see the values of τ' when the temperature T_{max} attained by the bath is lowered (indeed $T_{max} > T_F$). We observe that τ' largely increases when T_{max} approaches the melting temperature which is logical because the heat fluxes are reduced, the temperature gradients being smaller.

Above, we have concluded that upon heating we have a narrow front moving from the inner side of the cylinder where the droplets are melting. It has been shown [6] that, even when T_{max} is low, the front is always narrow. Its moving from the inner side of the cylinder to the axis is only slowed down. This result is different from the result upon cooling [1], showing that the phenomenon is quite different.

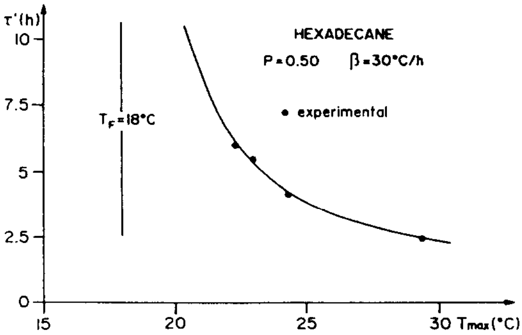

FIG. 6. Calculated and experimental values of τ' for different values of T_{max}, the maximum temperature of the bath.

5. CONCLUSION

In this second part, we have presented experimental results concerning the study of heat transfers inside an emulsion when the crystallized droplets melt.

The model presented is based on the resolution of the energy equation with a heat source (sink) depending on the local difference between the temperature of the emulsifying medium and the temperature T_F of the melting droplet. It confirms the shape of the curves giving the temperature at different radii of the cylinder vs time. We have a quasi plateau with a final temperature which is the melting temperature T_F. The experimental and calculated durations of the plateau are in good accordance and:

decreases when the heating rate increases;
decreases when the mass fraction decreases;
largely increases when the final temperature decreases.

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