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International Journal of Heat and Mass Transfer 48 (2005) 3212–3220

International Journal of HEAT and MASS TRANSFER

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Study of direct contact melting with hydrocarbon mixtures as the PCM

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Received 21 August 2003; received in revised form 8 December 2004
Available online 27 April 2005

Abstract

In this study, direct contact melting of hydrocarbon mixtures as phase change materials was investigated experimentally. Tetradecane and hexadecane binary mixtures, and pentadecane and octadecane binary mixtures were used as phase change materials, with various mixing ratios. It was found that the heat flux decreased significantly in the low surface temperature range. In addition, a rough and uneven melting surface was observed in the low surface temperature range. The convex portions at the melting surface were collected, and the ingredients of this region were measured by using differential scanning calorimetry (DSC). It was found that the DSC curve shifted to a higher temperature region, and the concentration of higher melting point material increased at the convex portions. Therefore, it seems that the melting point around the convex portions increased due to the higher concentration of higher melting point material, and this resulted in the decrease in the heat flux.

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1. Introduction

Recently, many studies on thermal energy storage systems have been carried out, in relation to the effective utilization of the energy. For the advancement of thermal energy storage systems using latent heat, not only studies on fundamental phenomena of solid–liquid phase changes, but also development of thermal energy storage materials having high densities for thermal energy and appropriate melting points, is necessary.

One thermal energy storage system is operated by repeated solidification and melting of the thermal energy storage material enclosed in a capsule. In this case, the PCM solid is pressed onto the heating wall by buoyancy or gravity force, and the melting process progresses. A very thin liquid film is then formed between the solid and the heating wall. Since heat is exchanged across this thin liquid film, a high heat flux can be obtained compared with a heat transfer that is, for example, dominated by natural convection. Therefore, the melting process is dominated by the phenomenon inside the thermal energy storage capsule. This phenomenon is known as direct contact melting and the phenomenon obtained by pressing a cylindrical solid onto a plate was first investigated both experimentally and analytically by Saito et al. [1–3]. They showed a relation between the heat flux, the Stefan number and the pressing force. Moallemi et al. [4] reported a similar relation. In these

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doi:10.1016/j.ijheatmasstransfer.2005.01.040

Nomenclature

c	specific heat, J/(kg K)
L	latent heat of melting, J/kg
P	average pressure, Pa
P^*	non-dimensional average pressure, $PR^2/\alpha\mu$
q	heat flux, W/m^2
q^*	non-dimensional heat flux, $qR/(\lambda\Delta T)$
R	radius of sample, m
Ste	Stefan number, $c(T_{\mathrm{surf}} - T_{\mathrm{m}})/L$
T_{H}	higher peak temperature of DSC output, °C
T_{L}	lower peak temperature of DSC output, °C
T_{m}	melting point, °C
T	temperature, °C
V	melting velocity, m/s

Greek symbols

α	thermal diffusivity of liquid, m^2/s
ΔT	difference between surface temperature and melting point, °C
ΔT_{hex}	difference between surface temperature and melting point of hexadecane, °C
λ	thermal conductivity of liquid, W/(m K)
μ	viscosity of liquid, Pa s
ρ	density kg/m^3

Subscripts

cal	calculated value
exp	experimental value
i	initial condition
l	liquid
s	solid
surf	surface of heating plate

studies, pure materials (such as octadecane and ice) were used as the PCM solid, where experiments and numerical analyses were carried out in order to understand a fundamental process of direct contact melting.

In relation to the development of thermal energy storage materials, many studies using paraffin wax hydrocarbon mixtures have been carried out. One of the characteristics of these hydrocarbon mixtures is that the melting point can be varied by changing the composition. Therefore, it is supposed that it is possible to operate the system efficiently by selecting an appropriate melting point. In previous studies on hydrocarbon mixtures, melting points and latent heats of melting of tetradecane and hexadecane mixtures were investigated by Choi et al. [5]. Bo et al. [6] investigated latent heats of fusion and the stabilities of mixtures of tetradecane and hexadecane. Wada et al. [7] measured thermal conductivities of binary and ternary mixtures of liquid hydrocarbons. In studies on solid–liquid phase changes of hydrocarbon mixtures, Webb et al. [8] investigated the solidification process of mixtures of hexadecane and octadecane.

As mentioned above, there are not enough investigations into the solidification and melting of hydrocarbon mixtures, although many researchers have attempted to investigate thermal properties of these mixtures.

Therefore, in this study, the direct contact melting of hydrocarbon mixtures is investigated experimentally. The results are examined with a view to understanding the characteristics of the melting process in composite materials, using binary hydrocarbon mixtures. Moreover, the experimental results are compared with analytical results for direct contact melting of pure materials, and applicable ranges of analytical results obtained in previous studies are investigated.

2. Experimental

2.1. Experimental apparatus and conditions

The experimental system consists of the main apparatus, a constant temperature bath and measuring instruments. The main apparatus is shown in Fig. 1. It is made of acrylic resin. A cylindrical sample was placed on a circular heating plate set horizontally. The heating plate is made of copper 100 mm in diameter and 16 mm in thickness. The surface temperature of the heating

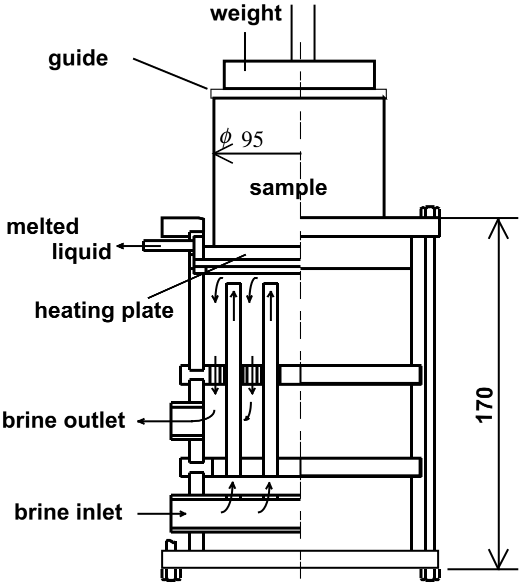


Fig. 1. Experimental apparatus.

plate was adjusted by controlling the temperature of the brine circulating beneath the heating plate. The brine temperature was maintained at a constant value throughout the experiment by using the constant temperature bath. Three sets of T-type thermocouples were installed in the heating plate as shown in Fig. 2. Each set consisted of two thermocouples, which were located at a depth of 2 mm from each surface. The three sets were installed at locations 25 mm from the center of the heating plate at 120° intervals in the angular direction. The temperature in the heating plate was measured by these thermocouples. The temperature distribution in the heating plate was assumed to be linear, and the surface temperatures were calculated from these values. In preliminary experiments, it was confirmed that the measurement error of the surface temperature of the heating plate was about ±0.1 °C. A guide was placed on the sample in order to make the sample move vertically and to assure that the force due to the weight acted uniformly on the top of the sample. Variation of sample height was measured at 20 s intervals by calipers which moved with the guide. Average pressure due to the load and the heat flux from the surface of the heating plate were calculated from the height and its variation, respectively.

In previous studies [1–3], authors showed that non-dimensional heat flux obtained from experiments was a function of the *Ste* based on the surface temperature and non-dimensional average pressure due to the load, when pure materials were used as the PCM. In this study, *Ste* and non-dimensional average pressure due to the load are also key parameters. *Ste* was calculated by using higher peak temperature and the latent heat of melting obtained by DSC measurement, and *Ste* was varied in the range from 0.03 to 0.4. The surface temperature of the heating plate was then set from 3 °C to 25 °C above the peak temperature obtained by DSC measurement. The average pressure was decided by the sum of gravitational forces due to the sample itself, the weight and the guide placed on the sample. Since the mass of the sample decreased with melting, the average pressure decreased over the course of the experiment. However, it was observed that the effect of the variation of the average pressure with melting was very small in the experiments. Therefore, the heat flux was measured in order to understand the effect of *Ste*, at a specific average pressure value. The average pressure was also varied as a parameter. The average pressure values were set at 5.96×10^2, 8.83×10^2, 1.20×10^3 and 4.50×10^3 Pa, respectively, and these values were varied by changing the mass of the weight.

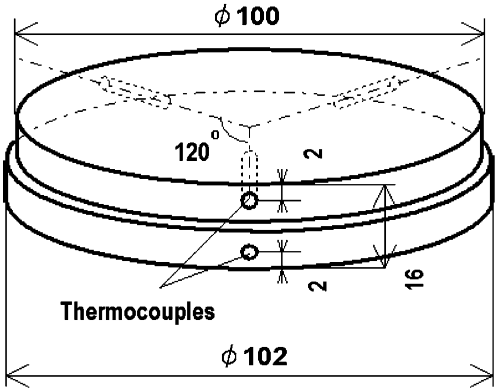


Fig. 2. Details of the heating plate.

2.2. Sample preparation

In this study, hydrocarbon mixtures were used as the PCM solid. The samples were either tetradecane and hexadecane mixtures, or pentadecane and octadecane mixtures. The components of these mixtures are hydrocarbons with carbon numbers from 14 to 18. The mixing ratios of the tetradecane–hexadecane mixtures were set at 2:8, 4:6, 6:4 and 8:2, and the mixing ratio of the pentadecane–octadecane mixture was set at 4:6.

It is known that the hydrocarbon solids can include a lot of air. Therefore, careful attention is needed during the solidification of the sample. Firstly, the sample in liquid form is put into a vacuum vessel. The solidification and melting phase changes are then repeated under vacuum, and dissolved air is removed from the sample. The liquid sample is then put into a cylindrical vessel 95 mm in diameter and 100 mm in height. The sample is solidified from the bottom of the vessel by using ice or liquid nitrogen, while it is heated from the top of the vessel by infrared lamp. After the whole sample has been solidified, the sample is removed from the vessel. The sample is then used for experiments, after the sample temperature has become uniform inside an incubator.

2.3. Sample properties

Since the samples used in this study are composite materials, not much is known about the sample properties. However, the compositions of the sample components are similar to each other, and some of their properties are also similar. Therefore, some of the sample properties were determined by using an arithmetic mean weighted by the mixing ratio, and others were measured.

Table 1 shows the properties of the pure materials. The specific heat values of the solid and the liquid, the thermal conductivity of the liquid, the viscosity and the density of the liquid were determined by the arithmetic means. Melting point, latent heat of melting and density of the solid were measured for the samples made as described in Section 2.2. The melting point and the latent heat of melting were measured by using differential scanning calorimetry (DSC). For example, Fig. 3

Table 1
Properties of pure materials

	Tetra-decane	Penta-decane	Hexa-decane	Octa-decane
Molecular formula	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$	$C_{18}H_{38}$
T_m, °C	5.5	10.0	18.15	28.1
L, kJ/kg	227	207	236	244
c_l, kJ/kg	2.16	2.21	2.09	2.18
c_s, kJ/kg	1.64	1.61	1.64	1.53
λ, W/(m K)	0.15	0.14	0.14	0.15
μ, Pa s	0.0023	0.00195	0.0023	0.0039
ρ_l, kg/m^3	759	776	773	777
ρ_s, kg/m^3	884		864	855

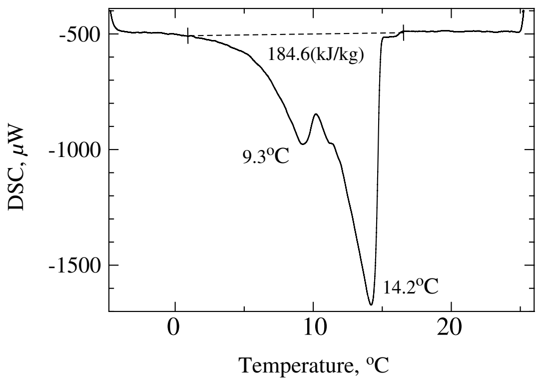


Fig. 3. DSC output curve of 2:8 mixture of tetradecane and hexadecane.

shows the DSC output curve of the 2:8 mixture of tetradecane and hexadecane. DSC output curve becomes flat when phase change does not occur in the sample, and the flat output line is a base line in the measurement. The output value of the base line is not 0, because the value is decided by the mass and the specific heat of the sample, and the heat capacity of the sample vessel. On the other hand, a remarkable variation from the base line in the output value of the DSC measurement is found when the phase change occurs. In pure materials, a sharp peak appears at the melting point. In contrast, as shown in Fig. 3, a peak curve with a wide temperature range appears in composite materials. The latent heat is obtained by integrating the peak range, and the melting point is taken as the peak temperature. When there are two peaks, as shown in Fig. 3, the higher peak temperature is used as the melting point of the material. In direct contact melting phenomena, the melted liquid forms very thin liquid film between solid surface and a heating plate, and the melting process progresses while the liquid squeezed out through the thin liquid film. Therefore, the melting temperature should be defined as the temperature at which the whole solid melts. Table 2 shows the sample properties. Using these properties, the heat flux was calculated by taking the variation in sample height with melting. These properties were also used in the analytical considerations described in the following section.

When liquid is solidified, the entire liquid is not solidified simultaneously, but the solid grows from the cooling surface. In these experiments, it was supposed that segregation of the sample occurred during solidification, because the samples were composite materials. Therefore, several grams of composite material were collected from cross sections of the samples prepared as described in Section 2.2, and their melting points and latent heats of melting were measured by using DSC, in order to confirm the sample composition. The positions used for collection are shown in Fig. 4. Fig. 5 shows DSC

Table 2
Properties of mixtures

	Tetradecane:hexadecane				Pentadecane:octadecane
Ratio	8:2	6:4	4:6	2:8	4:6
T_m, °C	2.7	5.0	8.6	14.2	20.1
L, kJ/kg	129.1	121.8	148.5	184.6	157.2
c_l, kJ/kg	2.15	2.13	2.12	2.1	2.19
c_s, kJ/kg	1.64	1.64	1.64	1.64	1.57
λ, W/(m K)	0.148	0.146	0.144	0.142	0.146
μ, Pa s	0.0023	0.0023	0.0023	0.0023	0.00345
ρ_l kg/m^3	761	765	767	770	776.5
ρ_s kg/m^3	817	795	806	839	815

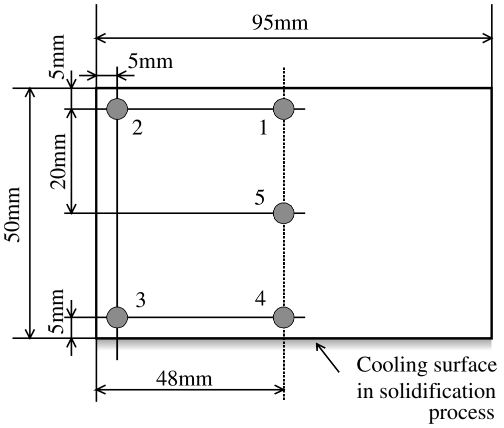


Fig. 4. Measurement points in a sample.

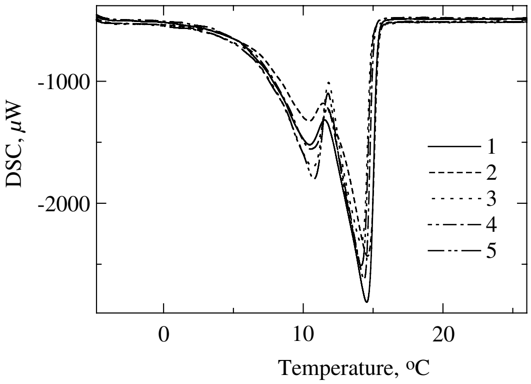


Fig. 5. DSC output curves for each point of Fig. 4 (2:8 mixture of tetradecane and hexadecane).

output curves of the 2:8 mixture of tetradecane and hexadecane for each position. From this figure, it is seen that the differences in the peak temperature are less than 0.5 °C. Moreover, the differences of the latent heat are less than 8 kJ/kg that corresponds to about 4% of the latent heat in Table 2. Thus, it is found that large scale segregation of the sample does not occur.

3. Results and discussion

3.1. Evaluation of experimental results

Previous studies on direct contact melting found that the non-dimensional heat flux was a function of the *Ste*, based on the surface temperature of the heating plate and the non-dimensional average pressure due to the load. In this study, characteristics of the melting process of the composite materials were considered by comparison with the melting process of pure materials. Therefore, the function for pure materials was applied to the direct contact melting of the composite materials, and differences between the pure material and the composite material were examined.

In previous studies by the authors, when the sample is cylindrical and a pure material, heat flux from the heating surface in quasi-steady state is expressed as follows [1–3];

$$
\begin{aligned}
q &= \frac{\lambda \Delta T}{R}\left[f(Ste)P^{*0.25}\,Ste^{-0.25}\right] \\
f(Ste) &= 0.915 + 0.168Ste - 0.00608Ste^{2.64}
\end{aligned}
\tag{1}
$$

This is an approximate equation from analytical results, when *Ste* ranges from 10^{-3} to 4.0 and P^* ranges from 10 to 10^{11}. It was found that the experimental and the calculated analytical results agreed with each other, when *Ste* ranged from 0.05 to 0.2 and P^* ranged from 6.0×10^8 to 5.9×10^{10}. In these experiments, it was found that the melting process progressed in a quasi-steady state. Thus, using higher peak temperature and latent heat of melting obtained by DSC, the heat flux q_{cal} can be calculated by using Eq. (1).

Experimental heat flux was calculated from the variation in the height of the sample, the surface temperature of the heating plate, and the initial temperature of the sample, as follows:

$$
q_{\mathrm{exp}} = V\{\rho_{\mathrm{s}}L + c_{\mathrm{s}}\rho_{\mathrm{s}}(T_{\mathrm{m}} - T_{\mathrm{i}}) + \tfrac{1}{2}c_l\rho_{\mathrm{l}}(T_{\mathrm{surf}} - T_{\mathrm{m}})\} \tag{2}
$$

Since the initial temperature of the sample is lower than the peak temperature range, the specific heat for the solid state must be considered. The sample moves downward with melting. The specific heat of the solid state can then be expressed as the second term on the right-hand side of Eq. (2), when it is assumed that the temperature distribution near the melting surface of the sample does not vary. When *Ste* is small, heat transfer in the liquid film is dominated by heat conduction, and it is supposed that a linear temperature distribution forms in the liquid film. Therefore, the specific heat for the liquid film can be expressed as the third term on the right-hand side.

The melting process is examined by using the ratio of q_{exp} to q_{cal} to confirm whether or not the approximate equation for the direct contact melting is applicable to the melting process of the composite materials. Namely, the ratio becomes 1 when the melting process of the composite materials is similar to the direct contact melting of pure materials.

3.2. Experimental results

Fig. 6 shows the relationship between the heat flux and the difference between the melting point and the surface temperature of the heating plate for the 4:6 mixture of pentadecane and octadecane. The increase of the heat flux with ΔT is the phenomena peculiar to the direct con-

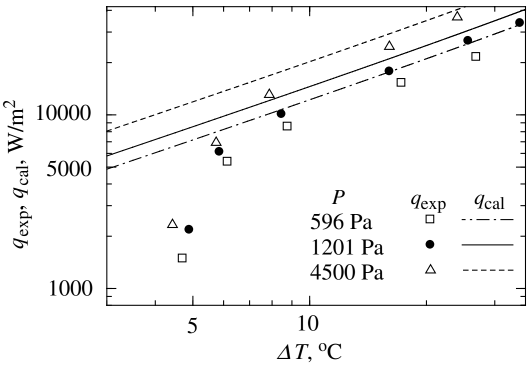


Fig. 6. Relation between q and ΔT (4:6 mixture of pentadecane and octadecane).

tact melting. On the other hand, the decrease of the heat flux q_{exp} compared with the heat flux q_{cal} in the low surface temperature range is caused by using the hydrocarbon mixture as the PCM.

Fig. 7(a) shows the relationship between the ratio of the heat flux and *Ste* for the mixtures of tetradecane and hexadecane, when the mixing ratios are 10:0, 8:2 and 6:4. Fig. 7(b) shows the relationship between the ratio of the heat flux and *Ste* for the 4:6, 2:8 and 0:10 mixtures of tetradecane and hexadecane. Fig. 7(c) shows the result for the 4:6 mixture of pentadecane and octadecane. The mixing ratios of 10:0 and 0:10 mean that the sample is a pure material. It was found that Eq. (1) is applicable to pure materials of tetradecane and hexadecane, since the heat flux ratio becomes almost 1. In the case of composite materials, the heat flux decreased in the small *Ste* range compared with the calculated value, and the *Ste* range in which the heat flux decreased varied with the mixing ratio. Moreover, the heat flux decreased in the small *Ste* range for the 4:6 pentadecane and octadecane mixture. Therefore, it was found that the decreases in the heat flux in the small *Ste* range are not a phenomenon peculiar to the mixtures of hexadecane and tetradecane, but are a characteristic of hydrocarbon mixtures. In the large *Ste* range, the experimental results were almost identical to the calculated values. The heat flux tendencies were similar to those of pure materials, and the heat flux was proportional to $\Delta T^{0.75}$ and $P^{*0.25}$.

Fig. 8 shows the relationship between the heat flux ratio and the mixing ratio of tetradecane and hexadecane, when *Ste* values are 0.05 and 0.2. When *Ste* was 0.2, the experimental heat flux decreased to 70% of the calculated value, and the peak of the decrease was at 40% hexadecane concentration. In contrast, the heat flux decreased to 20% when *Ste* was 0.05.

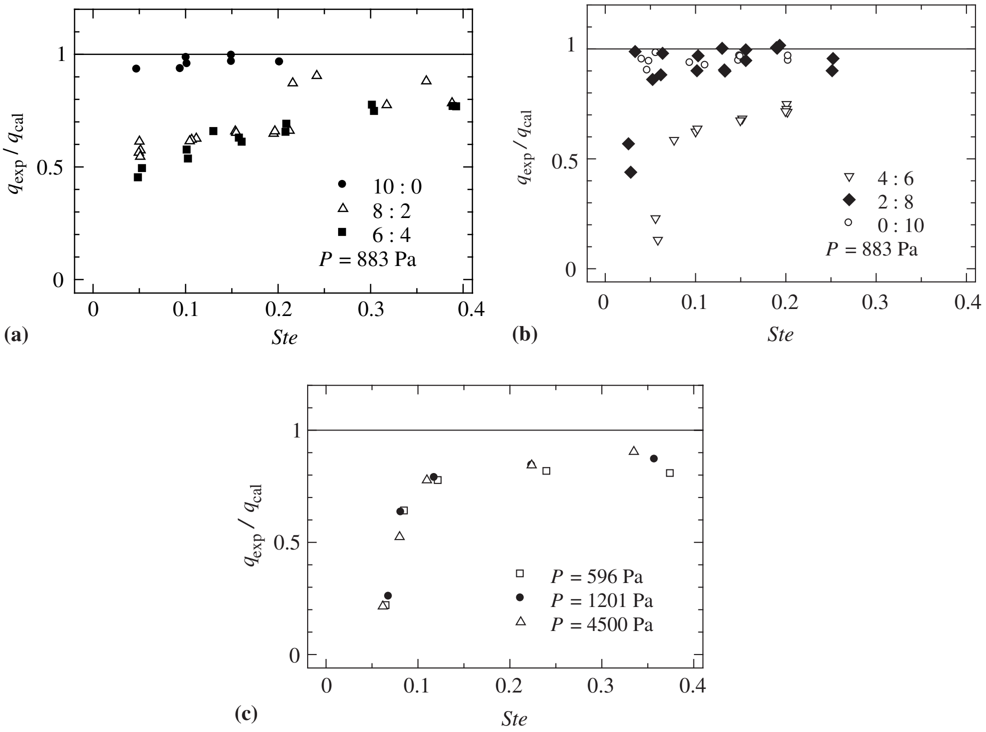


Fig. 7. Relation between q_{exp}/q_{cal} and *Ste*. (a) Mixtures of tetradecane and hexadecane, (b) mixtures of tetradecane and hexadecane and (c) 4:6 mixture of pentadecane and octadecane.

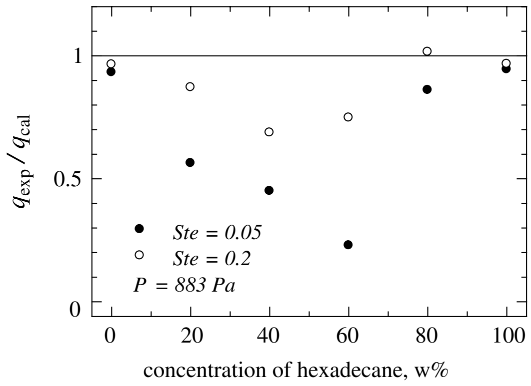


Fig. 8. Relation between q_{exp}/q_{cal} and mixing ratio.

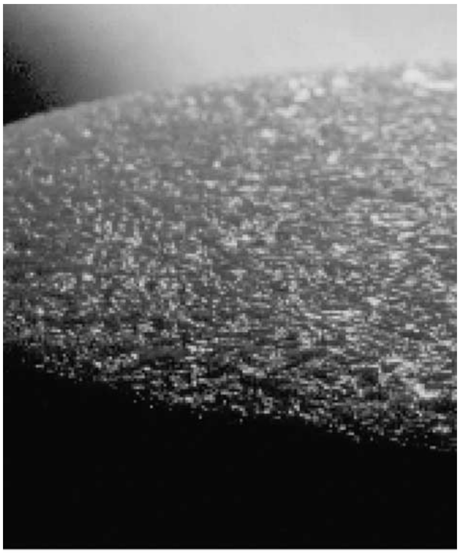
3.3. Melting surface observations

Observations of the melting surface under conditions at which the heat flux decreased by a large amount were carried out, and small scale unevenness was observed under several conditions. Fig. 9 shows photographs of the melting surfaces of pentadecane and octadecane mixtures, when *Ste* was 0.05 and 0.23, respectively. It was found that small scale unevenness formed at the melting surface when *Ste* was 0.05. In other mixtures, unevenness at the surface was also observed when the heat flux ratio decreased by less than 50%.

The convex portion which is shaved off with a knife from the uneven surface was collected and was measured by DSC in order to confirm its composition. Fig. 10 shows the DSC output of the convex portion, and the mixture of pentadecane and octadecane. From this figure, since the result for the convex portion has a high peak temperature, it is found that the ratio of octadecane is higher than in the overall mixture.

3.4. Heat flux decrease factors

It was observed that the heat flux decreased in the small *Ste* range, as compared with that in the high *Ste* range. Therefore, factors that affect the heat flux decrease will be discussed by considering the case of the pentadecane–octadecane mixture. Small scale segregation seemed to form at the melting surface, as shown in Fig. 11. When the surface temperature of the heating plate is low, the melting velocity is small. In this case, unevenness forms at the melting surface due to differences in the melting velocity, since there is a difference in the melting point between each small scale segregation. Here, the thickness of the liquid film is about 0.05 mm in the condition in which the decrease of the heat flux occurs, and the size of the segregation is about 1 mm from Fig. 9. Since the thickness of the liquid film is thinner than the size of the segregation, liquid that mainly includes octadecane melts at region A in Fig. 11. Because the melting temperature of the segregation approaches the melting point of octadecane in region A due to the phase equilibrium relationship, it is considered that the effective ΔT decreases, and, as a result, the heat flux decreases.



(a) *Ste* = 0.05

(b) *Ste* = 0.23

Fig. 9. Melting surface of pentadecane–octadecane mixture.

However, under some conditions, the unevenness did not form at the melting surface despite the small *Ste*. In these instances, the heat flux ratio decreased from 50% to 70%. Thus, it seems that formation of the unevenness depends on the size of the small scale segregation and the mixing ratio. The decrease of the heat flux is caused by the existence of the small segregation at the melting surface. The formation of the unevenness is not an

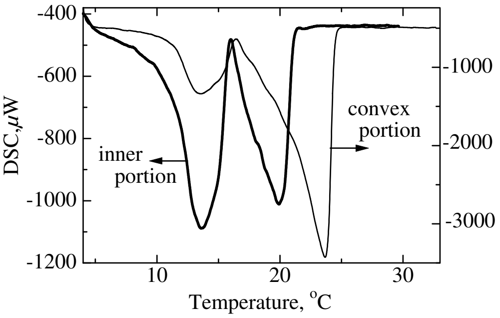


Fig. 10. DSC output curves for samples from the convex portion of melting surface and from an inner portion of pentadecane–octadecane mixture.

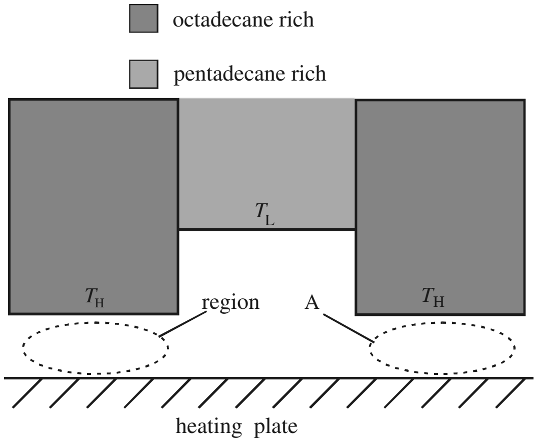


Fig. 11. Phenomena at the melting surface.

immediate cause, though it seems to promote the decrease in the heat flux.

On the other hand, when the surface temperature is high, the melting velocity becomes larger and the small scale segregation effect does not appear. As a result, the concentration in the liquid film becomes uniform, and the experimental heat flux is similar to the calculated value based on past studies.

Some samples of about 0.5 mg were taken from a cross section of the solid mixture and were measured by using DSC, in order to confirm when the small scale segregation formed. Fig. 12 shows several DSC outputs of the samples taken from the 4:6 mixture of pentadecane and octadecane. It was found that various kinds of segregation pre-existed in the sample. Moreover, since one of them was similar to the convex portion shown in Fig. 10, it was found that the segregation formed in the solid mixture during the solidification process.

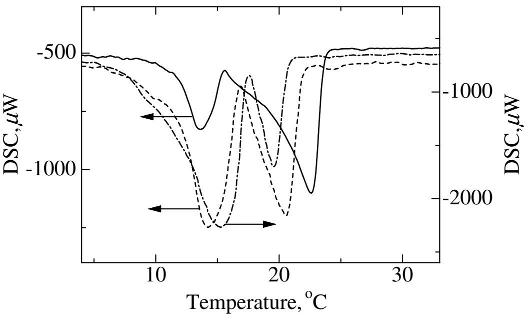


Fig. 12. DSC output curves for samples picked up from cross section (4:6 mixture of pentadecane and octadecane).

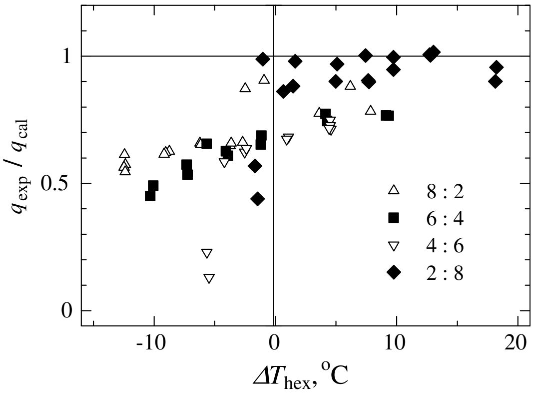


Fig. 13. Relation between q_{exp}/q_{cal} and melting point of hexadecane (4:6 mixture of pentadecane and octadecane).

Fig. 13 shows the relationship between the ratio of q_{exp} to q_{cal} and the temperature difference between the surface of the heating plate and the melting point of hexadecane (which has the higher melting point than the tetradecane). From this figure it can be seen that the heat flux decreases significantly in the range that is lower than the melting point of hexadecane. Therefore, it is found that the direct contact melting phenomena of mixtures depend on the higher melting point. On the other hand, the heat flux decreases slightly when the surface temperature of the heating plate is higher than the melting point of hexadecane.

From above considerations, it was found that mixtures can be treated as pure materials in an actual thermal energy storage system using hydrocarbon mixtures, if the heating surface temperature can be kept at more than melting point of the materials composing the mixture. Then, the melting amount can be expected by the analysis of direct contact melting. However, the decreases of the melting amount might happen, when the heating temperature is not sufficient.

4. Conclusion

The direct contact melting of hydrocarbon binary mixtures was investigated experimentally in order to understand the characteristics of this melting process in composite materials. The experimental results were compared with calculated analytical results for direct contact melting of pure materials, and an applicable range of analytical results obtained from previous studies was investigated. It was found that when the surface temperature was high, the non-dimensional heat flux for the melting process could be expressed as a function of *Ste* and non-dimensional average pressure. On the other hand, when the surface temperature of the heating plate was low, it was observed that the heat flux decreased compared with pure materials. Moreover, the factors affecting the decrease in the heat flux were discussed, and it was suggested that the decrease was caused by the formation of a concentration distribution in the liquid film due to small scale segregation in the sample.

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