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# Subcooling in PCM emulsions—Part 1: Experimental

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ABSTRACT

Many phase change materials (PCM) tend to subcool in microscopic geometries, even if they show negligible subcooling in macroscopic geometries. This paper presents an experimental study on subcooling and nucleation in paraffin-in-water emulsions. Different material systems with the average droplet size from 0.2 to 12.5 μm were prepared and analyzed. An increased subcooling up to 15 K was observed for small droplets. The paraffin, surfactant and nucleating agent also have impacts on the subcooling. The nucleation theory and the evaluation of the experimental results will be presented in Part 2.

## 1. Introduction

Thermal energy storage using the latent heat associated with a phase transition has recently gained considerable attention due to the high energy storage density. Latent heat storage materials, also named phase change materials (PCM), can absorb or release large amounts of heat during phase transformation like solid–liquid, liquid–gas or solid–solid transition. However, most PCM have a low thermal conductivity which results in a low heat transfer rate. PCM emulsions and microencapsulated PCM are often used to improve the heat transfer between the PCM and the ambient by increasing the surface to volume ratio of the PCM. However, it has to be kept in mind, that PCM in such microscopic geometries can behave different than in macroscopic geometries. From nucleation theory, subcooling in small volumes is expected to be more severe than in large volumes. Additionally, an ensemble of many separated PCM volumes as in an emulsion should show effects similar to slow crystal growth, because crystal growth beyond the droplet boundary is restricted [1].

Subcooling means that a liquid can be cooled below its melting point without causing crystallization. This effect is not expected in latent heat storages because it will additionally enlarge the operating temperature range of the systems. Several studies on subcooling of PCM emulsions and microencapsulated PCM have been reported in literature. Inaba et al. [2] presented the subcooling phenomenon of tetradecane and tetradecane-in-water emulsions. The emulsions comprised a collection of tetradecane droplets having the arithmetic mean diameter of 3.4 μm. The subcooling degree of the small tetradecane droplets in water (emulsion) showed a higher value ($\Delta T = 5.8$ K) than for the bulk tetradecane ($\Delta T = 2.6$ K). Nakahira et al. [3] studied the thermal properties of pentadecane, microencapsulated pentadecane slurry (particle sizes from 1 to 5 μm in diameter) and pentadecane in water emulsion by a differential scanning calorimeter (DSC). It was observed that pentadecane in emulsion and in microcapsule had both the main melting peak at approximately 10 °C as in the bulk. However, they had the main freezing peak at about 0 °C, which was much lower than the bulk pentadecane at 10 °C. Royon and Guiffant [4] studied the subcooling phenomenon of a paraffin-in-water emulsion with the mean diameter of 2 μm by using a DSC and an agitated tank. A quantitatively good agreement was observed between both experiments. The subcooling was determined 5.6 K by DSC and 5.3 K with the agitated tank. Kudo et al. [5] conducted cooling experiments to determine the subcooling degree of docosan-in-water emulsions with different droplet diameters. The average droplet diameter of the five samples was from 3.3 to 48.2 μm. Two equilibrium temperatures were experimentally observed in the samples except for the one with the average diameter of 3.3 μm. It was indicated that the higher one near the solidification temperature of docosan ($T_f = 43$ °C) is caused by heterogeneous nucleation and the lower one ($T_f = 33$–$38$ °C) is caused by homogeneous nucleation. Emulsions with smaller sizes have a greater subcooling during the homogeneous nucleation than those with larger sizes.

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**Nomenclature**

| | |
|---|---|
| $\Delta T$ | subcooling (K) |
| $T_m$ | melting temperature (°C) |
| $T_n$ | nucleation temperature (°C) |

Although many researchers reported the subcooling phenomenon in PCM dispersions, few of them studied the effects of droplet sizes and compositions on the nucleation and subcooling. In this work, different paraffin-in-water emulsions with various droplet sizes were prepared and their thermal properties were analyzed. An experimental study was performed to investigate the influence of different compositions and droplet sizes on the subcooling in PCM emulsions.

## 2. Materials and methods

### 2.1. Materials

A paraffin-in-water emulsion is a colloidal system where microscopically fine paraffin droplets (dispersed phase) are distributed in water (continuous phase) by using a surfactant. Regarding the compositions, the effects of different paraffins and surfactants as well as addition of a nucleating agent were studied. To investigate different paraffin volumes, emulsions were prepared with various techniques, resulting in different droplet size distributions.

### 2.1.1. Continuous phase

The continuous phase was tap water in all cases.

### 2.1.2. Dispersed phase

The dispersed phase was paraffin, which is one of the typical organic PCM. The normal paraffins of type $C_nH_{2n+2}$ are a family of saturated hydrocarbons with very similar properties. Three paraffins were used for preparing the emulsions: two pure paraffins tetradecane $C_{14}H_{30}$ and hexadecane $C_{16}H_{34}$, purchased as analytical grade materials from a chemical supplier, and a commercial paraffin blend RT20 manufactured by Rubitherm GmbH [6].

### 2.1.3. Surfactant

Surfactants are usually used to form a stable emulsion. They are amphipathic molecules consisting of a non-polar hydrophobic part and a polar or ionic part (hydrophilic). The surfactant molecules are adsorbed at the interface between water and oil to reduce the interfacial tension, thus stabilizing the droplet surfaces and thereby the emulsion. The surfactants used for the paraffin-in-water emulsions were the anionic surfactant SDS (sodium dodecyl sulfate), the nonionic surfactant Tween40 (polyoxyethylene sorbitan monopalmitate), and as third a surfactant mixture recommended by Inaba et al. [2], consisting of the nonionic surfactant polyethylene glycol-stearyl-ether and the anionic surfactant alkylbenzenesulfonate in the weight ratio of 10 to 1.

### 2.1.4. Nucleating agent

A nucleating agent can be used to prevent subcooling. It offers the necessary seeds inside of the paraffin droplets to start the nucleation and thus is acting as a nucleating catalyst. A nucleating agent should have a higher phase change temperature than the PCM. A paraffin wax with a freezing peak point of 50 °C was selected as nucleating agent in this study [7].

### 2.2. Methods

After preparation, the emulsions to be investigated were characterized with respect to their droplet size distributions. Then, their phase change behaviors and especially subcooling were investigated. All samples presented in this paper were stable for at least some days and after certain thermal cycles in DSC measurements, but could be destroyed by improper thermal treatment. In particular, an upper temperature boundary, that is a maximum temperature, was found to be 70 °C. The lower temperature boundary is defined by the fact that the continuous phase of the emulsion, i.e. water, should not be frozen. Thus, a minimum temperature of −10 °C can be reached due to the subcooling of water. In all stable emulsions prepared for this work, the surfactant layer between the droplets did not rupture and each droplet was isolated from the other droplets during the measurements. It can be assumed that the crystallization occurred only inside of the single droplets and they behaved independent of each other [8], such that the thermal behavior of the emulsion was caused by the multitude of its single droplets.

### 2.2.1. Emulsification

To form a paraffin emulsion, energy is needed for premixing the compositions and for dispersing the paraffin into fine droplets. There are various systems available for emulsification. In this study, two systems were used to prepare the paraffin emulsions:

(1) an ultrasonic generator, type Sonopuls HD3100 by Bandelin operating at 20 kHz and with a variable power of 10–100 W;
(2) rotor-stator systems, type Polytron PT1300D by Kinematica AG with a rotation speed from 7000 to 30,000 per minute, and type ULTRA-TURRAX T25 by IKA-Labortechnik with a continuously variable drive in the range of 9000–24,000 rotations per minute.

### 2.2.2. Droplet size analysis

The droplet size distribution was determined by using a laser diffraction particle size analyzer of type Malvern Mastersizer 2000. This analyzer has a broad measuring range from 0.02 to 2000 μm. The accuracy is ±1% on the mean droplet size $d_{50}$ and the instrument-to-instrument reproducibility is better than 1% RSD (riffle sample divider) on the $d_{50}$ by using the Malvern Quality Audit Standard.

### 2.2.3. Thermal analysis

To determine the melting and nucleation temperatures, a heat flux DSC type 204 Phoenix by Netzsch with aluminium crucibles having a height of about 1 mm and width of 4 mm was used. The temperature and sensitivity calibration were carried out by using the standard materials potassium nitrate ($KNO_3$), indium (In), bismuth (Bi), tin (Sn), zinc (Zn), caesium chloride (CsCl), mercury (Hg) and cyclohexane ($C_6H_{12}$). The temperature program for each material was created in such a way that the complete melting process was evaluated. The heating/cooling rate was 1 °C/min for the calibration. Measurements for all materials were conducted with 3 heating and 2 cooling segments so that the melting process was measured three times. Only the values from the 2nd and 3rd heating were evaluated. The extrapolated onset point and peak area of the melting curves were obtained with an analysis program built into the DSC. Here, the onset point of a DSC curve was defined as the intersection between the tangent to the maximum rising slope of the peak and the extrapolated sample baseline. The temperature calibration curve was created by entering the determined onset values for all calibration materials and the sensitivity calibration curve was obtained by entering the values of the peak area.

The scanning rate for all DSC measurements in this study was 2 °C/min. The onset point of a DSC curve was used to report the

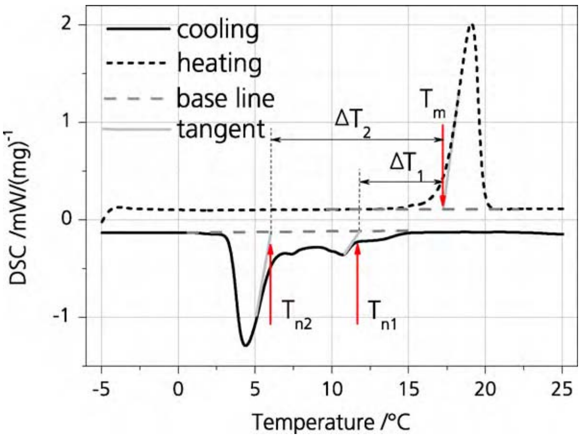

**Fig. 1.** DSC curves and subcooling of a hexadecane emulsion with the surfactant mixture, indicating the melting temperature $T_{\mathrm{m}}$ and two nucleation temperatures $T_{\mathrm{n1}}$ and $T_{\mathrm{n2}}$ by arrows.

melting/nucleation characteristics, because it depends little on the heating/cooling rate. The melting onset point was defined as the melting temperature $T_{\mathrm{m}}$ and the freezing onset point as the nucleation temperature $T_{\mathrm{n}}$. The difference between the melting and nucleation temperature was considered as subcooling. Fig. 1 shows for example the DSC curves of a hexadecane emulsion, in which the melting and nucleation temperature as well as the subcooling are indicated. This sample has a melting temperature $T_{\mathrm{m}}$ of 17.3 °C and two nucleation temperatures of 11.6 °C ($T_{\mathrm{n1}}$) and 6.0 °C ($T_{\mathrm{n2}}$), respectively, so that the sample has two subcooling degrees, namely 5.7 K ($\Delta T_1$) and 11.3 K ($\Delta T_2$). This cooling peak spectrum is caused by different seed types, which will be further discussed in detail in Part 2.

## 3. Results

### 3.1. Emulsions with different paraffins and SDS as surfactant

Three emulsions each containing 1 weight part paraffin, 2 weight parts water and 2 wt% SDS as surfactant were prepared by using the Polytron PT1300D at the same rotation speed of 24,000 rpm. The paraffins used are presented in Section 2.1.2. The emulsions cover a similar droplet size distribution of 0.6–10 μm as depicted in Fig. 2. The phase change temperatures of the paraffins and emulsions were determined by DSC measurements. As an example, the DSC curves of hexadecane (dash lines) and its emulsion (solid lines) are shown in Fig. 3. It can be seen that the emulsion has a slightly lowered melting temperature and a distinctly reduced nucleation temperature than the bulk hexadecane. The melting and nucleation temperatures of the samples as well as the temperature change from the bulk form to emulsion are listed in Table 1. The finely dispersed paraffins have nucleation temperatures 10–13 K lower than the bulk (for the tetradecane emulsion only the 2nd freezing peak is considered). Compared to the paraffins in their bulk forms, the tetradecane and hexadecane emulsion have slightly lower melting temperatures, while the RT20 emulsion shows a higher melting temperature. The reason could be that RT20 has a wide phase change temperature range as a mixture and it is difficult to define the melting temperature by using the onset point.

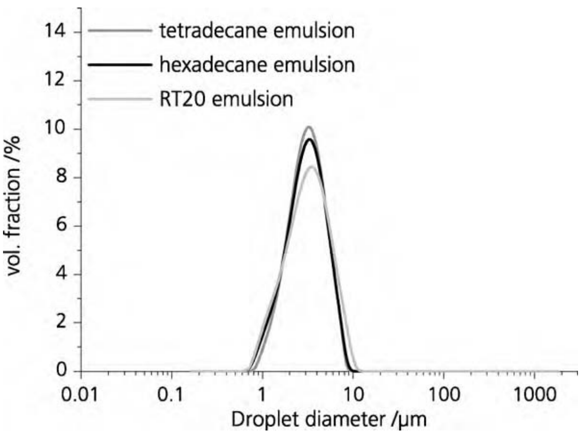

**Fig. 2.** Droplet size distribution of the emulsions containing tetradecane, hexadecane and RT20, all with SDS as surfactant.

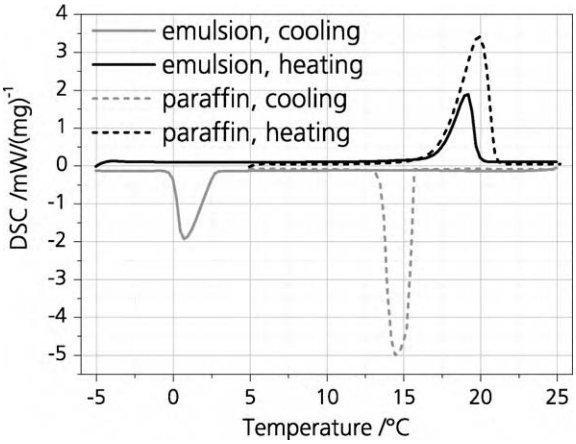

**Fig. 3.** DSC curves of hexadecane and hexadecane–water emulsion.

### 3.2. Hexadecane emulsions with different surfactants

In order to investigate the surfactant effect on subcooling, three samples each containing 1 part hexadecane, 2 parts water were prepared with 2 wt% different surfactants as introduced in Section 2.1.3. The three samples were emulsified using the Polytron PT1300D at the same rotation speed of 24,000 rpm as before. The droplet size distributions of the samples differ slightly from each other (Fig. 4). Their melting and nucleation temperatures as well as subcooling were determined by DSC measurements and the results are given in Table 2. It can be seen that the emulsions have nearly the same melting temperatures as hexadecane but considerably decreased nucleation temperatures. The sample with SDS has the

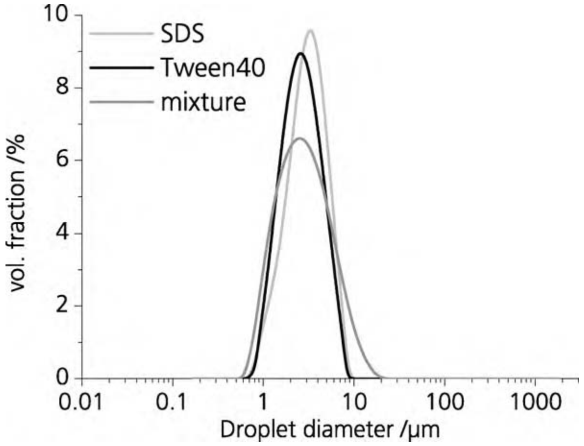

**Fig. 4.** Droplet size distribution of the hexadecane emulsions containing SDS, Tween40 and a surfactant mixture, respectively.

**Table 1**
Melting and nucleation temperatures, as well as the temperature change of the paraffins from the bulk to emulsion.

| Sample | Melting temp. (°C) | Nucleation temp. (°C) | Change melting (K) | Change nucleation (K) |
|---|---|---|---|---|
| Tetradecane | 2.0 | 1.5 | | |
| Tetradecane emulsion | 1.4 | −3.9 (1st peak)<br>−8.3 (2nd peak) | −0.6 | −5.4 (1st peak)<br>−9.8 (2nd peak) |
| Hexadecane | 17.4 | 15.5 | | |
| Hexadecane emulsion | 17.3 | 2.6 | −0.1 | −12.9 |
| RT20 | 17.5 | 21.9 | | |
| RT20 emulsion | 21.2 | 12.0 | +3.7 | −9.9 |

**Table 2**
Melting and nucleation temperatures, as well as subcooling of hexadecane and its emulsions with different surfactants.

| Sample | Melting temp. (°C) | Nucleation temp. (°C) | Subcooling (K) |
|---|---|---|---|
| Hexadecane (bulk) | 17.4 | 15.5 | 1.9 |
| SDS | 17.4 | 2.6 | 14.8 |
| Tween40 | 17.3 | 6.0 | 11.3 |
| Surfactant mixture | 17.3 | 11.6 (1st peak)<br>6.0 (2nd peak) | 5.7 (1st peak)<br>11.3 (2nd peak) |

lowest nucleation temperature (2.6 °C). For the sample with the surfactant mixture, two levels of nucleation temperature appear (Fig. 1): one is at 6.0 °C, which is equal to that of the sample with Tween40, and the other is at 11.6 °C.

### 3.3. Hexadecane emulsions with SDS as surfactants and different fractions of nucleating agent

To study the effect of the nucleating agent on subcooling, six emulsions each containing 1 part hexadecane, 2 parts water, 2 wt% SDS as surfactant and different fractions of the nucleating agent were prepared. The nucleating agent used was a paraffin wax with a freezing point of 50 °C, see also Section 2.1.4. Its concentration in the emulsions was 0.0, 0.8, 1.5, 3.0, 5.0 and 10 wt%, respectively. As depicted in Fig. 5, the paraffin droplets of all samples mainly cover a size range of 0.6–15 μm. However, three emulsions with 1.5, 5.0 and 10.0 wt% nucleating agent have a second small peak under 0.6 μm. The DSC heating (left) and cooling curves (right) are portrayed in Fig. 6. With increasing fraction of the nucleating agent, the melting peak shifts to low temperature range, but the freezing peak to high temperature range. All samples have two freezing peaks except for the one without nucleating agent. The samples containing 3.0, 5.0 and 10.0 wt% nucleating agent have the freezing peak spectrum in similar temperature ranges. The melting and nucleation temperatures as well as subcooling of the emulsions are listed in Table 3. There is a clear trend to lower melting temperatures with higher fraction of nucleating agent, up to 2 K lower for the sample with 10.0 wt% nucleating agent compared to that without nucleating agent. The emulsion without nucleating agent has only one freezing peak at 2.6 °C. With addition of 0.8 wt% nucleating agent, two nucleation temperatures at 2.6 and 7.7 °C are observed. The nucleation temperatures increase quickly when the fraction of the nucleating agent rises to 3.0 wt%, then the higher nucleation temperature near 13 °C tend to be constant and the lower one between 9 and 10 °C slowly rises when the nucleating agent increases from 3.0 to 10.0 wt%. The subcooling is reduced by about 12 K (1st peak) when the fraction of the nucleating agent reaches 3.0 wt%.

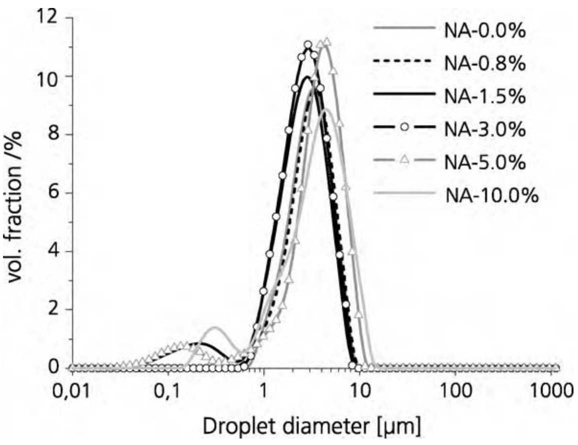

**Fig. 5.** Droplet size distribution of the hexadecane emulsions containing different fractions of the nucleating agent (NA).

**Table 3**
Melting and nucleation temperatures, as well as subcooling of the hexadecane emulsions with different fractions of the nucleating agent.

| Fraction of nucleating agent (wt%) | Melting temp. (°C) | Nucleation temp. (°C) | Subcooling (K) |
|---|---|---|---|
| 0.0 | 17.4 | 2.6 | 14.8 |
| 0.8 | 16.9 | 7.7 (1st peak)<br>2.6 (2nd peak) | 9.2 (1st peak)<br>14.3 (2nd peak) |
| 1.5 | 16.3 | 11.1 (1st peak)<br>3.5 (2nd peak) | 5.2 (1st peak)<br>12.8 (2nd peak) |
| 3.0 | 16.1 | 13.4 (1st peak)<br>9.3 (2nd peak) | 2.7 (1st peak)<br>6.8 (2nd peak) |
| 5.0 | 15.7 | 13.4 (1st peak)<br>9.5 (2nd peak) | 2.3 (1st peak)<br>6.2 (2nd peak) |
| 10.0 | 15.4 | 13.3 (1st peak)<br>9.9 (2nd peak) | 2.1 (1st peak)<br>5.5 (2nd peak) |

### 3.4. Hexadecane emulsions with different droplet sizes

In order to study the dependence between the droplet size and subcooling, eight samples were prepared with different methods

**Table 4**
Surfactant and preparation method of hexadecane emulsions.

| Method of preparation | Surfactant | Samples name |
|---|---|---|
| Ultrasound generator | SDS<br>Tween40 | SDS-US<br>Tween-US |
| Disperser, frequency 9 kHz | SDS<br>Tween40 | SDS-9k<br>Tween-9k |
| Disperser, frequency 24 kHz | SDS<br>Tween40 | SDS-24k<br>Tween-24k |
| Non-emulsified mixture | SDS<br>Tween40 | SDS-mix<br>Tween-mix |

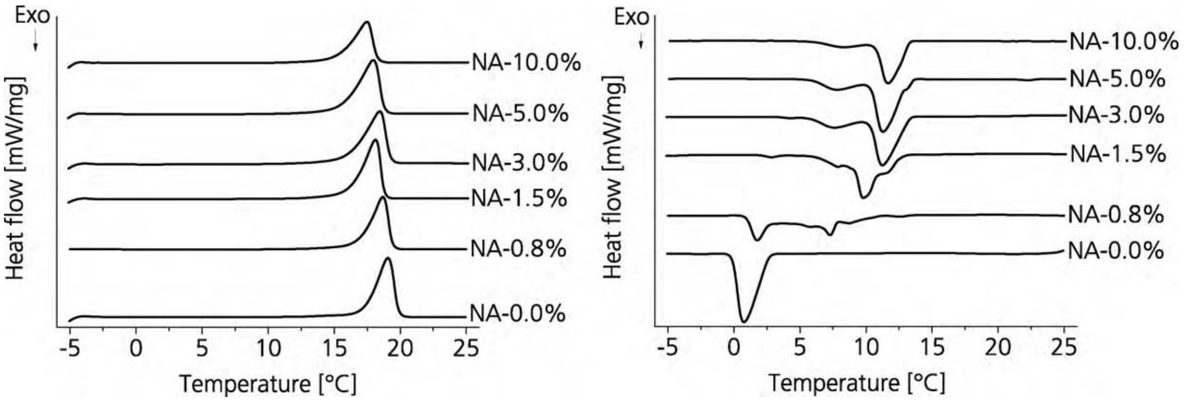

**Fig. 6.** DSC heating (left) and cooling (right) curves of the hexadecane emulsions with SDS as surfactant, containing different fractions of the nucleating agent (NA).

and using two surfactants (Table 4). In addition to the emulsions, also non-emulsified mixtures were prepared for each combination of substances.

Fig. 7 shows the droplet size distributions of the different hexadecane emulsions. With the ultrasonic treatment, the smallest drop sizes down to about 0.02 μm were achieved. To understand what this value means, the relation to the size of a hexadecane molecule is interesting. The length of a hexadecane molecule is about the number of C–C-bonds times their length, that is $16 \times 3\,\text{Å} = 4.8 \times 10^{-9}$ m. In Fig. 7 the minimum of the *x*-axis is set to 0.005 μm, corresponding to one molecule length. For the emulsion SDS-US with the smallest droplet size, the average droplet diameter (0.2 μm) is only about 40 molecule lengths. The shaded areas mark the range where 80% of the volume is found.

Fig. 8 shows the melting temperatures measured with DSC for the eight samples. For the emulsions, the ranges of droplet sizes are presented in Fig. 7. For the non-emulsified mixtures, the dimension of the DSC crucible was taken as droplet diameter. There is

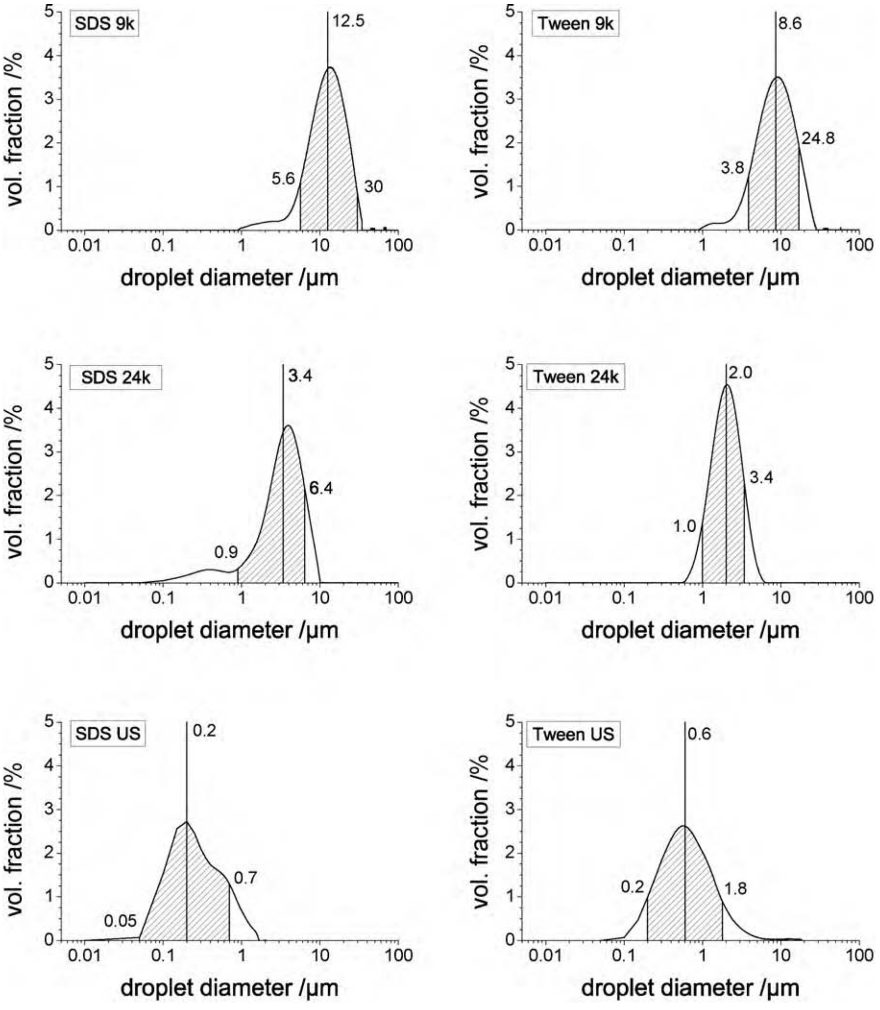

**Fig. 7.** Droplet size distributions of the different hexadecane emulsions.

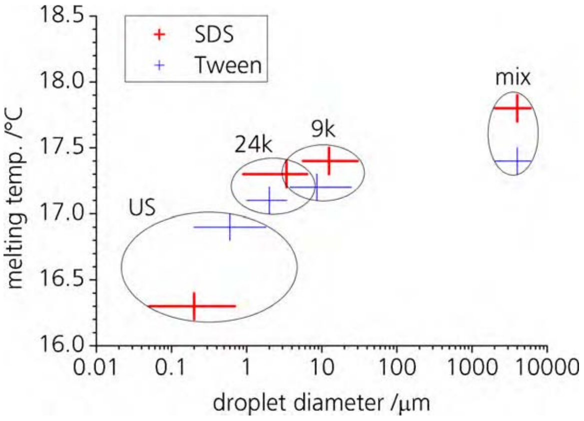

**Fig. 8.** Melting temperatures for the six different emulsions, as well as for hexadecane with the two emulsifiers in the non-emulsified form.

a clear trend to lower melting temperatures with smaller droplet diameters as is generally expected, up to 2 K lower for the smallest droplets compared to the non-emulsified form. Apparently the effect increases as soon as the dimension of the droplet gets below 10 μm. Except for the samples prepared with ultrasound, the melting temperature of samples with Tween40 is always lower than that of the SDS samples. This could be due to the smaller droplet sizes in SDS-US samples.

Fig. 9 shows the nucleation temperatures measured with DSC for the eight samples. The maximum of the *y*-scale corresponds roughly to the melting temperature of hexadecane. Here, the observed influence of the geometric dimension is dramatic and reaches about 15 K for the emulsion SDS-US with the smallest droplets. In addition, there seems again to be an influence of the surfactant. For example, the emulsion SDS-9k having droplets of about 12 μm diameter shows a nucleation temperature (5.2 °C) similar to the emulsion Tween-US having droplets of about 1 μm (5.6 °C).

Fig. 10 illustrates the subcooling of the eight samples. There is a clear tendency of an increase in subcooling with decreasing droplet diameter except for the emulsion SDS-US, which has a slightly smaller subcooling ($\Delta T = 14.1$ K) than the emulsion SDS-24k ($\Delta T = 14.4$ K). The difference between the two subcooling degrees lies in the range of the experimental uncertainty. The non-emulsified mixtures have subcooling of about 2 K, while the emulsions show a subcooling of about 6–15 K. Furthermore, it was observed that the emulsions with SDS have larger subcooling than those with Tween40.

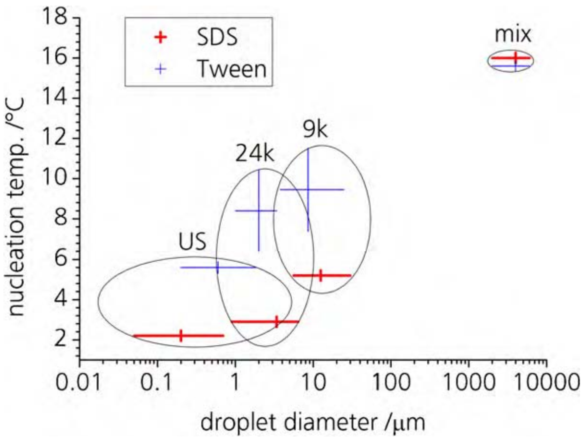

**Fig. 9.** Nucleation temperatures for the six different emulsions, as well as for hexadecane with the two emulsifiers in the non-emulsified form.

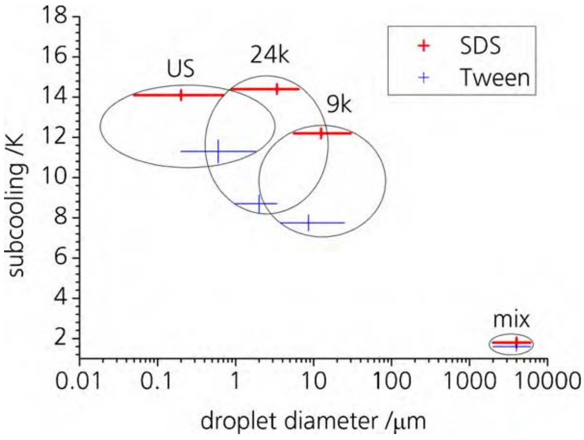

**Fig. 10.** Subcooling for the six different emulsions, as well as for hexadecane with the two emulsifiers in the non-emulsified form.

## 4. Discussion

The thermal properties of different paraffin-in-water emulsions have been investigated. The main results of the experiments are summarized as follows:

- Three paraffins (two pure and one blend) that show small subcooling (<2 K) in the bulk show large subcooling (9–15 K) in emulsion. Although paraffins have very similar properties, they have certain influence on the nucleation temperatures in emulsion. For the samples prepared with the same surfactant and having the similar droplet size distribution, the decrease in the nucleation temperatures is about 10–13 K from the bulk form to emulsion, depending on the paraffin sort.
- Surfactants have insignificant impact on the melting temperature, since the hexadecane emulsions prepared with three different surfactants (SDS, Tween40, surfactant mixture) show nearly the same melting temperature as the bulk hexadecane ($T_m = 17.4$ °C). However, the nucleation temperature and subcooling change with the surfactant sort. The subcooling varies from 11 K (Tween40, surfactant mixture) to 15 K (SDS).
- Subcooling can be reduced by using a nucleating agent. The nucleating agent and its fraction have important effect both on the melting and nucleation temperature. With increasing fraction of the nucleating agent, the melting temperature of the emulsions decreases, but the nucleation temperature increases. The subcooling can be distinctly reduced when the nucleating agent provides sufficient foreign seeds in the paraffin droplets. All emulsions containing the nucleating agent have a freezing peak spectrum. A spectrum of two freezing peaks was also observed in docosan-in-water emulsions with titanium oxide nanoparticles as nucleating agent by Kudo et al. [5].
- Droplet sizes and their distributions play a vital role both in the melting and nucleation temperature. Both temperatures decrease with reducing droplet size. The observed influence of the droplet diameter on the melting temperature is smaller than 2 K and the influence on the nucleation temperature reaches about 15 K for the emulsion with the smallest droplets. The effect was also observed in measurements on microencapsulated paraffin [3], where the nucleation temperature decreases by 10 K from the bulk form to microcapsule.

## 5. Conclusions

A large subcooling should be avoided in latent heat storage applications, because it will reduce the temperature stabilizing effect of PCM and consequently extend the charging/discharging temperature range. In this paper, an experimental study on the melting and nucleation temperature as well as subcooling of paraffin-in-water emulsions was presented. Stable emulsions were prepared with different paraffins, surfactants and various fractions of a nucleating agent. The impact of these compositions on the thermal behavior was observed. In addition, hexadecane–water emulsions were prepared using two different surfactants and two different methods, establishing the average droplet size of about 0.2–12.5 μm. The investigated emulsions subcool up to 15 K. The theoretic background of nucleation and subcooling in emulsion will be sketched and put in relation to the experimental results in Part 2.

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