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DSC (Differential Scanning Calorimetry) used to follow the evolution of W/O emulsions versus time on ground and in space in the ISS

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Abstract. The evolution of W/O emulsion versus time in microgravity conditions has been studied in the framework of the FASES (Fundamental and Applied Studies on Emulsion Stability) project sponsored by the *European Space Agency* (*ESA*). The objective of this study was to investigate the evolution of W/O emulsions made of water + paraffin oil + SPAN 80® under purely diffusive conditions (no gravity driven effects) and to compare with evolution of similar emulsions observed on ground. A correlation between the state of dispersion of water and either the freezing temperature during cooling, or the freezing time at a fixed temperature was used to follow the emulsion evolution versus time. For that purpose, two identical calorimeters were built by *Airbus* (formerly *EADS*) with the support of the French company *SETARAM*: The Flight Model (FM) located onboard the International Space Station (ISS) and the Engineering Model (EM) located at the TELESPAZIO Centre in Naples. Dedicated cells were filled on ground with different formulations of W/O emulsions and identical experiments were performed with the FM and the EM models in order to highlight the differences in emulsion evolution. On ground, the experiments were performed by cooling and heating the calorimeter between 40 °C and −60 °C but due to technical constraints in the FM, the experiments performed in the FSL (Fluid Science Laboratory) of the ISS were limited to a lowest temperature of −22 °C. The results obtained with the FM confirmed the formation of emulsions in the dedicated cell with the selected stirring system in space. These results also demonstrated that it is possible to detect the freezing and the melting of the water droplets with the designed calorimeter either during cooling and heating phases or versus time during a temperature holding period at −22 °C. Furthermore, the comparison between both results obtained with the EM on ground and with the FM in space revealed distinct behaviours. This study drove us to focus on other mechanisms than sedimentation and convection to account for the destabilization of these kinds of emulsions.

1 Introduction

The aim of this article is to describe and compare the results obtained when studying the evolution versus time of emulsions maintained either on ground or in microgravity conditions in the International Space Station (ISS). This study is a part of the project FASES (Fundamental and Applied Studies on Emulsion Stability) sponsored by *ESA* (*European Space Agency*) the purpose of which being to outline a correlation between the emulsion stability and the interfacial properties of the emulsions under study [1]. Water-in-Oil emulsions were chosen insofar as they are among the most often encountered in the petroleum industry, especially during the production phase. In fact, water-in-oil emulsions tend to form spontaneously during the extraction of petroleum and its treatment in surface facilities because of the presence of native compounds which act as surfactants (resins, asphaltenes, naphthenic acids, fine solids, etc.) [2,3]. So, in the field of crude oil production and processing, the challenge is to obtain on the one hand crude oil without water to meet the specifications required for transport and refining and, on the other hand, water without oil for reasons of environmental constraints. An optimized separation of crude oil and water is of prime importance to warrant the quality of separated phases at the lowest cost. Crude-oil dehydration is generally performed using a combination of mechanical, electrical,

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Table 1. Chemical properties of the surfactants (sorbitan esters) 108 used to prepare.

Supplier name	Chemical name *CAS no.*	Molecular formula	HLB	Molecular weight (g.mol^{-1})	Visual aspect at 20 °C	Supplier
span 20®	Sorbitan monolaurate *1338-39-2*	$C_{18}H_{34}O_6$	8.6	346.46	viscous liquid	*Sigma-Aldrich*
span 40®	Sorbitan monopalmitate *26266-57-9*	$C_{22}H_{42}O_6$	6.7	402.57	powder	*Koch-Light*
span 60®	Sorbitan monostearate *1338-41-6*	$C_{24}H_{46}O_6$	4.7	430.62	powder	*Koch-Light*
span 65®	Sorbitan tristéarate *26658-19-5*	$C_{60}H_{114}O_8$	2.1	963.54	powder	*Sigma-Aldrich*
span 80®	Sorbitan monooleate *1338-43-8*	$C_{24}H_{44}O_6$	4.3	428.6	viscous liquid	*Fluka*
span 83®	Sorbitan sesquioléate *8007-43-0*	$C_{66}H_{126}O_{16}$	3.7	1175.7	viscous liquid	*Sigma-Aldrich*
span 85®	Sorbitan trioléate *26266-58-0*	$C_{60}H_{108}O_8$	1.8	957.49	viscous liquid	*Sigma-Aldrich*

thermal, and chemical methods. Better knowledge of the mechanisms responsible of the emulsion destabilization is a way to improve the emulsions breaking processes. Different most often cited mechanisms that could lead to emulsions breaking are Ostwald Ripening, aggregation and sedimentation. All of them can be the cause of the coalescence of the droplets and finally the formation of a bulk phase due to the rupture of the film surrounding the droplets. It is not obvious to show the relative importance of these mechanisms in ground conditions, while in space conditions, sedimentation and convection that could lead to aggregation are suppressed and focus can be put on the other mechanisms. Therefore, it is expected that emulsions will show a better stability in space if at least the mechanisms of aggregation and sedimentation are eliminated.

In this context, the first point was to find an apparatus that could be able to follow the evolution of the emulsion in space. Previous works dealing with the characterization of water-in-oil emulsions versus time have shown that the so-called DSC (Differential Scanning Calorimetry) test is a powerful means to get reliable data on ground [4]. Therefore, this technique was proposed for studying dense emulsions, and a calorimeter was designed to be built on ground and launched in the FSL (Fluid Science Laboratory) of the ISS. Another one was also built in order to test the evolution of the emulsions on ground and to compare the results with the ones obtained in space.

Another crucial point concerns the emulsion preparation. In the project, emulsions are made on ground, and samples of these emulsions are put in the cells built specially to be inserted into the two calorimeters. The formulations of the emulsions were a great challenge of this study and some of the results obtained are described in this article. The formulations were defined in our lab by using the DSC test on commercial calorimeters and other techniques as bottle tests and optical microscopy.

2 Materials and methods

2.1 Materials

To be in agreement with the specifications of the FASES project, pure deionised water and a non-toxic oil were used to prepare surfactant solutions and water-in-oil emulsions. The deionised water with a resistivity of 18.2 MΩcm was produced by a Lab purification chain provided by *Veolia Water* (France). In addition, the oils used must not crystallize in the temperature range between 20 and −60 °C, so as not to interfere with the interpretation of the DSC results by overlapping the crystallization signal of water. So, first experiments were performed with various alkanes as hexane, heptanes, methylcyclopentane, and methylcyclohexane supplied by *Merck*, or more complex oils as silicone and paraffin oils supplied by *Fluka*. To aid emulsification, a surfactant was introduced in the continuous water phase prior mixing. Several surfactants of the sorbitan ester type, as described in Table 1, were used in order to study their influence on the water-in-oil emulsions evolution.

2.2 Emulsion preparation

A miniature metal cell fitted with a magnetic bar stirrer was designed (Fig. 1) and provided by *Airbus* (formerly *EADS-ASTRIUM*) for the FASES project, in order to directly prepare water-in-oil emulsions on ground and in space by mixing. These cells were prefilled on ground by pouring the required amount of water and the oil + surfactant phases with a syringe at room temperature. Identical formulations and replicated cells were used for experiments on ground and in space. Before emulsifying, samples were destabilized at 50 °C during 5 h to have water and oil phases fully separated and define a time zero. Emulsions were emulsified in the dedicated cells following a nominal agitation procedure of 1600 rpm during 30 min or a reduced agitation procedure involving less energy. After emulsifying at 40 °C, cells were stored at 40 °C during different ageing times.

A preliminary study was performed in our laboratory in order to make a first screening of formulations. Various compositions of water-in-oil emulsions were prepared by mixing surfactant with oil, and then adding deionised water using an Ultra Turrax T25 high speed blender Janke&Kunkel homogenizer at 25,000 rpm for 5 min at room temperature.

2.3 Bottle test

The bottle test method was used to indicate the emulsion stability by monitoring the extent of phase separation with time. Emulsions were stored in 10 mL graduated glass test

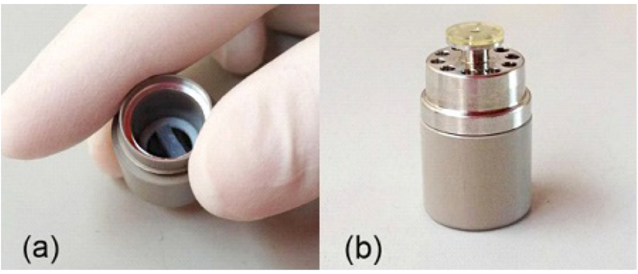

Figure 1. Images of miniature cell designed and provided by Airbus for the FASES Project to prepare emulsions on ground and in space. a) the integrated magnetic agitator, b) the protective lid on.

tubes at room temperature 20 °C ±2 °C. The percentage of each phase (emulsion, oil and water phases) was measured at regular time intervals and reported during at least 120 h.

2.4 Microscopy

The optical microscope was used to directly observe the state of dispersion of emulsions and to estimate their droplet size distribution. A Labophot-2 Nikon optical microscope (Japan) equipped with an ExwaveHAD Sony color video camera (Japan) was used. In addition, a thin glass slide was used to cover the emulsion sample in order to optimize the optical observation. It was verified that this operation did not induce a modification of the droplet diameter.

2.5 DSC test

The DSC test is performed on a sample emulsion taken time to time to see the emulsion evolution versus time. The sample introduced in a calorimeter is submitted either to a regular cooling–heating cycle or either maintained at a fixed subambient temperature in order to detect the freezing–melting transitions of the dispersed droplets. This technique allows the detection of the relatively important amount of energy during freezing and melting transitions of water. The freezing of water droplets is a stochastic process which depends on ice nucleation mechanism with time, droplet volume or cooling rate. The DSC test is based on the correlation between the droplet freezing probability and its volume during experiments carried out either during a regular cooling over time or at a fixed temperature over time. Consequently, undercooling state of water and freezing temperatures below the liquid/solid equilibrium temperature are observed. More details about the freezing of droplets dispersed within an emulsion can be found in a dedicated publication [5].

2.5.1 DSC test during cooling

The observed freezing delay is the result of the nucleation phenomenon and the necessary formation of an ice germ to enhance the freezing of a water droplet. Due to its small size, capillary phenomena have to be taken into account, and it is found that the probability of its formation is temperature and size dependent. The large number of droplets in the water-in-oil emulsion makes it possible to obtain statistical data on water dispersion in emulsion with DSC tests [6]. To interpret the DSC results, two extreme situations are considered as references: #1 the emulsion is essentially made of microsized and well isolated from each other water droplets, and #2 the emulsion is completely broken and made of two distinct water and oil bulk phases. Typical DSC cooling curves obtained for an emulsion containing microsized water droplets and completely broken emulsion are given in Figure 2.

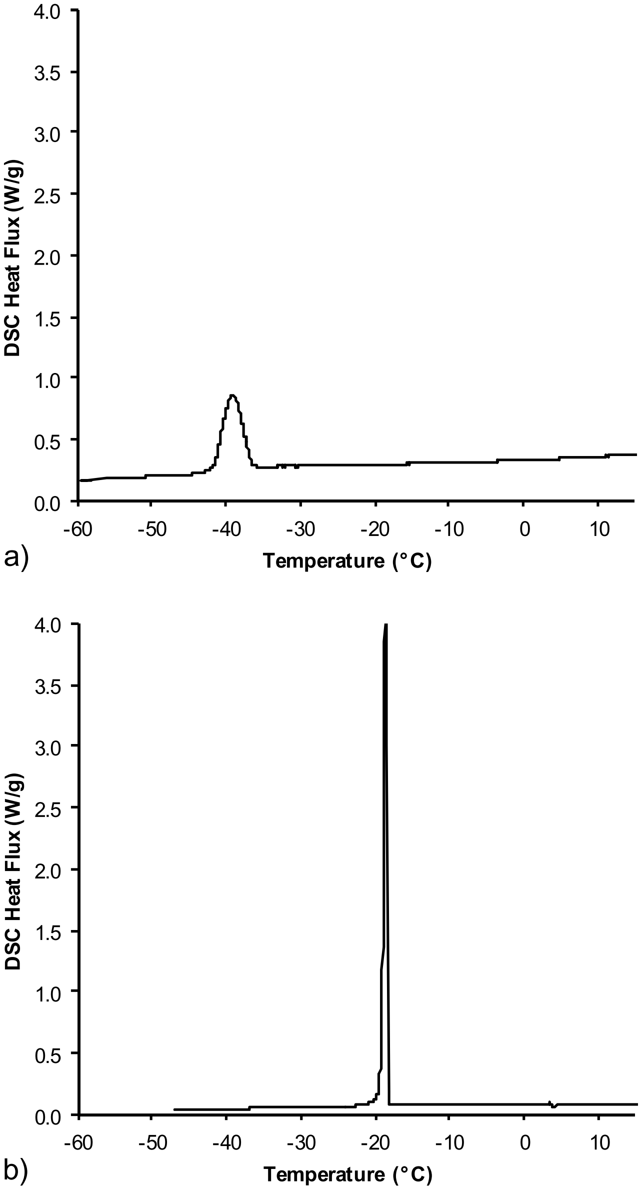

Figure 2. Representative DSC cooling curve obtained for the freezing of a) microsized water droplet dispersed in emulsion, b) broken emulsion made of water and oil distinct bulk phases (emulsions made of water, paraffin oil and span80).

The DSC cooling curve of microsized water droplets is characterized by a wide exothermic signal found between −36 °C and −42 °C and centered around −38 °C, designed as the "most probable" freezing temperature. The melting transition of the whole water droplets is represented by an endothermic signal beginning at 0 °C.

For a completely broken emulsion, the DSC cooling curve is characterized by a narrow exothermic signal corresponding to the water in bulk phase, and the freezing temperature is higher than the "most probable" temperature of microsized droplets dispersed in emulsion. By integrating energy signals, it is easy to verify that the frozen water volume is equivalent to the total volume of the water droplets initially dispersed in the emulsion sample put in the crucible of the calorimeter.

The shape of the freezing signal is narrow in the case of the completely broken emulsion because the formation of only one ice germ in the volume is necessary to induce the whole water bulk phase freezing. On the contrary, the freezing signal of water microsized droplets is bell-shaped and the freezing transition is progressive because the formation of one ice germ leads to a single droplet's freezing. The formation of an ice germ in each water droplet is required to freeze all the water droplets dispersed in the emulsion.

2.5.2 DSC test at a fixed temperature

As nucleation results of a kinetic phenomenon, freezing is also expected versus time when an emulsion is maintained at a fixed temperature less than 0 °C. It has been shown that the time needed for nucleation is all the higher as the temperature is close to 0 °C, since the size of the needed germ is increasing drastically when this temperature is reached. At 0 °C, which is the ice/liquid water equilibrium temperature, the size of the germ is theoretically infinite.

The number of droplets that solidify between t and t + dt is given by:

$$dN = N(t + dt) - N(t) = JV(N_0 - N(t))dt \qquad (1)$$

J being the nucleation rate, V the volume of the droplets, $N(t)$ the number of frozen droplets at time t and N_0 the total number of droplets. At a fixed temperature, the nucleation rate J is a constant versus time and the integration of relation 1 is straightforward as far it is assumed that at time 0, all the droplets are liquid when T is not too close to −40 °C.

$$Ln\left(1 - \frac{N}{N_0}\right) = -JVt \qquad (2)$$

From Equation (2), it is expected that the percentage of frozen droplets at time t is given by an exponential curve. This has been checked for fixed temperature near −40 °C. For temperature closer to −38 °C the times involved are shorter. The observation by microscopy of the freezing of individual water droplets has been done by Wood and Walton, 1970 [7]. The results obtained at −35.6 °C for various size groups of water droplets show that the smaller are the droplets, the higher are the times to get the freezing (Fig. 3).

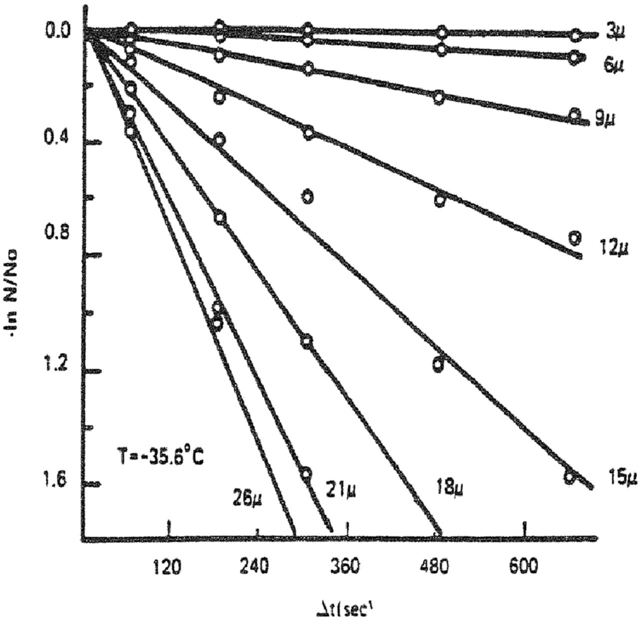

Figure 3. Crystallization frequency as a function of time for various volume groups obtained in an isothermal experiment. Adapted from [7].

Nevertheless, experimental results performed on water emulsions have shown that droplets freezing can be obtained at −21 °C and even at −10 °C with precooled treatment of the emulsion [5,8]. The times involved can be very important, around 400 h are needed to obtain 50% of the droplets frozen at −21 °C. It is also expected that this time will be the higher with smaller droplets. Therefore, the breaking of the emulsion could be observed by a sharp release of the freezing energy in a rather short time. For these reasons, it is difficult, on an experimental point of view, to follow the evolution of the emulsion versus time from the totally dispersed water as microsized droplets except if the temperature is very near −38 °C. Moreover, when the waiting time to get the freezing of droplets is too long, it is not possible to follow the freezing of the droplets in the calorimeter blocked during this kind of experiment. Therefore, another process was proposed. Several cells filled with the emulsion to be studied are stored in a thermostat, the temperature of which being fixed at the chosen temperature to study the freezing. From time to time, a cell is withdrawn from the thermostat and inserted in the head of the calorimeter which is at the same temperature than the thermostat. Afterwards, the emulsion is regularly heated and, by studying the energy absorbed during melting, it is possible to get the amount of frozen droplets. Repeating this experiment at different times on the stored cells, it is possible to get the proportion of water frozen in the emulsion versus time. Figure 4 displays an example of results obtained for the variation of the proportion of frozen water droplets versus time at a constant temperature of −21 °C [8].This technique was not retained to follow the emulsion evolution on ground as far it is easier to get a quick freezing in the temperature range between 25 °C and −60 °C. But this technique was used in the FSL as it was not possible to reach −60 °C, the lowest temperature that could be reached being −22 °C. For comparison, the same protocol was used on

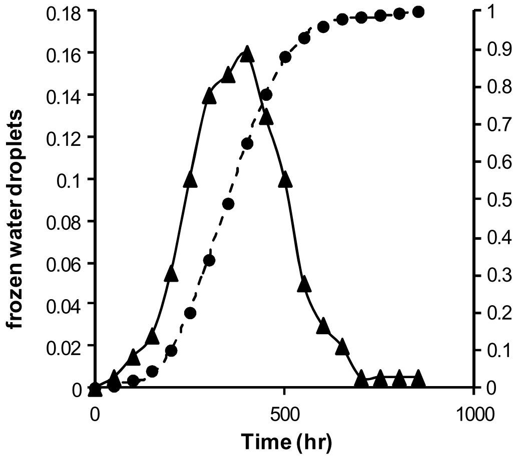

Figure 4. Nucleation of ice within water droplets. Variation of the proportion x of frozen water droplets versus time at a constant temperature of −21 °C. ▲) differential curve (left axis) and ●) integral curve (right axis). Adapted from [8].

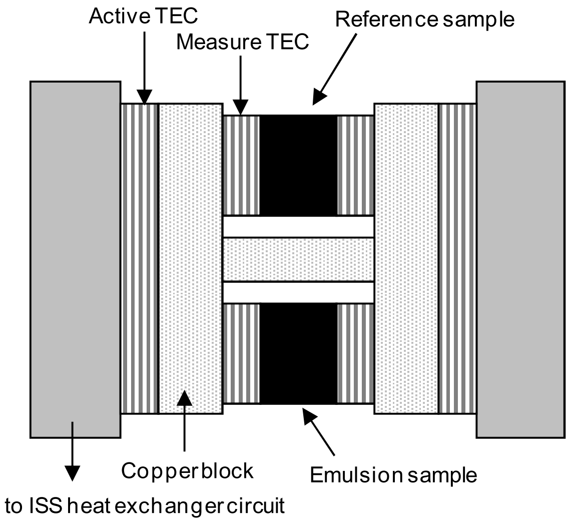

Figure 5. Design of the calorimeters built by *Airbus* and *SETARAM* for the FASES Project.

ground. More details are given in the next section devoted to FASES devices and procedures.

2.5.3 FASES devices and procedures

Two specific and identical calorimeters were built by *Airbus* (formerly *EADS*) with the collaboration of the French company *SETARAM*. The Flight Model (FM) was devoted to experiments in the Fluid Science Laboratory (FSL) of the ISS in space, while the Engineering Model (EM) was located at the TELESPAZIO Centre in Naples to carry out experiments on the ground. Each model consists of a calorimeter head to perform DSC tests, a Thermal Control Unit (TCU), and a cells transportation system. Dedicated and full cells were introduced in each device before launching. The sketch of these calorimeters is given in Figure 5.

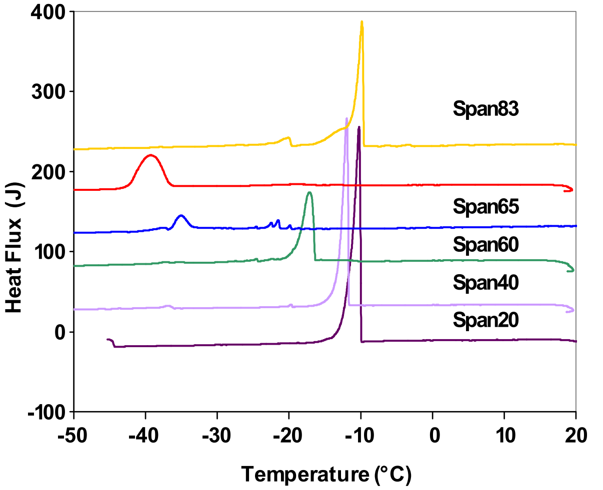

Figure 6. DSC curves of water-in-paraffin oil (30%vol water / 70%vol paraffin oil + 3%vol sorbitan ester type surfactants) obtained with a commercial DSC calorimeter [9].

After different ageing times at 40 °C in the TCU, the dedicated FASES project cells containing the emulsion were inserted in the head of the calorimeters (FM or EM). In the EM, a cycle of cooling and heating from 40 to −50 °C at a rate of 0.5 °C/min was scheduled in order to freeze and melt the droplets dispersed in emulsions. In the FM, the cell is regularly cooled from 40 to −22 °C. The cell is maintained at this temperature during 7220 s. Afterwards, the cell is heated to 40 °C at a rate of 0.5 °C/min. It is during the holding at −22 °C, that the freezing of the droplets is expected to occur. As it was stated before, a sharp freezing signal will be the signature of a broken emulsion, whereas a bell-shaped signal is the signature of the freezing of the individual droplets as shown on Figure 4, therefore demonstrating the presence of an emulsion.

3 Results and discussion

3.1 Emulsions formulations

The choice of emulsion formulations has been determined from preliminary experiments [9–11]. Droplet size distribution was observed by optical microscopy, stability versus time was monitoring by bottle test method and the morphology was analyzed by a cooling and a heating cycle with a commercial DSC calorimeter. Results indicated that only paraffin oil was suitable with the FASES project specifications: hexane and heptane are too volatile, while methylcyclopentane and methylcyclohexane are inflammable. As illustration, Figure 6 shows DSC curves obtained after a cooling and heating cycle from 20 to −60 °C for water-in-paraffin oil containing various sorbitan ester type surfactants.

Result obtained by DSC indicates that only emulsion prepared with Span80® and Span65® are characterized by a bell-shaped signal at very low temperature during the cooling process, representative of a well-dispersed emulsion. In comparison, the freezing signal is centered on −39 °C in the case of emulsion stabilized with Span80®

Table 2. Compositions of water-in-oil emulsions studied on ground and in space.

Sample	Water ($\%_{\mathrm{vol}}$)	Paraffin Oil phase($\%_{\mathrm{vol}}$)	Span80 Surfactant ($\%_{\mathrm{vol}}$ in oil phase)
1	3	97	0.1
2	3	97	0.5
3	3	97	1
4	3	97	3
5	10	90	0.1
6	10	90	0.5
7	10	90	1
8	10	90	3
9	30	70	0.1
10	30	70	0.5
11	30	70	1
12	30	70	3
13	50	50	0.1
14	50	50	0.5
15	50	50	1
16	50	50	3

and −35 °C for emulsion prepared with Span65®. These most probable temperatures of crystallization supposed that emulsion stabilized by Span80® is made of micro-sized droplets of water while emulsion prepared with Span65® is composed of larger water droplets. Conversely, DSC exothermic signals of emulsions mixed with other sorbitan ester type surfactants (Span83®, Span60®, Span40® and Span20®) are narrow and obtained between −10 °C and −16 °C, corresponding to completely destabilized emulsion. So, in the context of the FASES project and parallel experiments performed on ground and in space, paraffin oil and Span80® were chosen to make emulsions and the compositions retained in agreement with the other teams working in the FASES project are indicated in Table 2.

3.2 Definition of time zero

As the aim of the study was to follow the evolution of the emulsion versus time, it was necessary to define time zero. For that purpose, a destabilization procedure consisting of maintaining samples in the TCU at 50 °C during 5 h without agitation was systematically applied to completely break the possible emulsions produced by shaking during transport. This destabilization test aimed to separate water and oil phases and time zero was chosen from this state for evolution studies of emulsions with time. Therefore, tests were performed to check this destabilization state. Figure 7 shows DSC curves obtained after destabilization test applied to sample #14, corresponding to $50\%_{\mathrm{vol}}$ water/$50\%_{\mathrm{vol.}}$ paraffin oil containing 0.5% of Span80, in space in the FM (Fig. 7a) and on ground in the EM (Fig. 7b)

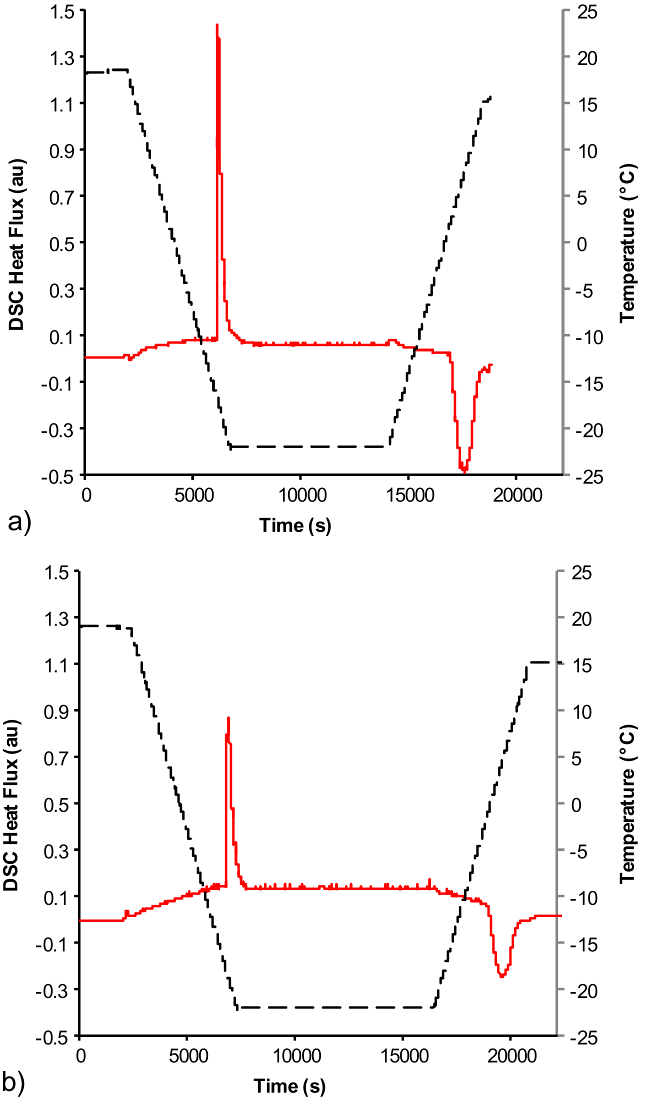

Figure 7. DSC curves of sample #14 (50%vol water / 50%vol paraffin oil + 0.5%vol Span 80) obtained directly after the destabilization test a) in space in the FM and b) on ground in the EM calorimeter.

In both cases, DSC curves of sample #14 are characterized by a narrow exothermic signal corresponding to the water in bulk phase. Identical DSC curves were obtained for others samples. These preliminary DSC analyses indicated that a storage of 5 h at 50 °C was adequate to completely break the emulsions and define time zero, both on ground and in space.

3.3 Stirring test

Two stirring procedures, nominal and reduced, were applied to make emulsion and compare the amount of energy required to emulsify on ground with gravity and in space under microgravity condition. Nominal stirring was 1600 rpm during 30 min whereas reduced stirring was progressively increased to 1000 rpm during 5 min. Figure 8 displays DSC curves obtained after stirring test applied to

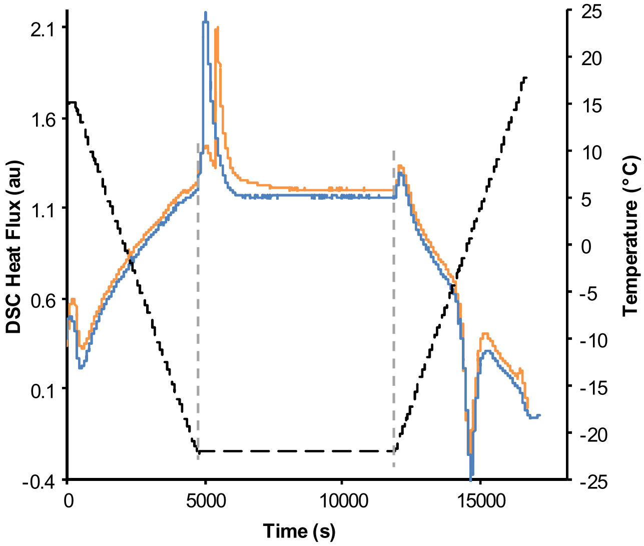

Figure 8. DSC curves of samples #8 (10%vol water / 90%vol paraffin oil + 3%vol Span 80) obtained directly after the nominal (blue line) and reduced (orange line) stirring test on ground in the EM calorimeter.

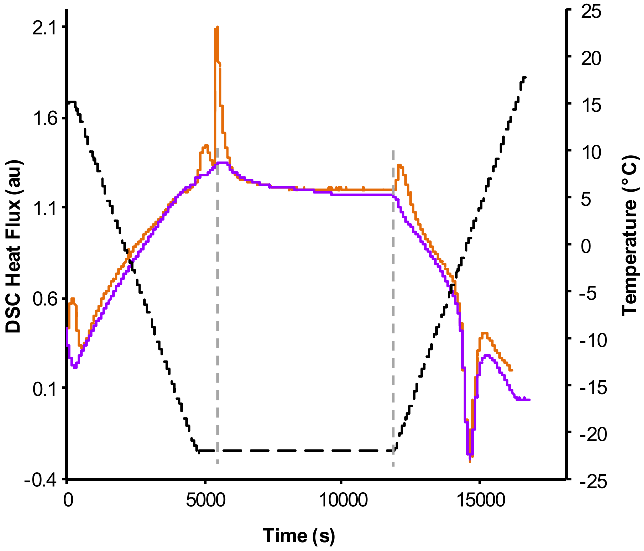

Figure 9. DSC curves of samples #8 (10%vol water / 90%vol paraffin oil + 3%vol Span 80) obtained directly after the reduced stirring test in space in the FM calorimeter (purple line) and on ground in the EM calorimeter (orange line).

#8 sample, corresponding to $10\%_{\text{vol}}$ water/$90\%_{\text{vol.}}$ paraffin oil containing 3% of Span80, on ground in the EM.

These tests performed on ground show that, in these conditions of stirring, no emulsion was obtained, as a sharp peak was found showing the presence of bulk water instead of dispersed water. Nevertheless, the effect of reduced stirring on emulsion formation under microgravity conditions was interesting to observe. Therefore, a reduced stirring procedure involving even less energy was applied to make emulsion with sample #8 in the FM calorimeter. The new reduced stirring test consisted of a stirring of 50 rpm during 1 min. Figure 9 displays the DSC curves obtained after reduced stirring test applied to #8 samples on ground in the EM (for comparison purpose) and in space in the FM.

In comparison, DSC curve of sample #8 analyzed in space in the FM following the application of the reduced stirring procedure shows a shell-shaped signal. The signal's shape is the one expected from the model (Fig. 4) described for the freezing of droplets hold at a fixed temperature. Therefore, it is representative of well-dispersed droplets in emulsion. So, these results show that very low energy was enough to emulsify sample#8 under microgravity conditions and, more importantly, the emulsion was found to be more stable when prepared in space than in ground. It is interesting to note that the melting signals are superimposed. This result indicates that the same amount of water is present in the compared emulsions, prepared and analyses on ground or in space.

3.4 Surfactant concentration effect

In this section, some examples are given about the results obtained with various concentrations of Span80 that were used to prepare samples in order to study the effect of the surfactant amount to emulsify water and paraffin oil, and therefore, the stability of the emulsions versus time. The samples #5 to #8, corresponding to $10\%_{\text{vol}}$ of water and $90\%_{\text{vol}}$ of paraffin oil with 0.1, 0.5, 1 or $3\%_{\text{vol}}$ of paraffin oil respectively, were analyzed by DSC on ground in the EM and in space in the FM. The samples were emulsified according to the previously defined reduced stirring procedures. As illustration, Figure 10 shows the DSC curves relative to samples #7 and #8 after mixing procedure applied in space in the FM.

In the FM, contrary to DSC curve of sample #8, DSC curve of sample #7 is distinguished by a narrow exothermic signal arriving early on the isothermal stage, relative to the water in bulk phase. Similar signals were obtained for samples #5 and #6 in the same conditions. These results indicated that a minimum amount of $3\%_{\text{vol}}$ of span80 surfactant in the paraffin oil was required to emulsified $10\%_{\text{vol}}$ of water in paraffin oil in space. Identical experiments were carried out on ground in the EM and all DSC curves obtained corresponded to water in bulk phase, as expected according the previous results (Fig. 8).

3.5 Stability test

Two consecutive DSC cycles consisting of cooling, isothermal stage at −22 °C and heating sequences were applied of well-dispersed droplets of sample #8 to study the stability of emulsion in space condition. The sample #8 ($10\%_{\text{vol}}$ water/$90\%_{\text{vol.}}$ paraffine oil + 3%Span80) was prepared according the reduced stirring procedure and analyzed twice in the FM calorimeter. Corresponding DSC curve of the first cycle experiment was previously presented in Figures 9 and 10 (purple line). Figure 11 displays the cycling DSC curves of sample #8.

In contrast to the wide peak obtained during the first DSC analysis, the curve obtained during the second DSC cycle is bell-shaped and starts at the end of the isothermal stage. This bell-shaped signal, as it is described in Section 2.5.2, is representative of an emulsion composed of fine and well-dispersed droplets. The point to notice is

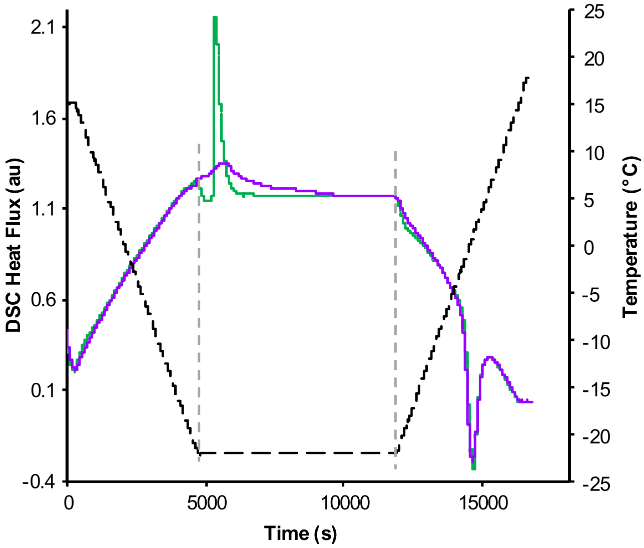

Figure 10. DSC curves of samples #7 (10%vol water / 90%vol paraffin oil + 1%vol Span 80, green line) and #8 (10%vol water / 90%vol paraffin oil + 3%vol Span 80, purple line) obtained directly after the reduced stirring procedure (50rpm during 1min) in space.

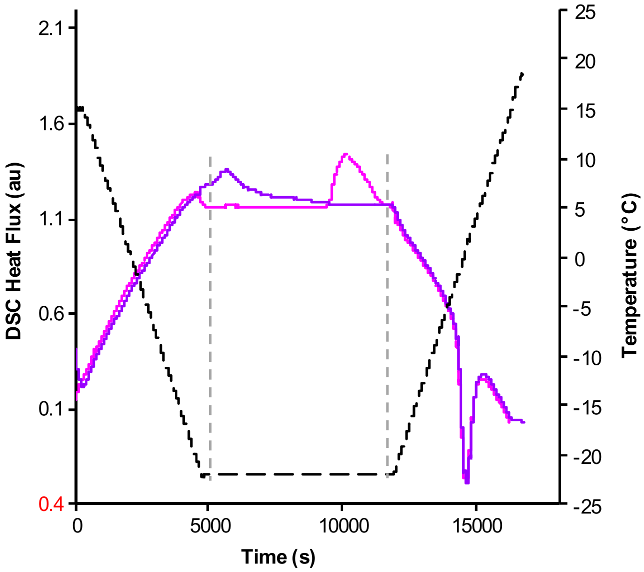

Figure 11. DSC curves of sample #8 (10%vol water / 90%vol paraffin oil + 3%vol Span 80) obtained during the first cycle (purple line) and the second cycle (pink line) in space in the FM calorimeter.

that it is possible to detect individual progressive freezing of the droplets versus time. A different behaviour of the emulsion at the second cycle was found, but is not necessarily representative of an evolution of the emulsion maintained at 40 °C towards smaller droplets, as theory indicates. The test itself could be a perturbation for the emulsion during the test. Similar phenomena have been noticed on ground after cooling–heating cycles performed on emulsions frozen at a fixed temperature [5]. It would have been interested to perform more experiments to see what is going on in microgravity conditions.

4 Conclusion

The experiments reported in this article show that it is possible to observe in space the freezing of water droplets versus time at the fixed temperature, namely −22 °C. This result confirms the one obtained on ground for emulsions maintained at −21 °C, but for more stable emulsion. The bell shape of the freezing signal evidences the presence of an emulsion and therefore this test could be used to follow the evolution of the emulsions versus time. However, the experiment is much more difficult to set up and interpret than the one consisting of detecting the total freezing of the dispersed water during a regular cooling. That is why this protocol has not be proposed when it is possible to set up a regular cooling heating cycle between 40 °C and −60 °C. The test with a stage at a fixed temperature was proposed only because the initially planned test was not possible due to a failure of the device in the FSL. Nevertheless, the presence of an emulsion, found to be more stable than when prepared on ground, was evidenced. Additional experiments at fixed temperatures would be relevant in order to confirm the enhanced stability of the emulsions formed under microgravity conditions, and to explain the effect of a second freezing cycle performed on an emulsion that has been previously frozen at a fixed temperature.

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