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Theoretic Prediction of Melting Temperature and Latent Heat for a Fatty Acid Eutectic Mixture

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ABSTRACT: To determine the thermal properties of eutectic mixture of fatty acids by theoretic calculations, a formula of predicting thermal properties of eutectic mixture was selected and validated, and then the melting temperature and latent heat of eutectic mixture of fatty acids were calculated. From the calculation, the result of the theoretic calculation agrees well with that of the previous experiments. For the 15 eutectic mixtures of fatty acids, the minimum and maximum of the melting temperature are (10.2 and 51.5) °C, respectively. The minimum and maximum of the latent heat are (138.6 and 187.5) $J \cdot g^{-1}$, respectively. The eutectic mixtures of fatty acids are suitable for heating, a heat water system, phase wallboard, concrete and phase clothes, and other engineering applications.

1. INTRODUCTION

A eutectic mixture is a composition of two or more components, each of which melts and freezes at the same temperature, and among the mixtures combined by the two or more components with different proportions, the eutectic mixture has the lowest melting temperature and the best thermal reliability. The melting temperature of the eutectic mixture is termed as the eutectic point.[1]

Compared with other potential latent energy storage candidates, fatty acids have some desirable properties, such as little subcooling, reversible melting, and freezing behavior. A fatty acid eutectic mixture as a new PCM (phase change material) has also gained popularity in recent years.[2−7] An investigation on stearic acid (SA), lauric acid (LA), myristic acid (MA), and palmitic acid (PA) was conducted by Ahmet et al.[8] The melting temperature and latent heat of four eutectic mixtures were measured by DSC thermal analysis. The proportions, melting temperatures, and latent heat for the three eutectic mixtures (LA-SA, MA-PA, PA-SA) of these four materials (LA, SA, MA, PA) were measured by differential scanning calorimetry (DSC) analysis. Lv et al.[9−11] investigated the thermal performance of CA (capric acid)-LA eutectic mixture. The scanning rate is 0.2 $°C \cdot min^{-1}$. The results show that the CA-LA binary system forms a eutectic with the mixture ratio of 66:34 wt %, which melts at 19.67 °C and has a latent heat of 126.562 $J \cdot g^{-1}$, and the gypsum-PCM composite's melting temperature and latent heat are 17.984 °C and 39.828 $J \cdot g^{-1}$, respectively. Costa et al.[12] obtained the phase diagrams of seven fatty acid binary mixtures by DSC. The mixtures were formed by capric acid with lauric acid, myristic acid, plamitic acid, or stearic acid and by lauric acid with myristic acid, plamitic acid, or stearic acid.

On the other hand, the experimental data on the thermal properties of eutectic mixtures are subject to the experimental sample purity and the measurement error of DSC, and the experiment is also expensive and time-consuming. In comparison, a theoretic calculation can provide a quick, accurate, and low cost approach. This paper selects and verifies a theoretical prediction formula for melting point and latent heat of eutectic mixtures. Then the proportioning, melting temperature, and the latent heat of 15 fatty acid binary eutectic mixtures are theoretically calculated. Finally, the article summarizes the distribution of the melting temperature and latent heat and then analyzes the engineering applications of fatty acid binary eutectic mixtures.

2. CHARACTERISTICS OF FATTY ACIDS

Among fatty acids, CA, LA, MA, PA, and SA are widely used as PCM. All fatty acids have the carboxyl group, which is an important factor in determining their chemical properties. Table 1 shows the reported results of fatty acids as PCM.

3. CALCULATION OF MELTING TEMPERATURE AND LATENT HEAT OF EUTECTIC MIXTURES

3.1. Selection and Verification of Calculation Formula. The calculation formula is developed by ref 13. For the binary mixture, the formula for the liquid phase line is as follows.

$$\begin{cases} -\dfrac{H_A}{T_A}(T_m - T_A) + RT_m \ln(1 - X_A) + G_{A,ex} = 0 \\ -\dfrac{H_B}{T_B}(T_m - T_B) + RT_m \ln(1 - X_B) + G_{A,ex} = 0 \end{cases} \quad (1)$$

For the fatty acids, $G_{A,ex} = G_{B,ex} = 0$. The eutectic point is an intersection point at which the liquid phase lines A and B intersect. So the phase diagram can be plotted by the following formula.

$$T_m = \left[\frac{1}{T_i} - (R \ln X_i)/H_i\right] \qquad i = A, B \quad (2)$$

wherein T_m is the melting temperature of mixture, K, T_i is the melting temperature of the i-st substance, K, X_i is mole fraction of

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Table 1. Basic Calculation Parameters on Fatty Acids as PCMs

	BS (methyl stearate)	PA	MA	SA	LA	CA
melting point (°C)	19	58.9	52.2	69.1	42.4	31.6
latent heat of fusion ($J \cdot g^{-1}$)	140	189.6	182.6	201.8	186.4	152.6
molecular weight	340.57	256.42	228.37	284.48	200.32	172.27

Table 2. Comparison on Properties of the MA-PA Eutectic Mixture[a]

	MA-PA	melting temperature	latent heat
	wt %	°C	$J \cdot g^{-1}$
experimental data	58.0:42.0	42.6	169.7
calculated value	58.2:41.8	42.1	178.2
absolute error	0.2	0.5	0.3
relative error	0.3 %/0.5 %	1.2 %	5.0 %

[a] 0.3 %/0.5 %, 0.3 % is the computing result relative to 58.0, while 0.8 % is relative to 42.0.

the i-st substance, H_i is the latent heat of the i-st substance, $J \cdot mol^{-1}$, and R is gas constant, 8.315 $J \cdot mol^{-1} \cdot K^{-1}$.

On the basis of the calculation formula, the phase diagram can be plotted, and the eutectic point of the binary eutectic system can be determined. The formula on the latent heat of the multiplex eutectic system is as follows.

$$H_m = T_m \sum_{i=1}^{n} \left[\frac{X_i H_i}{T_i} + X_i (C_{PLi} - C_{PSi}) \ln \frac{T_m}{T_i} \right] \quad (3)$$

wherein H_m is the latent heat of the mixture, $J \cdot mol^{-1}$, C_{PLi} is the specific heat at constant pressure of the i-st substance at liquid state, and C_{PSi} is the specific heat at constant pressure of the i-st substance at solid state.

If the molecular weight of every component is big enough, the error of the formula for latent heat is rather small due to ignoring the sensible heat. As for the long-chain organic compounds, the error is less than 4 %.

$$H_m = T_m \sum_{i=1}^{n} \frac{X_i H_i}{T_i} \quad (4)$$

To verify the accuracy of the formula, its results have been compared with experiment data from ref 8. The literature investigated the eutectic mixture of MA and PA by experiment, including the proportion, melting temperature, and the latent heat. In the experiment, a General V4.1C DuPont 2000DSC instrument was used to measure the melting temperature and latent heat. Samples were measured in a sealed aluminum pan with a mass of 6.5 mg. The DSC thermal analyses were performed in the temperature range of (0 to 80) °C with a heating rate of 5 $°C \cdot min^{-1}$ and under a constant stream of nitrogen at atmospheric pressure. The molecular weight, melting temperature, and latent heat of MA are 228.37, 52.2 °C, and 182.6 $J \cdot g^{-1}$, respectively, and the corresponding parameters of PA are 256.42, 58.9 °C, and 189.6 $J \cdot g^{-1}$, respectively. Table 2 shows the comparison between the calculated result by formula 2 and 4 and experimental data.

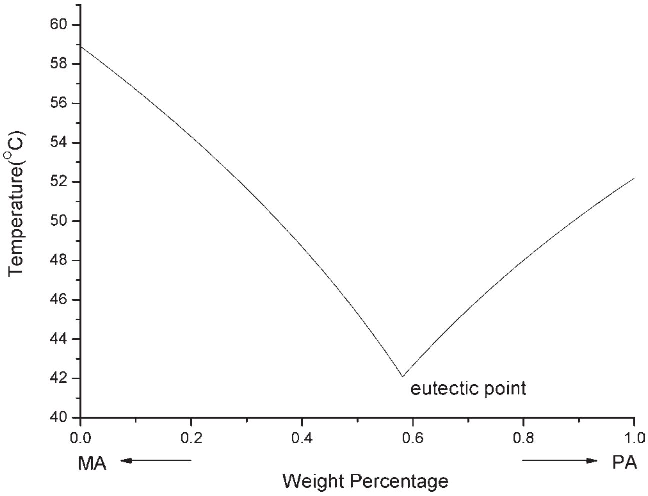

Figure 1. Calculation sketch of the ratio of MA-PA eutectic mixtures.

Table 3. Theoretical Value of the Ratio (wt %), Melting Point (°C), and Latent Heat of Eutectic Mixtures ($J \cdot g^{-1}$)[a]

	BS	PA	MA	SA	LA
PA	17.7/141.6				
	8.2/91.8				
MA	16.6/142.4	42.1/178.2			
	15.0/85.0	61.0/39.0			
SA	18.6/140.6	51.5/187.5	46.5/182.0		
	2.9/97.1	33.3/66.7	23.9/76.1		
LA	14.7/146.1	35.7/180.8	32.5/177.2	39.0/184.4	
	25.4/74.6	73.4/26.6	63.0/37.0	85.7/14.3	
CA	10.2/138.6	26.8/153.4	24.0/153.0	29.5/154.6	20.0/155.7
	45.6/54.4	84.8/15.2	76.8/23.2	92.9/7.1	66.3/33.7

[a] Take the first group data; for example, 17.7/141.6, 8.2/91.8 in the table denotes that the melting point, latent heat, and mole ratio of the PA-BS eutectic mixtures are 17.7 °C, 141.6 $J \cdot g^{-1}$, and 8.2:91.8, respectively.

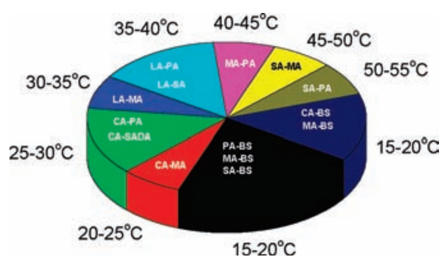

Figure 2. Distribution of melting temperature of the fatty acid eutectic mixtures.

Figure 1 is the calculation diagram of the proportion of MA-PA eutectic mixture, while Table 2 shows the comparison of properties of the MA-PA eutectic mixture. From Table 2, the calculated value is in good agreement with the experimental value; thus, the formula can be used to calculate the thermal properties of the fatty acid eutectic mixtures.

3.2. Calculation of Melting Temperature and Latent Heat. With Table 2, formula 2 and 4, the proportion, melting temperature,

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and latent heat of the fatty acid eutectic mixture were calculated and listed in Table 3.

Figure 2 shows the distribution of melting temperature of the fatty acid eutectic mixtures. It can be drawn a conclusion that, within the temperature range of (10.2 and 48.5) °C, there is at least one eutectic mixture at intervals of 5 °C, and among the 15 calculated fatty acid eutectic mixtures, the lowest latent heat is 138.6 $J \cdot g^{-1}$, while the highest is 185.5 $J \cdot g^{-1}$. In terms of practical application of PCMs, materials with the thermal properties are applicable to low temperature heating, hot water supply system, temperature-control concrete, and phase change clothing.

4. CONCLUSION

From the calculated results, the calculation is in good agreement with the previous experiment; thus, the formula can be used to calculate the thermal properties of the fatty acid eutectic mixtures.

Among the 15 calculated fatty acid eutectic mixtures, the lowest latent heat is 138.6 $J \cdot g^{-1}$, and the highest is 185.5 $J \cdot g^{-1}$. In terms of practical application of PCMs, fatty acid eutectic mixtures are applicable to low temperature heating, hot water supply system, temperature-control concrete, and phase change clothing.

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