Energy Conversion and Management 51 (2010) 1264–1269

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Experimental study on heat capacity of paraffin/water phase change emulsion

L. Huang [a,*], P. Noeres [b], M. Petermann [c], C. Doetsch [a]

[a] *Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Osterfelder Strasse 3, 46047 Oberhausen, Germany*
[b] *Franz-Bielefeld-Strasse 43, 45881 Gelsenkirchen, Germany*
[c] *Particle Technology, Ruhr-University Bochum, 44780 Bochum, Germany*

ARTICLE INFO

Article history:
Received 28 May 2009
Accepted 28 December 2009

Keywords:
Paraffin/water emulsion
Phase Change Material (PCM)
Phase Change Slurry (PCS)
Heat capacity

ABSTRACT

A paraffin/water phase change emulsion is a multifunctional fluid in which fine paraffin droplets are dispersed in water by a surfactant. This paper presents an experimental study on the heat capacity of an emulsion containing 30 wt.% paraffin in a test rig. The results show that the heat capacity of the emulsion consists of the sensible heat capacity of water and that of the paraffin as well as the latent heat capacity of the paraffin during the phase transition solid–liquid. The emulsion is an attractive alternative to chilled water for comfort cooling applications, because it has a heat capacity of 50 kJ/kg from 5 to 11 °C, which is two times as high as that of water in the same temperature range.

1. Introduction

Thermal Energy Storage (TES) is very important in many energy systems. The advantages of using TES systems are to balance the energy supply and demand, or to collect energy irregularly generated like solar energy for late use, or to transfer energy from manufacturers to consumers. With the growing demand for comfort cooling applications, the use of cold storage systems has been steadily increasing in recent years. The basic types of cold storage can be classified into sensible heat storages and latent heat storages [1]. In sensible heat storages, cold is stored by changing the temperature of a storage material like water or brines. Latent heat storages are based on the heat absorption when a Phase Change Material (PCM) undergoes a phase transformation, such as solid–liquid transition. Compared to sensible heat storages, latent heat storages have a high storage density with a small temperature swing [2]. However, PCM systems need an additional fluid for the heat transfer between the PCM and heat/cold sources due to the phase transition. The indirect heat transmission results in a decreasing heat transfer rate. Currently, the research on Phase Change Slurries (PCSs) has gained considerable attention. A PCS is a multifunctional system consisting of a Phase Change Material (PCM) as a dispersed phase and a carrier fluid as a continuous phase. PCSs have a high energy density because they store or transfer energy by using the sensible heat capacity of the carrier fluid and the PCM as well as the latent heat capacity of the PCM during its phase transformation. Additionally, a second heat transfer fluid is not necessary for PCS systems, because PCSs stay pump-able during the phase transition process.

There are two types of PCSs used in practical cooling applications. They are ice slurries and hydrate slurries. An ice slurry is a dispersion comprised of fine ice particles suspended in a solution of water and a freezing point depressant for preventing agglomeration of ice particles. The cooling capacity of ice slurry is four to six times higher than that of chilled water [3]. However, the operating temperature must be lowered under 0 °C to crystallize water which is too low for comfort cooling applications with a temperature range of 0–20 °C. A hydrate slurry is solid of crystalline compound of water as host molecule and low temperature boiling gases as guest molecule with a special form of molecular structure below a certain temperature at a constant pressure [4]. JFE Engineering Corporation in Japan has developed a hydrate slurry which is a mixed fluid consisting of an aqueous solution and particles of tetra-n-butylammonium bromide (TBAB) that holds latent heat within the same temperature range of 5–12 °C as chilled water used in air conditioning. This hydrate slurry has a cooling storage capacity which is 2–3 times as high as that of water [5]. However, TBAB is a hazardous material which is highly flammable and has toxic properties. When it is applied in cold supply networks, extensive safety-related measures must be taken.

Since 2006 paraffin/water emulsions have been studied as a PCS for comfort cooling applications at Fraunhofer UMSICHT. They are colloidal systems in which fine paraffin droplets are distributed in water and maintained in dispersion by a surfactant. The emulsions have melting temperatures in a range of 0–20 °C by selecting suitable paraffins. They contain no hazardous substance and are environmentally compatible. The previous work [6] reported that the emulsions with a paraffin concentration from 30 to 50 wt.% are

---

* Corresponding author. Tel.: +49 208 8598 1149; fax: +49 208 8598 1423.
E-mail address: li.huang@umsicht.fraunhofer.de (L. Huang).

0196-8904/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.enconman.2009.12.038

Nomenclature

$c_{p,i}$	specific heat capacity of components, J/(g K)
Δh_i	enthalpy change of components per mass, kJ/kg
$\Delta h_{f,i}$	heat of fusion of components per mass, kJ/kg
ΔH	enthalpy change, kJ
m	mass of components, kg
Q	heat, kJ
$\dot{Q}$	heat flow, kJ/s
Q_{loss}	heat loss, kJ
$\dot{Q}_{loss}$	heat loss flow, kJ/s
Δt	time interval, s
T	temperature, °C
T_c	extrapolated end temperature, °C
T_e	extrapolated onset temperature, °C
T_p	peak temperature, °C
ΔT	temperature difference, °C
u	flow rate, m^3/s
V	volume, m^3
X_i	weight fraction of components, wt.%

Greek letter

ρ	density, kg/m^3

Subscripts

e	emulsion
p	paraffin
pr	primary heat transfer fluid
sec	secondary heat transfer fluid
w	water

attractive alternatives to chilled water for comfort cooling applications because they have a relatively low viscosity and an energy density which is a minimum of two times as high as that of only water in the typical operating temperature range of 5–11 °C of chilled water systems. In this paper, an experimental study on the heat capacity of an emulsion containing 30 wt.% paraffin is presented.

2. Thermophysical properties of emulsion

The paraffin/water emulsions are composed of water as the continuous phase, a paraffin as the dispersed phase, a nonionic surfactant for stabilizing the two phases and a nucleating agent for preventing supercooling induced by small droplet sizes of the dispersed paraffin. The paraffin used is RT10 manufactured by Rubitherm GmbH. It is a mixture of different normal alkanes of type C_nH_{2n+2}. RT10 has a melting peak point of 9 °C and shows little supercooling. 19.3 liters of an emulsion containing 30 wt.% RT10, 1.5 wt.% surfactant and 1.5 wt.% nucleating agent were prepared for this study. When observing the emulsion under a light microscopy, the paraffin is dispersed in water in the form of spherical droplets with a diameter of 1–10 μm depicted in Fig. 1.

The thermal properties of the paraffin and emulsion were recorded with a Differential Scanning Calorimeter Netzsch DSC 204. The use of the extrapolated peak onset temperature T_e, the extrapolated end temperature T_c and the peak temperature T_p from DSC measurements is recommended when reporting the melting and freezing peak characteristics. T_e is the intersection between the tangent to the maximum rising slope of the peak and extrapolated sample baseline. The heat of fusion, namely the enthalpy change during the phase transformation, is obtained by estimating the peak area of a DSC melting curve [7]. The DSC melting and freezing curves of the paraffin and emulsion are shown in Fig. 2. Here, the phase transformation temperature range is defined as the temperature difference between T_e and T_c of a DSC curve. Fig. 2 gives an example of the characteristic temperatures of the melting curve of the emulsion. It was determined that RT10 has a heat of fusion of 145 kJ/kg from 2 to 12 °C, and the emulsion has a heat of fusion of 43 kJ/kg over the total melting temperature range of 4–11.5 °C.

The total heat capacity of the emulsion consists of the sensible heat capacity of water and that of the paraffin as well as the heat of fusion of the paraffin. The sensible heat capacities of the surfactant and the nucleating agent have not been considered because their concentrations are very low and they make minor contribution to the total heat capacity. In a temperature range from T_1 to T_2 ($T_1 < T_2$), the enthalpy change of the emulsion Δh_e can be estimated with the latent heat capacity $\Delta h_{f,e}$, the sensible heat capacity of water Δh_w and that of the paraffin Δh_p:

$$\begin{aligned}\Delta h_e &= \Delta h_{f,e} + \Delta h_w + \Delta h_p \\ &= X_p \cdot \Delta h_{f,p} + X_w \cdot c_{p,w} \cdot (T_2 - T_1) + X_p \cdot \bar{c}_{p,p} \cdot (T_2 - T_1) \qquad (1)\end{aligned}$$

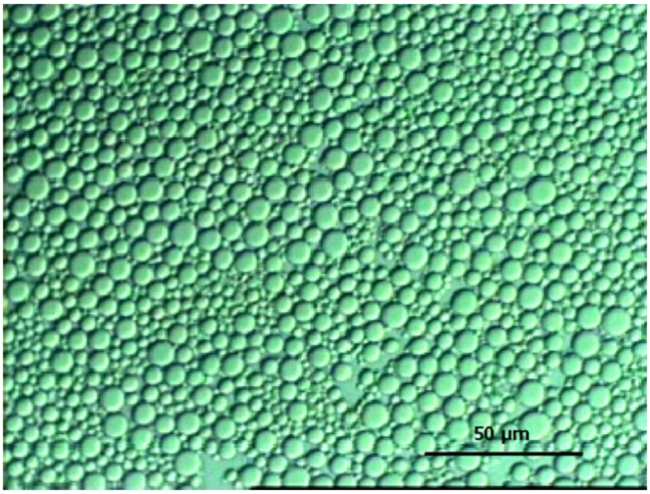

Fig. 1. Micrograph of the emulsion containing 30 wt.% RT10.

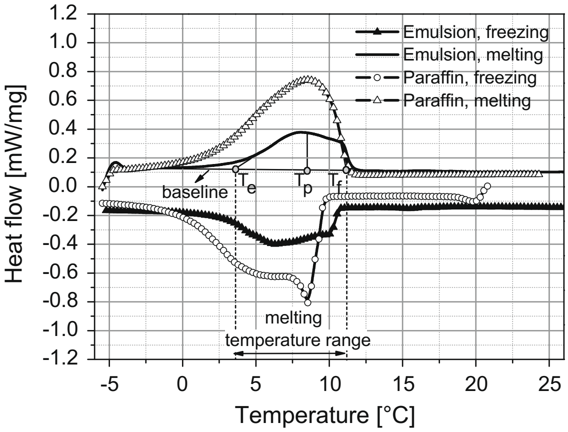

Fig. 2. DSC curves of the emulsion containing 30 wt.% RT10 and the characteristic temperatures of the melting curve at 2 °C/min scanning rate.

here X_p and X_w are the weight fraction of the paraffin and that of water, $\Delta h_{f,p}$ is the heat of fusion of the paraffin between T_1 and T_2, $c_{p,w}$ is the specific heat capacity of water and $\bar{c}_{p,p}$ is the average specific heat capacity of the paraffin in the solid and liquid state, which is 2.2 J/(g K) for the calculation. Fig. 3 shows the DSC melting curve and the integral curve of the emulsion at 2 °C/min scanning rate. In the typical operating temperature range of 5–11 °C for air conditioning, the emulsion has a heat of fusion of 35 kJ/kg determined by DSC and a total heat capacity of 55 kJ/kg calculated according to Eq. (1). In order to study the heat capacity of the emulsion under the similar operation conditions in practical applications, experiments were conducted in a test rig.

3. Experimental setup and calibration

A test rig depicted in Fig. 4 was built to study the heat capacity of the paraffin emulsion. The test rig is composed of a storage tank with a volume of 25 l, a thermostat Lauda RE 310 with a heating output of 2.25 kW and a cooling output between 0.27 and 0.50 kW in a temperature range of −40 °C to +200 °C, a plate heat exchanger Cetepac 310–10 having a volume of 0.45 l and a heat exchange area 0.24 m^2, and a Laing heating pump S4–36/360G with a capacity of up to 4 m^3/h. A Kobold plastic flow meter was used to determine the flow rate of the sample between the storage tank and the heat exchanger. It has a measuring range of 100–1000 l/h for water at 20 °C with scale divisions every 20 l/h. A flow meter Krohne type VA40 N19.26 was used to measure the flow rate of the primary heat transfer fluid between the thermostat and the heat exchanger. The flow meter has a measuring range of 63–630 l/h for water at 20 °C with scale divisions every 20 l/h. The temperatures of the primary heat transfer fluid and the sample were determined with the thermocouples NiCr–Ni (Type K) AL–KB-1.5-250-2-TT 465-cl.1 of Roessel Messtechnik GmbH & Co. The measuring range is −40 °C to +1000 °C and the maximal absolute error is ±1.5 °C. All of the elements and pipes are well insulated to reduce the heat loss.

A mixture of water and an anti-freezing agent BASF Glysantin Protect Plus G48 based on ethylene glycol was used as the primary heat transfer fluid and circulated between the thermostat and the heat exchanger. The sample was considered as the second heat transfer fluid and circulated between the storage tank and the heat exchanger. The flow rate of the sample was adjusted by setting the input valve to the pump. The flow rates of the sample and the primary fluid were read every 5 min. The temperatures of the sample in the middle of the tank, in the inlet and outlet of the tank, as well as the temperatures of the primary fluid in the thermostat, in the inlet and outlet of the heat exchanger were recorded every 60 s by a computer.

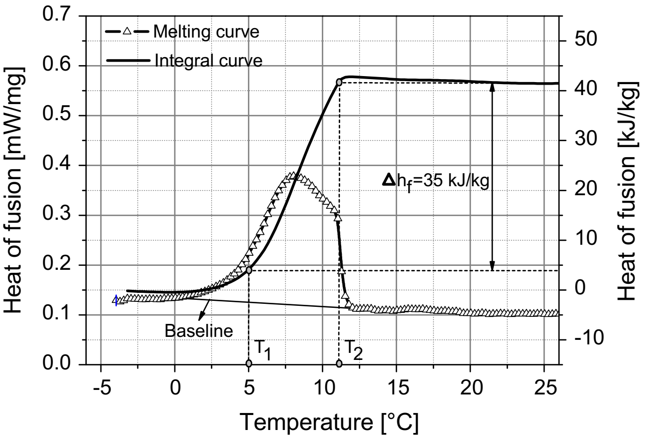

Fig. 3. DSC melting curve and integral curve of the emulsion containing 30 wt.% RT10 at 2 °C/min scanning rate.

The storage tank, the pump and the heat exchanger were regarded as a thermodynamic system as portrayed in Fig. 5. On the one hand, the amount of heat transferred from or released to the primary fluid Q_{pr} is equal to the sum of the enthalpy change of the secondary fluid ΔH_{sec} in the tank and the heat loss Q_{loss} according to the law of the conservation of energy,

$$Q_{pr} = \Delta H_{sec} + Q_{loss} \tag{2}$$

On the other hand, the heat amount of the primary fluid Q_{pr} is the sum of the product of the heat flow $\dot{Q}_{pr}$ and the time interval Δt of 60 s. The heat flow $\dot{Q}_{pr}$ can be estimated with the specific heat capacity of the primary fluid $c_{p,pr}$, the temperature difference between the inlet and outlet of the heat exchanger $T_{pr,inlet}$ and $T_{pr,outlet}$, the flow rate u_{pr} and the density ρ_{pr} of the primary fluid:

$$Q_{pr} = \sum \dot{Q}_{pr} \cdot \Delta t = \sum c_{p,pr} \cdot (T_{pr,outlet} - T_{pr,inlet}) \cdot u_{pr} \cdot \rho_{pr} \cdot \Delta t \tag{3}$$

The average sensible heat capacity of the primary fluid $c_{p,pr}$ was determined to be 3.51 J/(g K) between 0 and 25 °C by DSC measurements. From Eqs. (2) and (3), the enthalpy change of the secondary fluid per mass Δh_{sec}, namely the heat capacity, is obtained as:

$$\begin{aligned}\Delta h_{sec} &= \frac{\Delta H_{sec}}{m_{sec}} = \frac{Q_{pr} - Q_{loss}}{\rho_{sec} \cdot V_{sec}} \\ &= \frac{\sum c_{p,pr} \cdot (T_{pr,outlet} - T_{pr,inlet}) \cdot u_{pr} \cdot \rho_{pr} \cdot \Delta t - Q_{loss}}{\rho_{sec} \cdot V_{sec}}\end{aligned} \tag{4}$$

where m_{sec}, ρ_{sec} and V_{sec} are the mass, the density and the volume of the secondary fluid respectively.

Nineteen liters of water were used for calibrating the test rig before the experiment with the emulsion. The water was first cooled from 30 °C to 4.7 °C and afterwards heated to 30 °C again. In order to determine the heat loss of the system Q_{loss}, the water temperatures in the tank measured with the thermocouple were compared with those calculated according to the following equation:

$$T_2 = \frac{\Delta h_w}{c_{p,w}} + T_1 \tag{5}$$

here T_1 and T_2 are the end and start temperatures of water in the tank every time interval Δt of 60 s, Δh_w is the enthalpy change of water calculated according to Eq. (2) without considering any heat loss, $c_{p,w}$ is the specific sensible heat capacity of water of 4.19 J/(g K). The heat flow $\dot{Q}_{pr}$ as well as the water temperatures measured and calculated according to Eq. (5) are plotted against the time during the cooling and heating processes. The curves are shown in Figs. 6 and 7. The heat loss is caused by the pump and the heat transfer between the sample and the environment. The heat loss flow $\dot{Q}_{loss}$ was 50–300 W during the test process, which changed proportionally with the temperature difference between the sample and the environment. The heat loss amount Q_{loss} was 45–50% relative to the total heat amount during the cooling process and 10–15% during the heating process, because the cooling power of the test rig is lower than the heating power and it took a longer time for the cooling process than for the heating process.

On the one hand, the heat capacity of water was obtained according to Eq. (4), which is considered as the experimental value. On the other hand, the enthalpy change of water Δh_w in a certain temperature range can be estimated using the sensible heat capacity of water $c_{p,w}$ and the temperature difference ΔT. Rearrangement of Eq. (5) gives:

$$\Delta h_w = c_{p,w} \cdot \Delta T = c_{p,w} \cdot (T_2 - T_1) \tag{6}$$

The heat capacity calculated according to Eq. (6) is regarded as the theoretical value. Fig. 8 shows the experimental and theoretical values of the heat capacity of water versus temperature. The

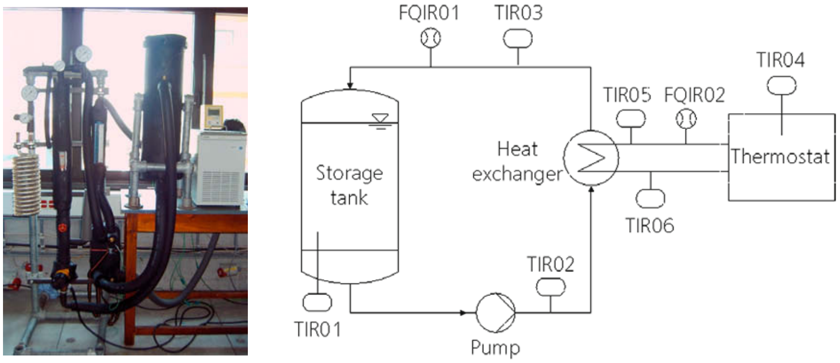

Fig. 4. The test rig for studying the heat capacity of the emulsion.

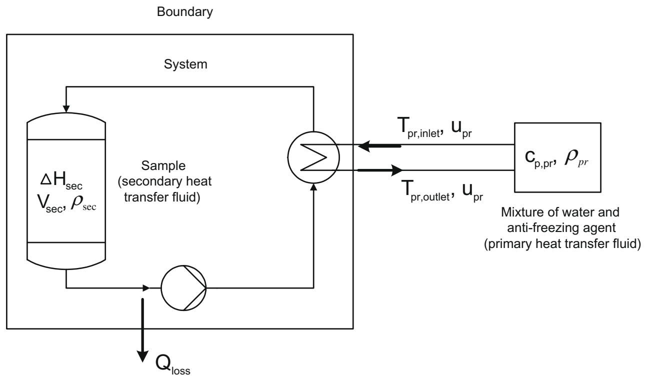

Fig. 5. Thermodynamic system for determining the heat capacity of the emulsion.

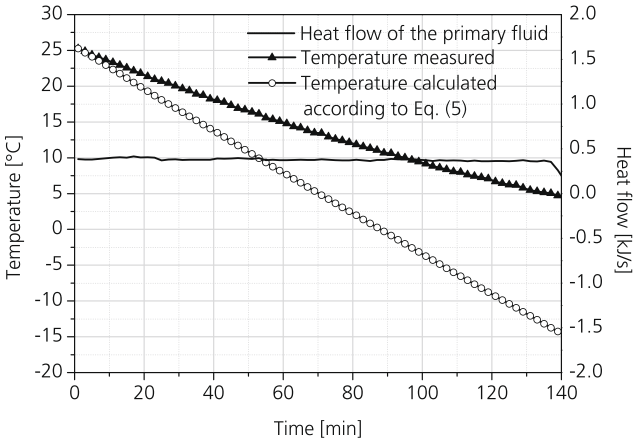

Fig. 6. The heat flow and the water temperatures in the tank measured and calculated according to Eq. (5) during the cooling process.

temperatures of 5.1 °C and 25.3 °C are taken as the start temperature T_0 during the heating and cooling processes respectively. Thus, the enthalpy changes at these two temperatures are zero. From Fig. 8 it can be seen that the experimental values of the heat capacity agree well with the theoretical ones. The results show that the test rig and the measuring systems can be used for studying the heat capacity of the emulsion.

4. Experimental results

19.3 l of an emulsion containing 30 wt.% RT10, 1.5 wt.% surfactant and 1.5 wt.% nucleating agent were investigated in the test rig.

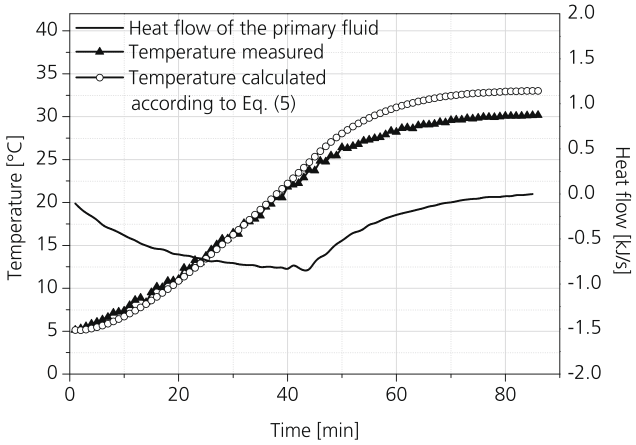

Fig. 7. The heat flow and the water temperatures in the tank measured and calculated according to Eq. (5) during the heating process.

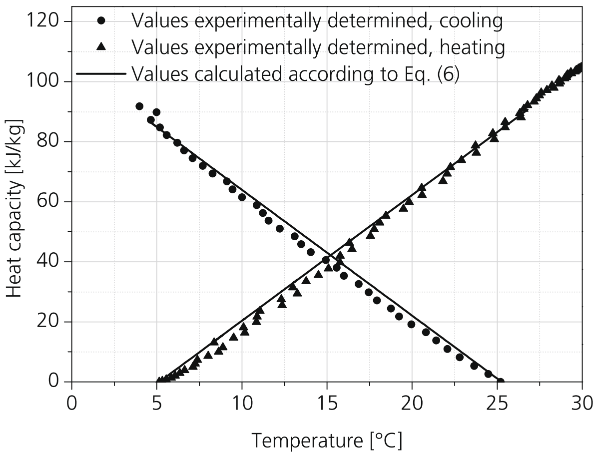

Fig. 8. The heat capacity of water experimentally determined and calculated according to Eq. (6) versus temperature during the heating and cooling processes.

The emulsion was cooled and heated to freeze and melt the paraffin for determining the heat capacity during the phase transformation. The melting process of the emulsion occurs over a temperature of 4–11.5 °C depicted in Fig. 2. Thus, the emulsion was firstly cooled from 25 °C to 5 °C and afterwards heated to 25 °C again. For a cold storage and transfer fluid, the cooling process is regarded as the charging process and the heating process is the discharging process. The heat capacity of the emulsion was experimentally determined according to Eq. (4). As shown in Figs. 9

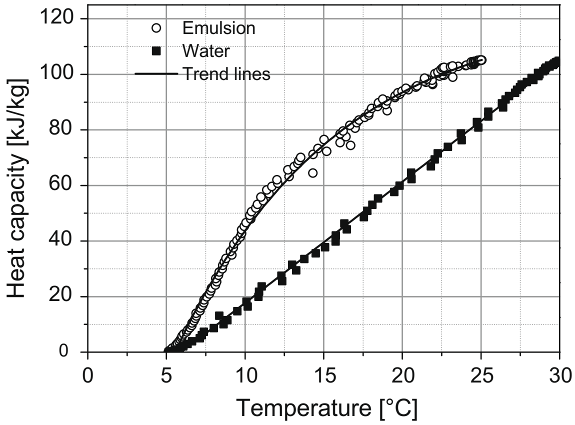

Fig. 9. The heat capacity of the emulsion containing 30 wt.% RT10 compared to that of water during the discharging process.

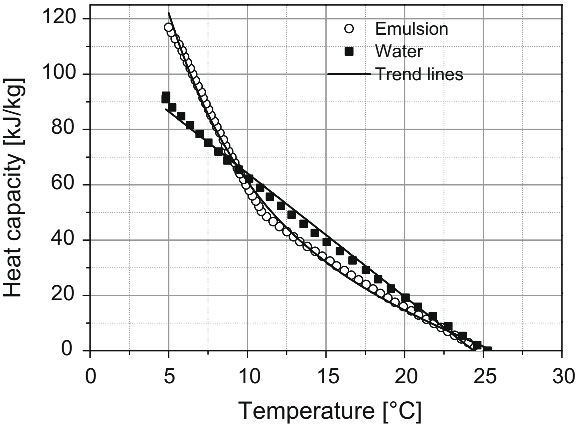

Fig. 10. The heat capacity of the emulsion containing 30 wt.% RT10 compared to water during the charging process.

and 10, the values of the heat capacity are plotted against the temperature measured in the middle of the tank during the discharging and charging processes compared to those of water. The enthalpy change of the emulsion at 5 °C in the discharging process and that at 25 °C in the charging process are taken as zero. The same percentages of the heat loss ΔQ_{loss} were considered in the calculation as those for water. During the discharging process, the emulsion has a heat capacity of 50 kJ/kg from 5 °C to 11 °C, which is two times as high as that of water. During the charging process, the emulsion has a slightly lower heat capacity than water until the paraffin begins to solidify. The heat capacity of the emulsion increases sharply during the phase transition process.

The heat capacity of the emulsion can be calculated with the sensible heat capacity of water, the latent and sensible heat capacities of the paraffin RT10 according to Eq. (1). The values of the heat capacity determined with the test rig are compared with those estimated according to Eq. (1) as represented in Fig. 11. The values of the heat capacity experimentally determined are within ±10% deviation of those calculated (see the following section also).

5. Experimental errors and error analysis

The heat capacity of the emulsion was experimentally determined with the test rig. It was obtained with the volume V_e and the density ρ_e of the emulsion, the density ρ_{pr}, the flow rate u_{pr}, the specific heat capacity $c_{p,pr}$ and the temperature difference ΔT of the primary heat transfer fluid the heat loss Q_{loss} and the time interval Δt according to Eq. (4). The volume of the emulsion V_e was determined with a graduated cylinder having a measuring range of 0–5000 ml with scale divisions every 100 ml. The acceptable deviation between the volumes designed and actually used was ±100 ml. The densities of the emulsion ρ_e and the primary fluid ρ_{pr} were obtained with a gas pycnometer and they have a relative error of ±0.1% on the values measured. The flow rate of the primary heat transfer fluid u_{pr} was directly read from the flow meter Krohne N19.26. The relative error is ±1% on the value recorded. The specific heat capacity of the primary heat transfer fluid $c_{p,pr}$ was determined by DSC measurements and the relative error is ±3.5% on the value obtained. The temperatures were recorded by using the thermocouples NiCr–Ni (Type K) and the maximal absolute error of the temperatures is ±1.5 °C. According to the propagation of errors, the maximal relative error of the heat capacity is ±10% on the values determined with the test rig. Fig. 11 shows that the values experimentally determined are within ±10% deviation of the values calculated according to Eq. (1). It means that the heat capacity of the emulsion can be estimated with Eq. (1).

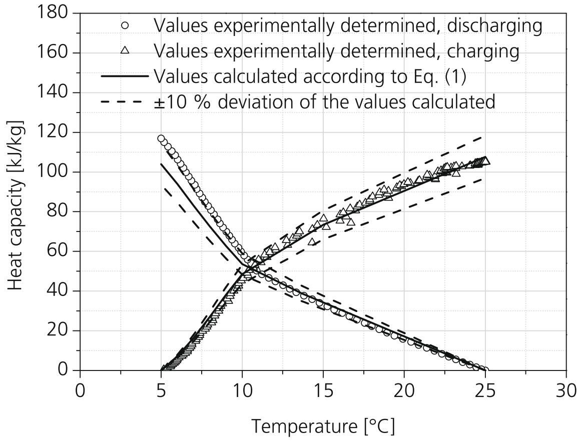

Fig. 11. The heat capacity of the emulsion containing 30 wt.% RT10 experimentally determined and calculated according to Eq. (1) versus temperature.

6. Conclusion

In this paper, a paraffin/water emulsion containing 30 wt.% paraffin RT10 having a melting peak point of 9 °C was studied as a Phase Change Slurry (PCS) for comfort cooling applications. It comprises a collection of small paraffin droplets, having a diameter of 1–10 µm, and dispersed in water by a nonionic surfactant. The phase transition temperature ranges and the heat of fusion of the emulsion were determined by DSC measurements. The emulsion has a heat of fusion of 43 kJ/kg over the total melting temperature range of 4–11.5 °C. In order to determine the heat capacity of the emulsion under similar operation conditions in practical applications, experiments were carried out in a test rig. It was found the heat capacity of the emulsion experimentally obtained agrees well with the sum of the heat of fusion determined by DSC measurements as well as the sensible heat capacity of water and that of the paraffin according to Eq. (1). In a temperature range of 5–11 °C for air conditioning, the emulsion has a heat capacity of 50 kJ/kg which is two times as high as that of water. The study shows that the paraffin/water phase change emulsion is an attractive alternative to chilled water for comfort cooling applications and enables cold storage and transportation at a high energy density.

Acknowledgments

This study was supported by the Project Management Jülich (PTJ) and Federal Ministry of Economics and Technology (BMWI).

References

[1] Saito A. Recent advances in research on cold thermal energy storage. Int J Refrig 2002;25:177–89.

[2] Sharma SD, Kitano H, Sagara K. Phase change materials for low temperature solar thermal application. Res. Rep. Fac. Eng. Mie Univ. 2004;29:31–64.

[3] Ure Z. Slurry ice based cooling systems. In: Proceedings of the conference of commissions B2 & C2 with D1 & D2/3, Sofis, Bulgaria, 23–26 September, 1998, p. 172–9.

[4] Inaba H. The current trends in research and development on phase change material slurry. In: Egolf PW, Sari O, editors. Proceeding of the phase change material and slurry scientific conference & business forum, 23-26 April, Yverdon-Ies-Bains, Switzerland, 2003, p. 5–13.

[5] Ogashi H, Takao S. Air-conditioning system using clathrate hydrate slurry, JEF technical report, No. 3; 2004. <http://www.jfe-steel.co.jp/en/research/report/003/pdf/003-02.pdf>.

[6] Huang L, Petermann M, Doetsch C. Evaluation of paraffin/water emulsion as a phase change slurry for cooling applications. Energy 2009;34:1145–55.

[7] He B, Martin V, Setterwall F. Phase change temperature ranges and storage density of paraffin wax phase change materials. Energy 2004;29:1785–804.