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A STUDY OF THERMOGRAMS OBTAINED THROUGH DIFFERENTIAL SCANNING CALORIMETRY OF AN EMULSION OF A SUPERCOOLED LIQUID

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ABSTRACT

To study the breakdown of the supercooling of drops of liquids dispersed in an emulsifying medium, the heat involved at the time of the change in state has been measured by differential scanning calorimetry (DSC).

In order to determine the number of drops crystallizing either as a function of temperature and of time during a continuous cooling or as a function of time at a fixed temperature, the heat generated by the thermal phenomenon itself has been determined by an analysis of the principle of DSC and the basic equations of the apparatus which has been used. The limits of the validity of the methods exposed have also been indicated.

Provided that the signals obtained during either cooling or heating are correctly (and differently) delimited, it has been proved possible to measure directly the total heat of crystallization.

I. INTRODUCTION

The study of the supercooling of liquids with volumes of the order of magnitude of μ^3 shows that it is necessary to examine a large number of samples to achieve a statistical analysis of the resulting data[1]. A quick and simple method consists of dispersing the liquid into drops in an emulsifying medium. The change in state of the drops goes with the releasing of calorific energy and can therefore be detected by differential thermal analysis (DTA) or differential scanning calorimetry (DSC) of the emulsion.

These analyses provide thermograms that reveal the existence of a signal or peak whose position in the temperature curve gives indications about the degree of metastability of the dispersed liquid.

However, in a more thorough study of the phenomenon, it is essential for instance to be able to specify the number of drops crystallizing as a function of temperature or time. Thus, naturally enough, one is led to achieve an accurate study of the signal observed. As differential thermal analysis fails to be satisfactory[2], it was differential scanning calorimetry that we decided upon to achieve this study. In effect, we shall see that owing to the low thermal inertia of the enthalpimetrical analyser utilised, a thorough study of the metastable states can be achieved. Effecting our experiments on the Perkin-Elmer DSC, we have, in this paper, in the light of the theory expounded by Gray[2], intended to achieve an analysis of the signals obtained in the course of thermal processes applied on such heterogeneous bodies as emulsions, so that we could retrace the properties of the dispersed liquid.

II. RECALLING OF THE THEORY OF THE DSC-BASIC EQUATION

A thorough study of the working principle of the apparatus has been effected by Watson et al.[3], and by O'Neill[4]. A simple generalized theory for the analysis of dynamic thermal measurements has been proposed by Gray[2].

Making use of his notations, we can propose the diagram of the apparatus in Fig. 1.

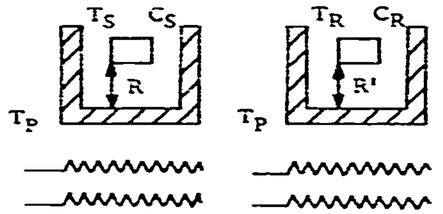


Fig. 1. Scheme of the apparatus. C_S = Total heat capacity of the sample plus container; C_R = total heat capacity of the reference (container empty); T_S = temperature of the sample; T_R = temperature of the reference; T_P = temperature of both sample holders; R, R' = thermal resistance through which the thermal energy flows to or from the sample, or to or from the reference, respectively.

The quantities dh/dt, the heat generated ($dh/dt > 0$) or absorbed ($dh/dt < 0$) by the sample per unit time, dq/dt, the difference of energies exchanged between the sample and reference and the sample holders $dT_P/dt = \dot{T}_P = C^{te} > 0$ (heating), < 0 (cooling) or $= 0$ (isothermic measurement) are related by the following relation:

$$\frac{dh}{dt} = -\frac{dq}{dt} + (C_S - C_R)\dot{T}_P - RC_S\frac{d^2q}{dt^2} \quad (1)$$

This relation is deduced from the two following ones:

$$\begin{cases} \dfrac{dh}{dt} = C_S\dfrac{dT_S}{dt} - \dfrac{T_P - T_S}{R} & (2) \\ 0 = C_R\dfrac{dT_R}{dt} - \dfrac{T_P - T_R}{R'} & (3) \end{cases}$$

which express the conservation of energy for the sample and the reference[2].

dh/dt then results as the sum of three terms, the first being the signal measured from the zero signal line, the second being the baseline displacement due to the difference in heat capacity between the sample and the reference and the third being the slope of the recorded curve multiplied by the constant RC_S.

It is to be noted that the resulting formula involves that C_R is constant whereas C_S may possibly vary with time.

When $dh/dt = 0$ and $t \gg RC_S$, the equation is written:

$$\frac{dq}{dt} = (C_S - C_R)\dot{T}_P \tag{4}$$

III. STUDY OF THE THERMAL SIGNAL RESULTING FROM THE CHANGE IN STATE OF THE DISPERSE PHASE OF AN EMULSION SUBJECTED TO CONTINUOUS COOLING

(*A*) *Determination of heat released at supercooling breakdown*

Figures 2 and 3 are an example of the thermograms observed in the case of two steadily cooled emulsions of benzene and water. The baselines before and after crystallization are not in direct time with each other. This is a result of the difference in specific heat of the supercooled liquid emulsion and the crystallized drops emulsion. Let C_{SL} and C_{SC} be the two corresponding total heat capacities; if we suppose in a first appproximation that the granulometry of the emulsion is homogeneous and that the heat of crystallization varies only little with temperature during the lapse of crystallization of the drops, dh/dt is in direct ratio to the number of drops crystallizing per unit time, that is, dn/dt. So we can state:

$$\frac{dh}{dt} = \frac{dn}{dt} \cdot \rho \cdot v \cdot L_c \qquad \text{with} \qquad \int_{t_o}^{t_e} \frac{dn}{dt}\, dt = n$$

in which ρ = the volume density of the dispersed liquid;
n = the total number of drops;
L_C = the heat of crystallization per mass unit;
t_o = the beginning of crystallization;
t_e = the end of crystallization.

To determine L_c it is necessary among other things to know what heat has been utilized in the process of crystallization of the emulsion drops. We have intended to specify what area should be taken in order to determine the correct heat released at the time of crystallization. In the case of the melting of a pure body, Guttman and Flynn[5] have shown that whenever there is a difference in the specific heats of the melted and the solid body, it is essential to define the melting peak, as is shown in Fig. 4, if the quantity of heat absorbed in the course of melting is to be obtained. However, their calculations can only be applied to the particular case of a thermal phenomenon (sharp transition) occurring at a fixed temperature. Here the problem is different as drops crystallization occurs from the beginning, continuously. Thus, we

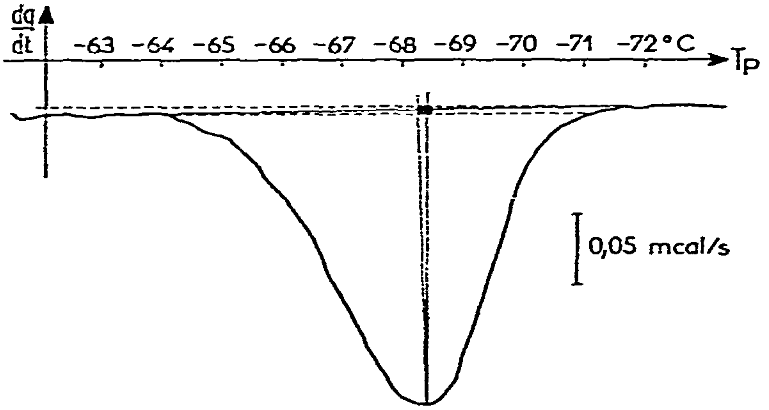
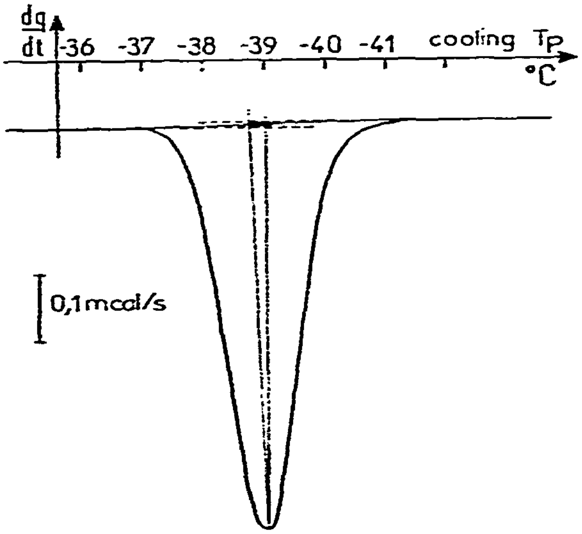


Fig. 2. Thermogram of a benzene emulsion obtained on cooling ($\dot{T}_P = -1.25\,°C\,min^{-1}$).



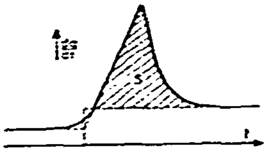


Fig. 3. Thermogram of a water emulsion obtained on cooling ($\dot{T}_P = -1.25\,°C\,min^{-1}$).

Fig. 4. Determination of the melting peak area (from Guttman and Flynn[6]).

shall have to consider a continuous variation of C_S instead of a discontinuous one as in the case of melting.

If we suppose that the variations of total heat capacity of the emulsion as a function of temperature are those indicated in Fig. 5, the quantity

$$S^* = \int_{t_0}^{t_e} \left[\frac{dq}{dt} - (C_S - C_R)\,\dot{T}_P \right] dt \qquad (5)$$

represents the hatched area in the same figure.

After relation (1), eqn (5) can be written as:

$$S^* = \int_{t_0}^{t_e} -\frac{dh}{dt}\,dt - \int_{t_0}^{t_e} RC_S \frac{d^2q}{dt^2}\,dt$$

The first integral represents $-\Delta H_c$, total heat released in the course of the change in state. We write the second integral under the form $-RI$, with

$$I = \int_{t_0}^{t_e} C_S \frac{d^2q}{dt^2}\,dt$$

An evaluation of this term characterizing the difference between S^* and $-\Delta H_c$ can be made in the following way.

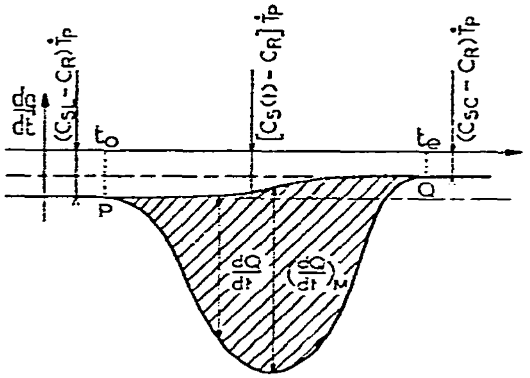


Fig. 5. Graphic determination of S^*.

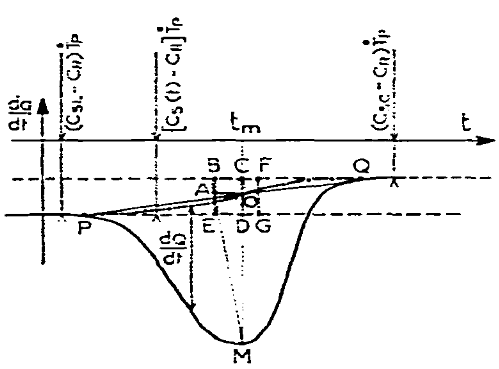


Fig. 6. Study of the determination of the crystallization peak area of a dispersed supercooled liquid.

First of all, it is important to note that, between the times t_0 and t_m, d^2q/dt^2 is $\leqslant 0$; and between t_m and t_e, d^2q/dt^2 is $\geqslant 0$ (t_m being the time corresponding to the minimum point M of the curve). Besides, the total heat capacity of the emulsion, that is $C_S(t)$ is comprised between both values of C_{SC} and C_{SL}, that is:

$$C_{SC} \leqslant C_S(t) \leqslant C_{SL}$$

In this case we can write:

$$I \geqslant C_{SL} \int_{t_0}^{t_m} \frac{d^2q}{dt^2}\,dt + C_{SC} \int_{t_m}^{t_e} \frac{d^2q}{dt^2}\,dt$$

and

$$I \leqslant C_S(t_m) \int_{t_0}^{t_m} \frac{d^2q}{dt^2}\,dt + C_S(t_m) \int_{t_m}^{t_e} \frac{d^2q}{dt^2}\,dt$$

In the type of experiments we have effected, the point M approximately corresponds to 50% of the quantity of crystallized liquid, so that:

$$C_S(t_m) \approx \frac{C_{SL}+C_{SC}}{2}$$

Using $\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_M = \left(\frac{dq}{\mathrm{d}t}\right)_M - [C_S(t_m)-C_R]\,\dot{T}_P$ (see Fig. 5)

we obtain $I \leqslant -C_S(t_m)(C_{SL}-C_{SC})\,\dot{T}_P$

and

$$I \geqslant \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_M (C_{SL}-C_{SC}) - C_S(t_m)(C_{SL}-C_{SC})\,\dot{T}_P$$

Therefore we can write:

$$-[S^* - RC_S(t_m)(C_{SL}-C_{SC})\,\dot{T}_P] \leqslant \Delta H_c \leqslant$$

$$-\left[S^* + R\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_M (C_{SL}-C_{SC}) - RC_S(t_m)(C_{SL}-C_{SC})\,\dot{T}_P\right] \tag{6}$$

The evaluation of the corrected terms can be effected from the following graphic determinations.

In Fig. 6, we have drawn from point M (minimum of the curve) a straight line whose slope is equal to $\dot{T}_P/R$ (we can form an idea of this quantity by studying the melting peak of a pure body, for instance In or Hg). As OM represents $(\mathrm{d}Q/\mathrm{d}t)_M$, OA represents $(R/\dot{T}_P)\,(\mathrm{d}Q/\mathrm{d}t)_M$. Besides, CD is equal to $(C_{SL}-C_{SC})\,\dot{T}_P$. Therefore,

$$R\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_M (C_{SL}-C_{SC}) = \text{area BCDE}$$

We can obtain an approximate value of $RC_S(t_m)$ by studying the downward slope of a melting peak[2].

Supposing that CF is equal to that quantity, we have then:

$$RC_S(C_{SL}-C_{SC})\,\dot{T}_P = \text{area CFGD}$$

Thus, we can see from the graph that:

$$-[S^* - \text{area CFDG}] \leqslant \Delta H_C \leqslant -[S^* + \text{area BCDE} - \text{area CFGD}].$$

This calculation is interesting as it shows how these areas can be reduced so as to make them so negligible that we can write with a good approximation:

$$\Delta H_c = -S^*$$

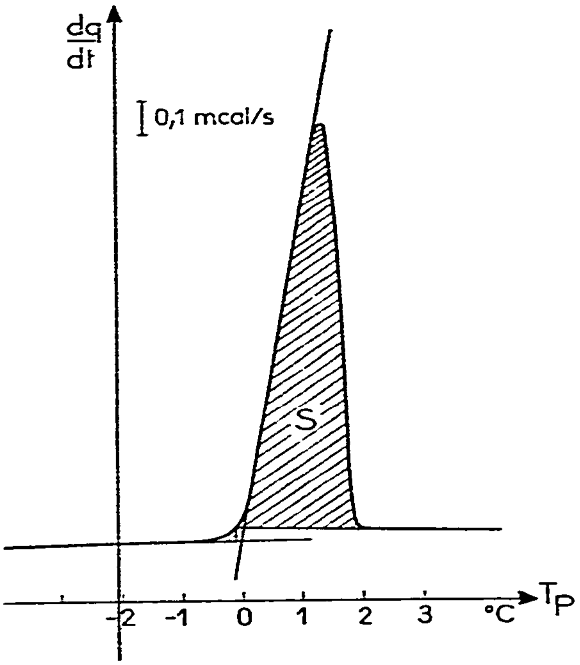
We can see that the safest method is to reduce the speed $|\dot{T}_P|$. In fact, in this case, FG will have decreased and the area CFDG will have decreased in proportion. Besides, if $|\dot{T}_P|$ is decreased, $t_c - t_o$ is increased and we can see experimentally that $(\mathrm{d}Q/\mathrm{d}t)_M$ is decreased. Then the area BCDE will be smaller. Therefore, we can see that we need a cooling speed low enough to be able to write:

$$\Delta H_c = -S^*$$

Besides, under these conditions, we can replace the plot of the curve POQ by the straight line PQ. This makes the determination of S^* easier (see Fig. 6).

Therefore, we can conclude that in the case of crystallization of drops dispersed within an emulsion, which can be effected in a lapse of time much longer than RC_S (from 1 to 2 min in our case), we are able, by determining the area of the thermal signal defined correctly, to go back directly to the heat released at the time of the change in state. Then we can think that it is possible to go back to the heat of crystallization at the temperature of the change in state. To achieve this, the quantity of material concerned in the transformation should be known, which may prove difficult as we dispose of an emulsion whose mass fraction is not known precisely. We prefer to make use of the method that also studies the signal observed during the melting of the crystallized drops.

The experiment shows that, as a rule, there is no noticeable delay in the melting of the crystallized drops[1]. Hence, all drops melt at the same temperature and we may in a first approximation consider that the transition from the crystallized drops emulsion to the liquid drops emulsion occurs at a fixed temperature. This is confirmed by the experiment, as the thermogram reveals a conventional melting peak,



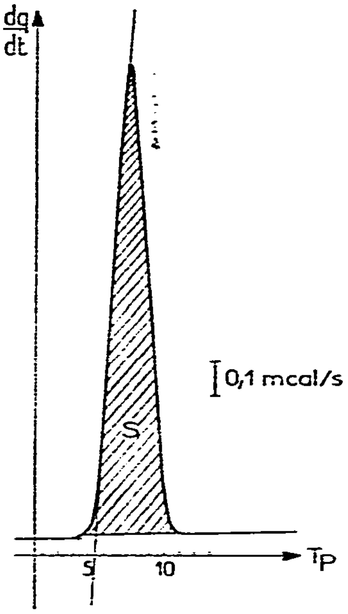


Fig. 7. Melting peak of dispersed ice ($\dot{T}_P = 1.25$ °C min^{-1}).

Fig. 8. Melting peak of crystallized benzene dispersed in a medium ($\dot{T}_P = 5$ °C min^{-1}).

which is shown by Figs. 7 and 8 relating to the melting of ice and crystallized benzene.

As is shown by Guttman and Flynn[5], the hatched area S in Figs. 7 and 8 represents the total melting heat ΔH_F. Referring to the melting latent heat per mass unit as L_F, we shall have:

$$L_C = -\frac{\Delta H_C}{\Delta H_F} L_F = -\frac{S^*}{S} L_F \tag{7}$$

Examples

Water crystallizing at about $-40\,°C$ gives $L_C = -0.70 \cdot L_F = +56$ cal g^{-1}.

Benzene crystallizing at about $-67\,°C$ gives $L_C = -0.90 \cdot L_F = +27$ cal g^{-1}.

(B) Determination of the temperatures of a change in state

The study of the mechanism of a change in state of the emulsion also necessitates the knowledge, at any time, of temperature. In particular, it is important to know the temperature of the emulsion at the time of the change in state.

The definition of $\mathrm{d}q/\mathrm{d}t$ gives:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{T_P - T_S}{R} - \frac{T_P - T_R}{R'}$$

After eqn (2), we can write $\mathrm{d}q/\mathrm{d}t = (T_P - T_S)/R - C_R \dot{T}_P$ in a steady state. From this we can deduce:

$$T_S = T_P - R\frac{\mathrm{d}q}{\mathrm{d}t} - RC_R \dot{T}_P$$

which can be written:

$$T_S = T_P - RC_S \dot{T}_P - R\left[\frac{\mathrm{d}q}{\mathrm{d}t} - (C_S - C_R)\dot{T}_P\right]$$

or also, when posing:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}q}{\mathrm{d}t} - (C_S - C_R)\dot{T}_P$$

$$T_S = T_P - RC_S \dot{T}_P - R\frac{\mathrm{d}Q}{\mathrm{d}t} \tag{8}$$

The quantity $\mathrm{d}Q/\mathrm{d}t$ can be evaluated graphically as has been indicated in Fig. 5.

$RC_S \dot{T}_P$ is a quantity >0 at heating and <0 at cooling, whose determination can be effected graphically from the melting peak.

The evaluation of $R\mathrm{d}Q/\mathrm{d}t$ gives us the rise in temperature of the sample resulting from the freezing of drops. For instance, at peak top (point M), we find:

$$R\frac{\mathrm{d}Q}{\mathrm{d}t} = 0.5\,^{\circ}\mathrm{C} \qquad \text{for water} \qquad (\dot{T}_{\mathrm{P}} = 1.25\,^{\circ}\mathrm{C\ min}^{-1})$$

$$R\frac{\mathrm{d}Q}{\mathrm{d}t} = 0.9\,^{\circ}\mathrm{C} \qquad \text{for benzene} \qquad (\dot{T}_{\mathrm{P}} = 5\,^{\circ}\mathrm{C\ min}^{-1})$$

Note: If we apply formula (8) to the upward slope of a melting peak, we find $T_{\mathrm{S}} = T_{\mathrm{F}}$, melting temperature of the body studied.

(*C*) *Determination of the number of drops crystallizing as a function of temperature or time*

Taking into account the hypotheses formulated in paragraph A, we know that between dn/dt, the number of drops crystallizing per unit time, and dh/dt there is a relation of the type

$$\frac{\mathrm{d}h}{\mathrm{d}t} = K\frac{\mathrm{d}n}{\mathrm{d}t}$$

Thus, knowing dh/dt we can go back to dn/dt. Gray[2] proposes to determine dh/dt graphically as a function of time, thus necessitating the knowing of RC_{S}, which can only be evaluated at melting temperature, hence at a different temperature. Because of the low thermal inertia of the apparatus, we have applied a method consisting of cooling until time t_{i} and then heating immediately so as to obtain melting. The area S_{i} of the corresponding melting peak is proportional to that quantity of liquid crystallized during cooling until time t_{i}. From formula (8) we can determine the temperature of the sample $T_{\mathrm{S}}^{\mathrm{i}}$ at time t_{i}. The curve S_{i}/S as a function of $T_{\mathrm{S}}^{\mathrm{i}}$ provides at any time, hence at any temperature, the proportion of liquid crystallized at $T_{\mathrm{S}}^{\mathrm{i}}$. Thus, we can plot the variations of S_{i}/S as a function of time or temperature:

$$\frac{S_{\mathrm{i}}}{S} = \frac{1}{n}\int_{t_0}^{t_{\mathrm{i}}} \frac{\mathrm{d}n}{\mathrm{d}t}\,\mathrm{d}t = \mathrm{f}(t_{\mathrm{i}}) = \varphi(T_{\mathrm{S}}^{\mathrm{i}}) \tag{9}$$

and from this integral curve, it is then possible to plot the differential curve and so to obtain dn/dt as a function of $T_{\mathrm{S}}^{\mathrm{i}}$.

It should be mentioned here that this determination should be made cautiously. In fact, as the apparatus does not directly provide T_{S} but T_{P}, it is important to know the temperature effectively reached by the sample when heated at time t_{i}.

Let us suppose that the sample is cooled at the speed $\dot{T}_{\mathrm{P}}$ until t_{i}, then heated at the speed $\dot{T}_{\mathrm{P}}'$ with:

$$\dot{T}_{\mathrm{P}}' = -k\dot{T}_{\mathrm{P}} \qquad (k > 0) \tag{10}$$

In order to make this study simpler, we will suppose that dh/d$t \approx 0$. We may think in fact that the conclusions of this study are not altered materially when dh/d$t \neq 0$.

From (8), we have the following relations:

$$\left.\begin{array}{ll} t<t_i & T_S = T_P - RC_S\,\dot{T}_P \\ t=t_i & T_S^i = T_P^i - RC_S\,\dot{T}_P \end{array}\right\} \tag{11}$$

and because of the linear variation of temperature T_P, for $t \geqslant t_i$, we have:

$$T_P = T_P^i + \dot{T}'_P(t-t_i)$$

Besides, from formula (2), we have for $\mathrm{d}h/\mathrm{d}t = 0$

$$\frac{T_P - T_S}{R} = C_S\frac{\mathrm{d}T_S}{\mathrm{d}t}$$

that is:

$$\frac{\mathrm{d}T_S}{\mathrm{d}t} + \frac{1}{RC_S}T_S = \frac{T_P}{RC_S}$$

For $t>t_i$, this relation is written:

$$\frac{\mathrm{d}T_S}{\mathrm{d}t} + \frac{1}{RC_S}T_S = \frac{1}{RC_S}\left[T_P^i + \dot{T}'_P(t-t_i)\right]$$

Taking into account the relations (11), the solution of this equation gives:

$$T_S = T_P + RC_S\left[\dot{T}_P - \dot{T}'_P\right]\mathrm{e}^{-\frac{t-t_i}{RC_S}} - RC_S\,\dot{T}'_P \tag{12}$$

We have plotted in Fig. 9 the variations of T_P as well as those of T_S as deduced from the formula above for $t>t_i$.

For $t-t_i \gg RC_S \approx 3$ sec

$$\mathrm{e}^{-\frac{t-t_i}{RC_S}} \to 0$$

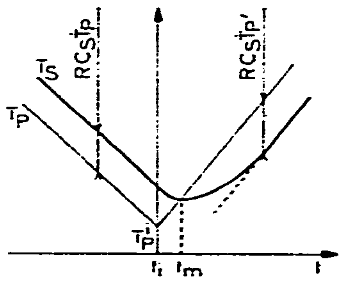
and the curve of T_S moves asymptotically towards the equation line

$$T_S = T_P - RC_S\,\dot{T}'_P$$

Thus we can see, as is shown by the plot of the curve, that T_S continues falling beyond T_S^i down to time t_m. In order that this falling should be as slight as possible, it is profitable to make $t_m - t_i$ as low as possible.

The time t_m will be determined by writing that at this instant $\mathrm{d}T_S/\mathrm{d}t = 0$. With $\dot{T}'_P = -k\dot{T}_P$ we find:

$$t_m - t_i = RC_S \log\frac{RC_S\,\dot{T}'_P\left(1+\frac{1}{k}\right)}{RC_S\,\dot{T}'_P} = RC_S\log\left(1+\frac{1}{k}\right) \tag{13}$$



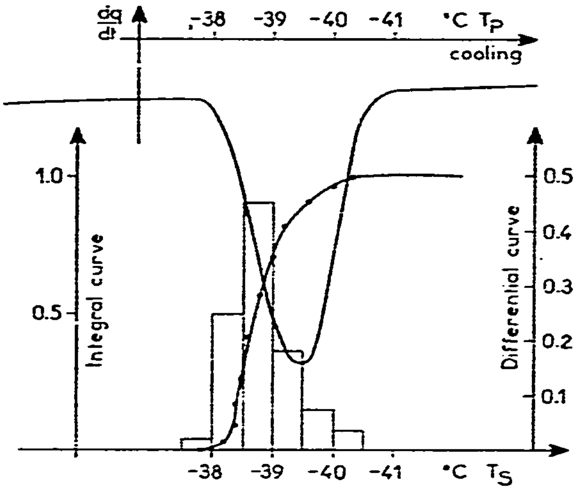
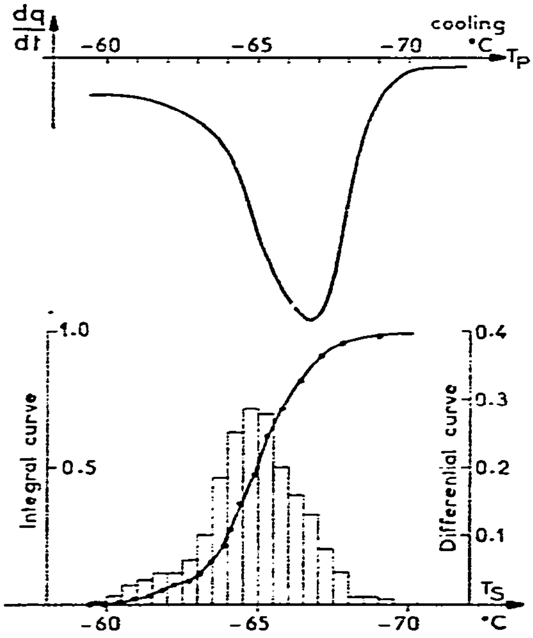


Fig. 9. Variation of T_S when $\dot{T}_P$ changes at t_i (cooling + heating).

Fig. 10. Determination of $\frac{dn}{dt}(T_S)$ (water, $\dot{T}_P = -1.25\,°\mathrm{C\,min}^{-1}$).



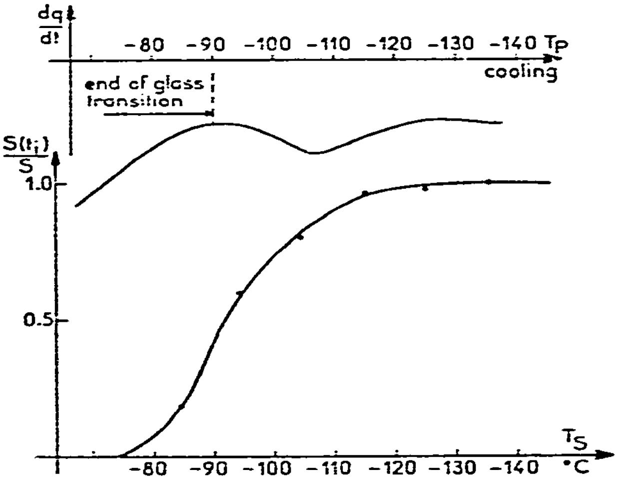


Fig. 11. Determination of $\frac{dn}{dt}(T_S)$ (benzene, $\dot{T}_P = -5\,°\mathrm{C\,min}^{-1}$).

Fig. 12. Determination of $\frac{dn}{dt}(T_S)$ (nitrobenzene, $\dot{T}_P = -20\,°\mathrm{C\,min}^{-1}$).

Example

$$\dot{T}_P = -5\,^\circ\mathrm{C\,min^{-1}}; \qquad \dot{T}'_P = 80\,^\circ\mathrm{C\,min^{-1}};$$

$$t_m - t_i = RC_S \log\left(1 + \frac{1}{16}\right) \approx \frac{RC_S}{16} \approx 0.2\ \mathrm{sec}$$

Thus we see that $t_m - t_i$ will be lower as k is greater.

Therefore, we come to the conclusion that we have to choose the highest possible ratio between the speeds of heating and cooling so that we can consider that the sample temperature actually reached in the course of cooling is that corresponding to the instant t_i.

This precaution being taken, it becomes possible, by the method described above, to go back to the quantity of liquid that has crystallized as a function of temperature. As an example (Figs. 10 and 11), we give the results obtained for a water and a benzene emulsion. We also have to remark that in the case of crystallization within a wide range of temperatures, that is with very low values of dh/dt, this is the only feasible method for studying the change in state of the disperse phase, as it often occurs that the specific heat of the pure emulsifying medium is not absolutely constant in this wide range of temperatures, and it is unnecessary to utilize the highest sensibility of the apparatus. The melting peak is always narrow and can always be seen, and its area can always be measured. This is, for instance, the case with nitrobenzene emulsified in a medium which presents unfortunately a glass transition at the beginning of the crystallization range (Fig. 12).

(*D*) *Isothermic experiments*

In a certain period of time the crystallization of the liquid dispersed in an emulsion maintained at a fixed temperature can also be studied by DSC analysis. A study along this line has been effected at temperatures higher than that corresponding to the beginning of crystallization in a dynamic study. The determination of the amount of liquid that crystallizes during this time has been effected in the following way.

Several cells filled with a fraction of the same emulsion are placed in a thermostat whose temperature is held between $T_0(t_0)$ and T_F so that the dispersed liquid is in a metastable state. After having maintained the cells in the thermostat during time t, one cell is taken out and introduced into the DSC-2 apparatus whose sample holder has been previously held at the temperature of the thermostat. From this temperature, the emulsion is heated and one notes the area $S(t)$ of the peak of melting. This area is proportional to the amount of liquid which has crystallized during time t. To know the whole amount of the dispersed liquid, the emulsion is cooled and heated once again. The cooling is performed until complete crystallization of the liquid in the emulsion is achieved. Let S be the area of the peak of melting observed during heating.

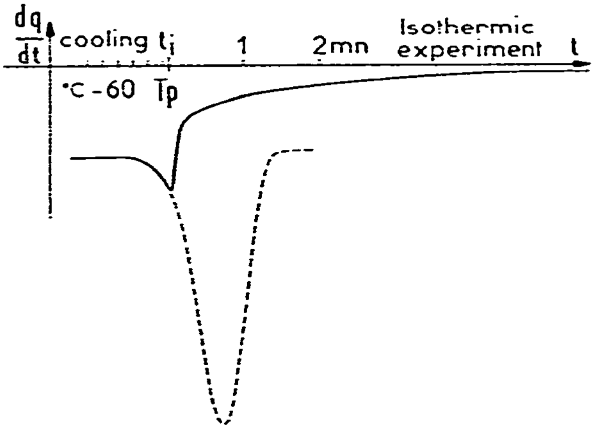
The proportion of liquid having crystallized during time t then equals the ratio:

$$\frac{S(t)}{S}$$

By studying the cells previously placed in the thermostat at different lapses of time t, it is possible to go back to the proportion of liquid which crystallized in a period of time at a fixed temperature.

When this study has to be effected at times t_i or temperatures T_i comprised between $T_o(t_o)$ and $T_e(t_e)$, the times involved are such that it is necessary to take some precautions. In Fig. 13 we have represented the thermogram obtained when cooling is stopped at $t_i > t_o$.

In fact, it is rather difficult to analyze the curve $dq/dt = f(t)$ for $t > t_i$, especially if $t_i > t_o$; that is the reason why we prefer to heat at the instant t and then measure the area of the melting peak $S(t)$. $S(t_i)$ will represent the quantity of liquid having crystallized at a temperature varying down to t_i; and $S(t) - S(t_i)$ will represent the quantity of liquid that has crystallized at a fixed temperature in time $t - t_i$.



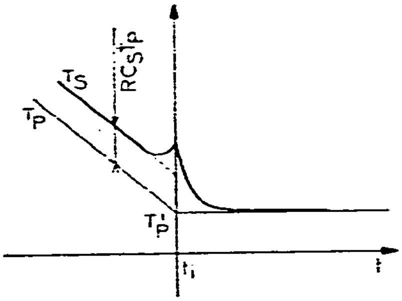


Fig. 13. Thermogram obtained with a benzene emulsion on cooling up to $t = t_i$ and on maintaining at fixed temperature for $t > t_i$.

Fig. 14. Variation of T_S when $\dot{T}_P$ becomes zero for $t \geq t_i$ after cooling up to t_i.

However, it is important to know the variations in temperature T_S of the sample when cooling is stopped at t_i. Supposing that $dh/dt \approx 0$ for $t > t_i$ and by using eqn (12) with $\dot{T}_P' = 0$, we have for $t > t_i$:

$$T_S = T_P^i + RC_S \dot{T}_P e^{-\frac{t-ti}{RC_S}}$$

We can see that if for $t_i > t_o \dfrac{dQ}{dt}(t_i) \neq 0$ we have:

$$T_S = T_P^i + \left[RC_S \dot{T}_P + \frac{R\,dQ}{dt}(t_i)\right] e^{-\frac{t-t_i}{RC_S}}$$

Therefore the temperature reached is not $T_S(t_i)$, but

$$T_P(t_i) = T_P^i$$

as is shown in Fig. 14.

Besides, this temperature T_P^i is not reached immediately, but after some time (about 2 or $3RC_S$). Thus our experiments will only be valid if crystallization is achieved in times much longer than $RC_S(dk/dt \approx 0)$.

IV. CONCLUSIONS

In conclusion, we see that the interpretation of thermograms obtained through DSC analysis of an emulsion is a tricky one, on account of the complexity of the phenomena studied.

As the determination of the heat involved at the time of the change in state is effected from the area of the thermal signal observed, it is essential to define this signal correctly. As the change in state of a supercooled liquid emulsion has specific characteristics of its own, we have been led to take the basic equations of the apparatus utilized so that we could define the area that is best to take in order to obtain a correct determination. In particular, we have come to the conclusion that the lower the cooling speed used, the better the determination.

We have seen that it is also possible to determine the number of drops crystallizing as a function of temperature T and of time t. This determination is effected by cooling the sample to temperature T at the speed $\dot{T}_P$, the emulsion being then heated at the speed $\dot{T}'_P$. The proportion of drops having crystallized at temperature T, that is:

$$\frac{n(T)}{n}$$

is then equal to $S(T)/S$, where $S(T)$ and S, respectively, represent the areas of the melting peaks obtained on cooling to temperature T and all emulsion drops have been crystallized. As there is a difference between the temperatures of the sample T_S and of the sample holders T_P, and the phenomena studied are a function of temperature, it is essential to specify what temperature has actually been reached by the sample during cooling. We have come to the conclusion that the ratio:

$$k = -\frac{\dot{T}'_P}{\dot{T}_P}$$

should be taken as large as possible.

It is important here to emphasize that the method of investigation is particularly interesting when the change in state covers a long span of time, with the signal observed being only slightly indicated.

The study in function of time, at a fixed temperature also necessitates some precaution, as the sample at the time of stabilization has a temperature different from that imposed by the sample holder. It is essential then to take into account the time-constants involved in the interpretation of the results obtained.

Moreover this study leads us to try to verify different models that can be proposed for the mechanism of crystallization of a supercooled liquid dispersed in a matrix.

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