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Differential thermal analysis, differential scanning calorimetry, and emulsions

Danièle Clausse

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Abstract This article is a review of some of the results we have obtained by studying various kinds of emulsions using techniques from the simplest one, a home-made differential thermal analysis to elaborated ones such as differential scanning calorimetry commercial devices. These techniques were used not only to determine energetic values but also essentially to show and quantify physical chemical phenomena such as undercooling, freezing, melting, mass transfer between droplets and solid formation involved in hydrate formation.

Keywords Emulsions · Undercooling · Mass transfer · Hydrate · DSC

Introduction

Emulsions are very well-known systems specially when referring to what is called simple emulsions. Generally speaking, they are composed of a continuous phase wherein droplets of a rather poor miscible liquid are dispersed. At least a third compound is needed in order to get a kinetically stable emulsion, namely a surfactant. The continuous phases are either oil for water in oil emulsion (W/O) or water for oil in water emulsion (O/W). The surfactant is a compound which shows the particularity to have a hydrophilic part and a hydrophobic one and by the way it will preferentially be found at the interface water–oil of the droplets. Nevertheless, when the interface cannot accept more molecules according to the equilibrium state, molecules gather in the continuous phase to give micelles that could play an important role in transport phenomena as it will be shown later on in this article. Less known are what has been referred as mixed emulsions. They have been introduced for getting controlled sized droplets or for studying mass transfer within emulsions on a fundamental point of view. They are composed of two populations of droplets having different compositions and giving rise to mass transfer which can be achieved in a rather short time when compared to classical osmosis device. Close to these systems are multiple emulsions as far they are made of two different composition phases separated by a third one. Two kinds of multiple emulsions are found: the emulsions referred as W/O/W made of oil globules wherein water is dispersed, these oil globules being themselves dispersed within an aqueous continuous phase and the other one referred as O/W/O made of water globules wherein oil is dispersed, the water globules being themselves dispersed within an oily phase. Mass transfer can occur between the inner and the outer phases of the globules as far the compositions are different. These systems are also referred as liquid membranes systems. More details about emulsions can be found in general books dealing with [1–3] showing a great contributions of scientists and by the way the great interest for studying such systems.

All kind of emulsions are known to be not stable systems and they evolve irreversibly to separate bulk phases. Nevertheless, it is possible to obtain kinetically stable systems that permit to study various phenomena that can be detected by calorimetry if they are accompanied by either a release or an adsorption of energy. The more obvious one is freezing and melting of the dispersed phase. This phenomenon will be examined in the first section of this article. As far freezing is the result of a nucleation phenomenon, specific properties are found. Two of them showing correlations between the droplets sizes, their

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D. Clausse (✉)
Dépatement du Génie des Procédés, Université de Technologie de Compiègne, 20529-60205 Compiègne Cedex, France
e-mail: Daniele.Clausse@utc.fr

composition, and their freezing temperatures have been considered to set up a technique to characterize others phenomena such as emulsion stability, mass transfer, and hydrate formation. After having described the technique referred as the “emulsion DSC test” these phenomena will be described in the next sections.

Freezing and melting of the dispersed phase of an emulsion: theoretical point of view

For theoretical purposes, the emulsions concerned are simple ones and focussed only on the dispersed droplets. The emulsion itself is considered as being a means to get a great number of droplets having the same surroundings. Therefore, they can be studied at the same time and statistical information about their freezing temperatures can be obtained avoiding long experiments dealing with isolated droplets which are not necessarily placed in the same conditions. We will see that this point is very important when nucleation phenomena showing kinetics aspects are involved. This way of doing so has been introduced in the fifties of the twentieth century by scientists working on undercooling of metals, the most known being mercury [4].

A compilation of the works done in the field can be found in articles dealing with the technique differential scanning calorimetry (DSC) applied to emulsions [5–9]. Just the main points will be given in this article in order to understand the phenomena occurring within in the emulsions. The model is the following:

Due to capillary phenomena based on the Laplace equation showing that there is a greater pressure inside a spherical particle, the equilibrium temperature with the surrounding is found to be the lower, the particle being the smaller. Therefore, referring to a liquid droplet, to get its solidification it is necessary to place the droplet in the favorable conditions to have the formation of a spherical solid particle that will form spontaneously in the droplet as a result of local fluctuations leading to a gathering of molecules to form the solid particle. When such a particle is greater than a critical size corresponding to what is called a germ, the solidification is obtained thanks to a very fast growing of the germ.

Considering water in oil emulsion, it is assumed that all the droplets have the same volume V and that a single germ is enough to induce the whole instantaneous freezing of each water droplet. The number of droplets that could freeze during dt is given by the number of germs that could be formed in the remaining still liquid droplets, namely:

$$\mathrm{d}N_t = N_{t+\mathrm{d}t} - N_t = J(N_0 - N_t)V\,\mathrm{d}t \tag{1}$$

J being the nucleation rate that gives at any temperature T, the number of germs formed by time unit and volume unit, N_0 is the total number of droplets, and N_t is the number of frozen droplets at time t and temperature T. From theoretical considerations dealing with nucleation in condensed system, J versus T is given by:

$$J = A \cdot \exp\left[-\frac{16\pi\gamma^3 V_s}{3L_\mathrm{f}^2 \ln^2(T/T_\mathrm{f})}\frac{1}{kT}\right] \tag{2}$$

where A is a pre-exponential factor, viscosity-dependent, V_s is the molar volume of the ice germ, γ is the interfacial energy of the interface between ice and the surrounding undercooled water, L_f is the molar water freezing energy at T and T_f the melting temperature of ice or the equilibrium temperature T_e between ice and liquid water equal to 273 K under atmospheric pressure. J cannot be calculated directly from this equation as far the interfacial energy is unknown. Nevertheless, its profile versus T can be deduced as it is shown in Fig. 1.

From this profile and the relation 1 it is possible to draw the variations of dN_t or the corresponding value ΔN for a finite temperature interval ΔT. When T is near the equilibrium temperature, J is nearly zero as far the corresponding germ which has to be formed is very large (at T_e the corresponding radius is infinite) and the energy required as well. It is necessary to reach temperature far to T_e to get a great increase of J but when all the droplets are frozen, it is the term ($N_0 - N_t$) which is null. It is deduced that ΔN must be varying for the various time intervals from zero to zero with a maximum as it is represented schematically in Fig. 2.

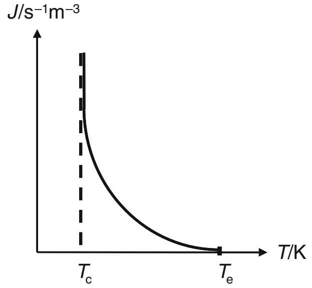

Fig. 1 Schematic profile of the nucleation rate versus temperature

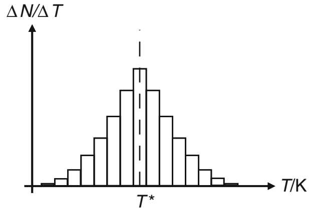

Fig. 2 Histogram of the droplets freezing temperatures

The first point to notice is that the droplets do not freeze at a same temperature. Nevertheless, the histogram shows a temperature T^* around which a maximum of droplets freeze in a relatively short temperature range. This temperature which has been referred as the most probable freezing temperature can be defined as being the temperature at which 50% of the droplets are frozen. It can be correlated to the radius R of the droplets as follows:

By integration of the relation 1, the percentage of frozen droplets N_t/N_0 at any temperature T during the regular cooling with a scanning rate written as: $\dot{T} = -\frac{\mathrm{d}T}{\mathrm{d}t}$, can be expressed as:

$$\ln \frac{N_t}{N_0} = -\frac{V}{\dot{T}} \int_{T_\mathrm{f}}^{T} J \, \mathrm{d}T. \tag{3}$$

The integration being made between the melting temperature T_f and T^*, it follows:

$$R^3 = 0,69 \frac{3\dot{T}}{4\pi \int_{T_\mathrm{f}}^{T^*} A \cdot \exp\left[-\frac{16\pi\gamma^3 V_s}{3L_\mathrm{f}^2 \ln^2(T/T_\mathrm{f})} \frac{1}{kT}\right] \mathrm{d}T} \tag{4}$$

Relation 4 shows that a correlation between R and T^* does exist. It shows that smaller the R is, the higher is the integral and therefore the difference between T and T^*.Therefore, by determining the water droplets freezing temperatures it is possible to get an information about how the water is dispersed within the emulsion.

Emulsion DSC test

DSC has been proposed to detect the freezing and the melting temperatures of the droplets. To obtain these temperatures, the emulsion is regularly cooled and the freezing is detected through the energy released thanks to a calorimeter in the head of which an emulsion sample is introduced.

The energy dh released by the freezing of dN droplets during the lapse of time dt is given by:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = V\rho L_s \frac{\mathrm{d}N}{\mathrm{d}t}, \tag{5}$$

V being the volume of the droplets assumed to be all the same, ρ being the mass by volume unit, and L_s the energy released by mass unit.

For regular cooling, the scanning rate being less than 5 K min^{-1}, dh/dt is given with a good approximation by dq/dt, electrical power registered by the calorimeter through the thermocouples placed around the head of the calorimeter containing the sample emulsion which is freezing. Therefore it can be expected that in these conditions, the shape of the freezing signal traducing the individual freezing of the droplets will show a shape close to the histogram one represented in Fig. 3 and T^* will be given by the apex of the signal with a good approximation.

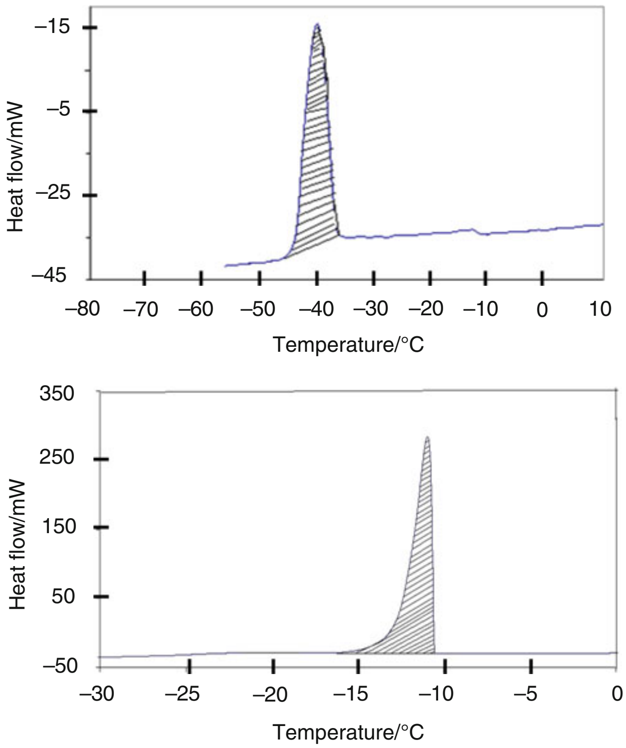

Fig. 3 Typical freezing curves of a water emulsion; *top*: all the water is emulsified as microsized droplets, *bottom*: any emulsification

During regular heating performed after freezing, all the droplets melt at the same temperature as far there is any nucleation phenomena inducing a delay respect to melting occurring therefore at 0 °C for all the droplets.

This technique permits to detect bulk water and emulsified water within an emulsion which is partially destabilized as it is shown thereafter. Figure 3 gives typical freezing curves obtained during the cooling of an emulsion.

The curve represented on the top is characteristic of the freezing of microsized water droplets as numerous previous experiments have shown. T^* corresponding to the apex of the bell-shape signal is found to be around −40 °C. The curve represented on the bottom shows water freezing at a highest temperature and furthermore the shape is asymmetric. It is characteristic of a fast release of energy due to the freezing of a unique water sample the volume of which being equivalent to the one of the whole water dispersed within the emulsion sample understudy. The volume being bigger and as far only one ice germ is enough to induce the sample freezing, the temperature is found around −15 °C in agreement with the cell volume which is around a few mm^3.

Figure 4 reproduces freezing curves of water in oil emulsions obtained after different times of preservation at room temperature.

It can be seen that just after the emulsion preparation, the droplets radii are around a few microns as far the water freezing temperature is found around −39 °C. When the test is performed 4 days later, the emulsion has changed a lot as far the freezing temperature is found at −12 °C showing that the emulsion is separated into two distinct phases. This technique has been proposed for following the evolution of emulsions in microgravity conditions in the frame of a project named Fundamental and Applied Studies on Emulsion Stability (FASES) supported by European Space Agency (ESA) and involving several research groups. The main objective is to show correlations between the evolution of the emulsion and the interfacial properties W/O, numerous works having shown that at least the interfacial tension is a parameter to consider [10, 11].

If instead of having pure water droplets, droplets made of an aqueous solution are dispersed, the way the droplets solidify is much more complicated as far two compounds A and B are involved and undercooling for the both compounds has to be considered. Figure 5 shows the equilibrium and metastable curves obtained when such systems are studied. The equilibrium curves Γ_e and Σ_e joining at the eutectic point E gives the composition of the solution in equilibrium either with solid A or solid B, respectively. Curves Γ and Σ give the most probable temperatures of solidification either for A alone or B alone versus the composition. These two curves join at point ε which is equivalent to the eutectic point E but is very different as far it is not an equilibrium point. Points α and β give the temperatures and compositions at which the dispersed solutions are expected to be totally solidified. When A is water and B a salt, curves Γ_e and Γ cut the axis corresponding to pure water at 0 °C and around −39 °C for microsized droplets. Curves Σ_e and Σ are truncated as far it is not possible to get very concentrated solutions without deterioration of the solutions.

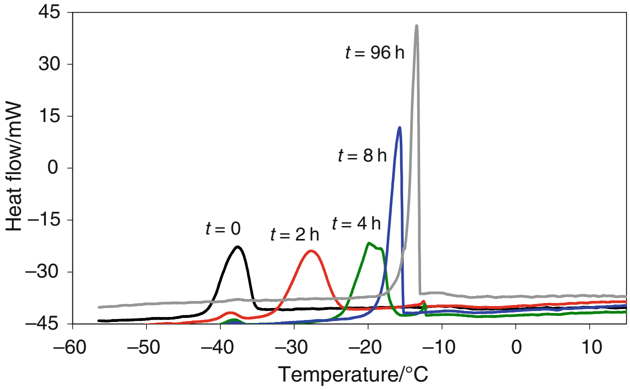

Fig. 4 Freezing curves of a water emulsion at different times of preservation at 20 °C

These curves can be drawn by performing a DSC test as it has been described for pure water emulsions. During cooling, solidification of either component A or B is observed depending on the droplets compositions. For $x < x_\varepsilon$ A will solidify first; and for $x > x_\varepsilon$ it is the solidification of B that will be observed first. The total solidification of the droplets could occur at a lowest temperature either at point α for $0 < x < x_{\alpha'}$ or at point β for $x_{\beta'} < x < 1$ or at the same temperature for $x_{\alpha'} < x < x_{\beta'}$. During heating as far there is any nucleation phenomenon, the equilibrium curves can be obtained. The detailed descriptions can be found in [6].

Differential thermal analysis (DTA) of emulsions containing droplets made of water and ammonium chloride

As far only temperatures determinations are required, DTA performed on an emulsion sample can be used. This study fully described in [12] is an example of what could be obtained with a very simple DTA device that needs a block of brass having the shape of a cylindrical ring containing three holes. One of the welds of a thermocouple is placed in one of the hole containing the emulsion sample and the other one is placed in the empty hole. A second thermocouple is used to measure the temperature, one of its welds being placed in the third hole and the other one in melted ice at 0 °C. The first thermocouple gives the temperature

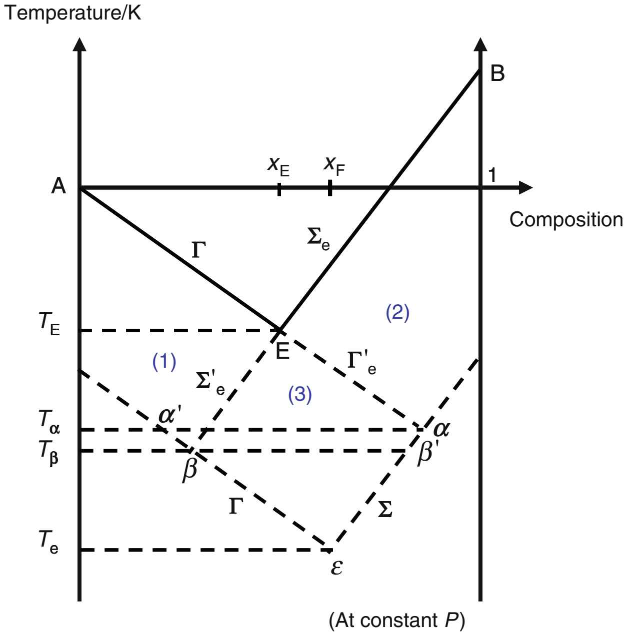

Fig. 5 Equilibrium and metastable curves for droplets containing components A + B

difference ΔT between the emulsion and the reference (empty hole). Thanks to nitrogen vapor generated by an electrical resistance immersed in liquid nitrogen, it is possible to cool the emulsion sample. A fixed cooling rate is difficult to obtain but nevertheless as far reproducible scanning rates can be provided it is possible to get reliable data or at least a general behavior. From the registered variations of ΔT versus T it is possible to get the most probable freezing temperature of the droplets from the temperature corresponding to the DTA signal apex. From the results obtained it was possible to draw the different metastable curves reproduced in Fig. 6.

X being the molar fraction of ammonium chloride, it can be seen that it is not possible to get directly an emulsion with droplets the composition of which being more than 0.15. The solution has to be heated before being dispersed and ammonium chloride solutions are known to do not bear high temperatures. In order to reach dispersed high concentrated solutions, an undersaturated solution at 20 °C was dispersed and afterward the emulsion was regularly agitated with a magnetic bar in order to create water evaporation and therefore a more concentrated solution. Already at that time it was found that water molecules can migrate through the oily continuous phase. By weighing regularly the emulsion, it was possible to deduce the concentration of the dispersed droplets. It was checked that the evaporation was quasi homogeneous among the droplets as far a rather symmetric DTA freezing signal was obtained during the cooling of an emulsion sample. From these experiments, it was shown that salt precipitation can be obtained either by cooling the emulsion the droplets having a known composition or by water evaporation until the salt precipitates in the droplets. This point was easy to detect as far the emulsion aspect is changing.

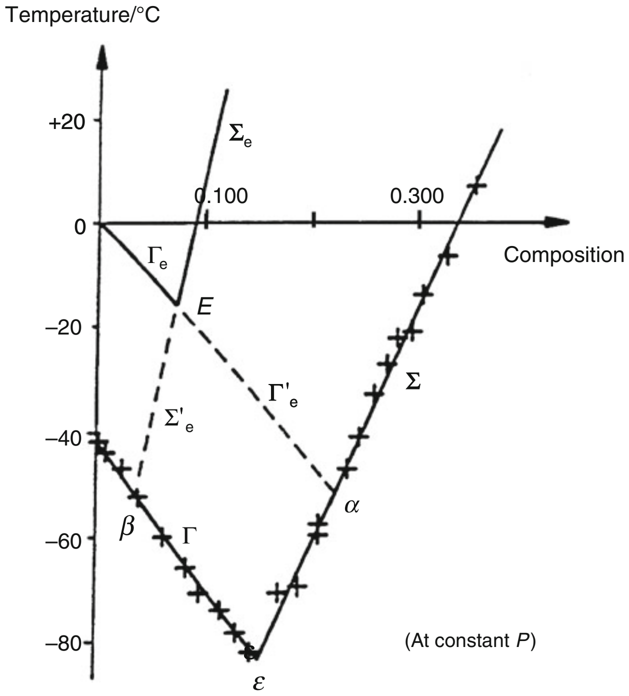

Fig. 6 Equilibrium and metastable curves for droplets containing water + ammonium chloride

Mass transfer within emulsions

The preceding example has shown that water molecules can migrate from the droplets toward the emulsion surface and afterward in the surroundings. This mass transfer is the result of the difference of the values of the water chemical potential between water in the solution and in the gaseous phase which is undersaturated regarding water. Another way to provoke mass transfer is to create a gradient of the chemical potentials of a component between two phases having different compositions regarding this component. This has been achieved by making either mixed emulsions or multiple emulsions. In the mixed emulsions, there are two droplet populations having different compositions and in multiple emulsions, the inner and the outer phases of the globules have different compositions. Should a mass transfer occur between either the droplets or the inner and the outer phases, a difference in the compositions of either the droplets or the phases should be noticed. According to the correlation between the freezing temperature and the composition, curve Γ Fig. 5, this change can be followed by performing time to time a regular cooling of the emulsion sample placed in the head of a differential calorimeter. For emulsions containing water droplets and urea + water droplets the resulting freezing curves are given in Fig. 7. The full description of the experimental study and of the model used can be found in [13].

Figure 7a gives the freezing curve for the emulsion containing pure water droplets. The freezing is found around −40 °C as expected. Figure 7b gives the freezing curve for the emulsion containing water + urea droplets. The freezing is found around −60 °C in agreement with the composition as it can be deduced from the corresponding Γ curve. DSC tests performed on emulsion samples taken at different times from the mother emulsion let at room temperature give the freezing curves represented in Fig. 7c, d, and e for 5, 35, and 65 min, respectively. The first point to notice is that there is an evolution of the freezing signals. The one dealing with pure water droplets do not change a lot regarding the temperature but its area is vanishing toward zero with time. The other one showing the freezing of water + urea droplets is changing regarding the freezing temperature which is higher and higher with time. These results have been interpreted considering a transfer of water molecules from the pure water droplets toward the water + urea droplets. This is in

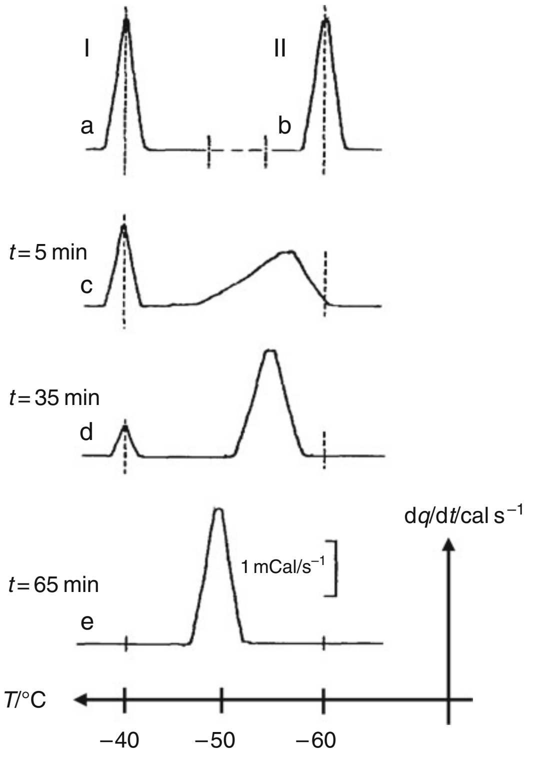

Fig. 7 Freezing curves of a mixed emulsion water + urea versus time

agreement with the rule that the water flux is in the opposite direction of the chemical potential gradient.

Similar results have been observed on O/W emulsions and on multiple emulsions either W/O/W or O/W/O [14–17]. The proposed models consider a facilitated transport mechanism due to the presence of micelles within the continuous medium [13–18].

DSC coupled with X-rays to study hydrate formation within emulsions

In this section, an example will be given to illustrate the problems that could be encountered when there is overlapping of thermal events that could be exothermic and endothermic in the same temperature range.

For obtaining full interpretation of the signals it is therefore necessary to use a complementary technique that could be used to study the same sample at the same time. This was done with the coupled technique DSC and X-rays were set up for studying other complex systems [19].

Trichlorofluoromethane (CCL_3F)

CCL_3F is known to form a hydrate at atmospheric pressure and at temperature around 8 °C. This system has been taken as model to study the formation of gas hydrate such as hydrate methane that is encountered in the petroleum industry. Hydrates create drastic problem as far they are solid and are an obstacle for the transportation of fluids in pipe lines.

During the hydrate formation, the energy released is high enough to be detected by calorimetry [20]. To get it water in oil emulsion is made (see the formulation on Fig. 8) and CCl_3F is introduced afterward to avoid evaporation. NaCl is added to water for enhance the emulsion stability and for studying its influence on the hydrate formation.

A sample of the obtained emulsion is introduced in the head of a DSC device which is cooled regularly. During the cooling, it is expected that water transforms into ice, that solid NaCl forms and that hydrate forms also. All these solid phases are expected to form as the result of nucleation phenomena and delays are expected according to the theory presented in the first section. Surprisingly, only one signal is obtained during cooling, signal that is identical to the one obtained when the aqueous solution is dispersed without addition of CCL_3F and during heating not only the progressive ice melting is observed but also an endothermic signal showing the melting of the hydrate. The question to solve was when does the hydrate form? To answer to this question, an emulsion sample was studied by DSC coupled with X-rays [21, 22]. One of the coupled freezing curve and X-rays diffractogram obtained is represented Fig. 9.

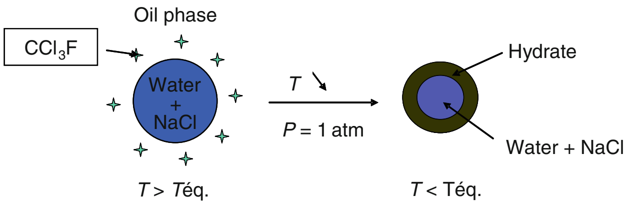

Fig. 8 Hydrate formation around a droplet

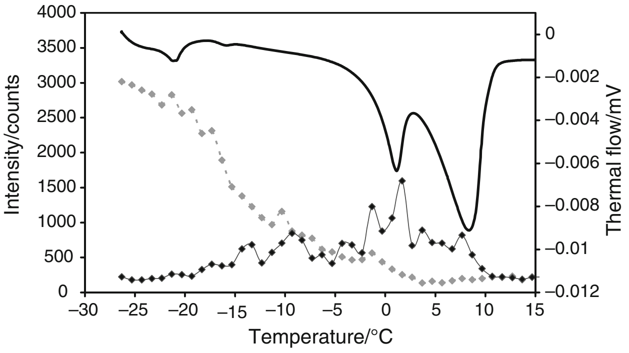

Fig. 9 DSC melting curve and X-rays intensity curves. *Continuous dark line*: melting curve; *black dots* and *lines*: intensity of hydrate line; *gray lines* and *dots*: intensity of hexagonal ice

Comparison between the DSC freezing curve and the lines intensity dealing with ice and hydrate shows the following results. Ice is melting regularly from the eutectic temperature (−21 °C) until around 0 °C a little less as far NaCl is present in the droplets. The lines dealing hydrate begin first to increase and after having reached a maximum they decrease. This means that first hydrate forms and afterward it melts according to the DSC melting curve. This result has been confirmed by performing experiments on the emulsion alone for comparison and on emulsions of dispersed saline solutions having different compositions [21, 22].

Conclusions

The results described in this article show that calorimetry is a very efficient technique for studying what can occur within emulsion when it is submitted to a regular cooling and heating. By studying the freezing and the melting of the dispersed droplets, it is possible first to determine the corresponding temperatures and to study the destabilization of the emulsion and to study mass transfer due to composition gradient of the solutions dispersed. As far quantitative values can be obtained it is possible to get model to describe the mass transfer occurring. Nevertheless, this technique cannot be sufficient enough when signals are overlapping and another technique is needed to interpret the results. The study of hydrate formation within emulsions is an example of this situation.

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