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Evaluation of the Thermal Properties of Ternary Mixtures of Fatty Acids for Green Thermal Energy Storage Application

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In the present study, experimental and thermodynamic aspects of solid-liquid equilibrium were evaluated for ten ternary fatty acid mixtures formed by capric, undecylenic, pentadecylic, margaric, and stearic acids, as potential phase change materials (PCMs). The latent heat and melting temperature of ternary fatty acids mixtures were obtained from differential scanning calorimetry (DSC). Furthermore, the coefficients of the non-random two-liquid (NRTL) thermodynamic model were calculated using a quasi-binary mixing rule to correlate the liquidus line of solid-liquid equilibrium for the studied ternary mixtures. The comparison between the results of the proposed thermodynamic model and the experimental data showed average absolute deviations lower than 1%, validating the correlated thermodynamic model. The melting temperatures of the ternary mixtures of the studied fatty acids were in the range of 281-315 K, and their melting enthalpies ranged between 26.09 and 45.74 kJ mol^{-1}, indicating that the studied mixtures had good potential to be utilized as low-temperature thermal energy storage materials.

Keywords: Eutectic point, NRTL model, Phase change material, Ternary system

INTRODUCTION

Energy markets in the world are in a state of change, and the energy demand is increasing around the globe [1]. Over the past three decades, avoidance of energy waste has become necessary due to global energy shortage, higher prices, and concerns about environmental problems. Additionally, there has been an increased call for technologies to enhance energy storage and minimize the gap between energy generation and consumption [2,3]. Phase change materials (PCMs) are considered as one of the most practical materials for thermal energy storage (TES) [3-8]. The TES by PCMs has received increasing interest as a new technology for energy storage. The most efficient PCMs for TES application have high latent heat, low cost, moderate phase change temperature, non-flammability, non-toxicity, and a uniform phase change [9].

PCMs are suitable for applying innovative energy-efficient materials in the field of energy storage, which encompasses waste heat, waste cold, and solar power [10-12]. Regarding solar energy, there is an increasing demand for the use of thermal energy in daily life, including drying, building comfort, water heating, *etc*. The application of solar energy can reduce an enormous amount of energy use in the world. The only problem with solar energy is its alternative nature, which can be overcome by storing it in materials such as PCMs for later use [13].

Fatty acids and their eutectic mixtures have been regarded as desirable PCMs for low/medium energy storage purposes. Given that the pre-eutectic point occurs in the solid-liquid equilibrium of fatty acid mixtures, activity models should account for the behavior of both solid and liquid phases [14-17]. While some studies have focused on models which only predict eutectic points [18,19], other

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studies have presented an approach to predict pre-eutectic points [20]. Belgodere *et al.* [21] conducted experiments to calculate the phase diagrams for some ternary systems, which included light fatty acids, at 308.15 K and ambient pressure. Moreover, Shilei *et al.* [22] examined the eutectic mixture of capric acid (CA) and linoleic acid (LA) and its thermal stability by phase change sequences. Sari [23] studied the melting temperature of the binary eutectic mixtures of margaric acid (MA) and stearic acid (SA), LA and pentadecanoic acid (PA), and LA and MA. Some fatty acid binary mixtures were prepared, and their phase-transition properties were determined using the Schröder-Van Laar equation [24]. Furthermore, Feldman *et al.* [25] produced several mixtures of SA and PA with methyl, butyl, and propyl alcohols, and determined their phase transition temperature and heat storage capacity. Mirpoorian *et al.* [26] predicted the solid-liquid phase equilibrium of some fatty acid binary mixtures by the differential scanning calorimetry (DSC) method. They provided a thermodynamic approach in which melting temperatures were considered as a function of mole fraction in the equilibrium. Finally, Karaipekli and Sari [27] tested the thermal and chemical cycling (5000 cycles) cooling and heating process to determine the thermal reliability of the binary mixtures of PCMs, including capric acid, lauric acid, palmitic acid, and stearic acid, which were all used in the current study. The test results showed that all binary mixtures of PCMs had good chemical stability and thermal reliability.

It should be noted that the temperature of pure PCMs does not allow them to be used directly for many TES applications. In this study, the mixtures, especially ternary mixtures, were developed based on commonly and commercially used fatty acids (*i.e.*, CA, LA, PA, MA, and SA) and investigated with different weight ratio percentages. The phase transitions of the ternary mixtures of CA, undecyclic acid (UA), PA, MA, and SA were experimentally examined by the DSC method, and their melting enthalpies were calculated based on the DSC results [28, 29]. Then, the adjustable parameters of the non-random two-liquid (NRTL) activity model were determined considering the experimental results of the ternary mixtures and utilizing a newly developed mixing rule. The eutectic point compositions of the ternary fatty acid mixtures were theoretically calculated by the developed activity model, and the results supported the validity of the model.

MATERIALS AND METHODS

Materials

CA, UA, PA, MA, and SA, with a purity of over 98%, were supplied from Merck and used without further purifications. Table 1 summarizes the physical properties of the fatty acids used in the present study.

The melting temperature of binary mixtures was theoretically calculated using the formula developed by Yuan *et al.* [30]. In addition, the following equation was used to calculate the liquid phase line of the binary mixtures:

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

Table 1. Thermal Properties of the Studied Fatty Acids

Material	IUPAC name	CAS number	Chemical formula	Melting temperature (K)	Latent heat of fusion (kJ mol^{-1})
CA	Capric acid	334-48-5	$C_{10}H_{20}O_2$	304.8	27.79
UA	Undecylenic acid	112-38-9	$C_{11}H_{20}O_2$	295.9	25.98
PA	Pentadecylic acid	1002-84-2	$C_{15}H_{30}O_2$	325.7	41.53
MA	Margaric acid	506-12-7	$C_{17}H_{34}O_2$	334.2	51.33
SA	Stearic acid	57-11-4	$C_{18}H_{36}O_2$	342.7	61.21

For fatty acids, $G_{A,ex} = G_{B,ex} = 0$ [30]. Schröder equation for the melting temperature of a mixture is expressed as follows:

$$T_m = \frac{1}{\left[\frac{1}{T_i} - \frac{R \ln x_i}{H_i}\right]} \quad (2)$$

where T_m is the melting temperature of mixture (K), T_i is the melting temperature of i component (K), and R is gas constant (8.314 J mol^{-1} K^{-1}). In addition, x_i and H_i indicate the mole fraction and latent heat (J mol^{-1}) of the i component, respectively.

Regarding ternary mixtures, the pseudo-component of each binary mixture was blended in eutectic mass ratio. Then, it was mixed with the third component in various combination ratios to provide the pseudo-binary system of fatty acids. The melting temperature and latent heat of the binary systems at their eutectic points are presented in Table 2 [26].

Uncertainty Analysis

The uncertainty of temperature and enthalpy obtained by Mettler Toledo DSC1 were ±0.2 K and ±3%, respectively. The sample was weighed by an electronic balance of 4 digits. The weight of each sample was recorded 3 times, and the average value was used for experiments.

Methods

In the present study, ten ternary fatty acid mixtures, which included CA+UA+PA, CA+UA+MA, CA+UA+SA, CA+PA+MA, CA+PA+SA, CA+MA+SA, UA+PA+MA, UA+PA+SA, UA+MA+SA, and PA+MA+SA, were examined in the form of pseudo-binary mixture case studies. Gravimetric and ultrasonic methods were used to prepare and mix fatty acid samples, respectively. In addition, the thermal properties of the mixtures were measured using a Mettler Toledo DSC1 (Switzerland) in the temperature range of -5-50 °C, with a heating rate of 0.2 °C min^{-1}, and a continuous nitrogen flow of 50 ml min^{-1}.

Figure 1 displays DSC thermograms of the ternary fatty acid mixtures. The eutectic points were precisely determined for all ternary fatty acid mixtures, with only one long peak in DSC curves.

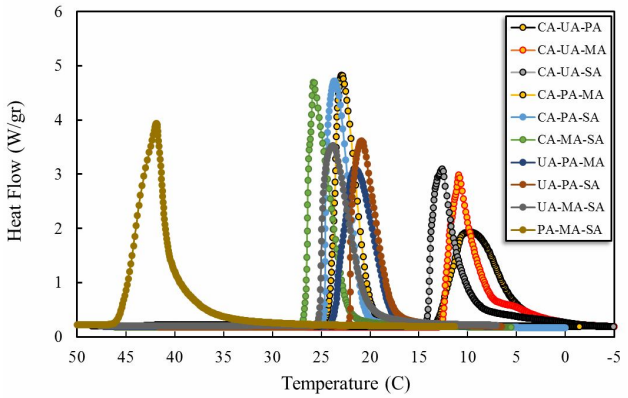


Fig. 1. DSC thermograms of the examined ternary mixtures.

THERMODYNAMIC MODEL

Based on the thermodynamic analysis, two regions of

Table 2. Thermal Properties of Binary Fatty Acid Systems [26]

Binary mixtures	Mass ratio	Eutectic temperature (K)	Latent heat (kJ mol^{-1})
CA-UA	0.457:0.543	284.7	25.04
CA-PA	0.764:0.236	297.5	30.29
CA-MA	0.869:0.131	300.9	30.53
UA-PA	0.794:0.206	295.0	27.92
UA-MA	0.889:0.111	298.2	27.91
PA-MA	0.643:0.357	316.5	43.30

solid-liquid equilibrium existed in *T*-*x* diagrams. Region I was related to a liquid line that began from $x_1 = 0$ up to the eutectic point, and Region II started from the eutectic point to $x_1 = 1$.

The equations for the solid-liquid phase equilibrium of the binary or pseudo-binary mixtures of fatty acids were as follows [31]:

Region I

$$T_m = \frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_2} - R\ln[(1-x_1)\gamma_2]} \tag{3}$$

Region II

$$T_m = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_1} - R\ln[x_1\gamma_1]} \tag{4}$$

where Δh_{fi} refers to the latent heat of fusion, and γ_i indicates the liquid-phase activity coefficient of i component. Additionally, T_i and T_m are the melting temperature of component i and mixture, respectively. In the above Eqs. (3) and (4)), the activity coefficient (γ_i) is a function of *T* and x_i. Thus, the temperature is an implicit parameter, which should be found by the iterative approach.

Latent Heat of Binary or Pseudo-Binary Mixtures

The following equation can be used to determine the latent heat of fusion for a binary mixture of fatty acids [32].

$$H_m = T_m \sum_{i=1}^{n}\left[\frac{x_i H_i}{T_i} + x_i (C_{PLi} - C_{PSi})\ln\frac{T_m}{T_i}\right] \tag{5}$$

where H_m is the latent heat of mixture (J mol^{-1}), and C_{PLi} and C_{Psi} are the specific heat at a constant pressure of component i in liquid and solid states, respectively. The second term of the equation (C_{PLi} - C_{PSi}) can be ignored in long-chain fatty acid compounds, resulting in the following equation:

$$H_m = T_m\left[\frac{x_1\Delta h_{f1}}{T_1} + \frac{(1-x_1)\Delta h_{f2}}{T_2}\right] \tag{6}$$

NRTL Model for Predicting Liquid Phase Activity

In binary systems, excess Gibbs free energy is calculated by the following equation presented by the NRTL [33].

$$\frac{g^E}{RT} = x_1 x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1 G_{12}}\right) \tag{7}$$

$$\tau_{21} = \frac{g_{21} - g_1}{RT} \tag{8}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{9}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{10}$$

where g^E is the molar excess Gibbs energy of the mixture (J mol^{-1}), g_{ij} is the energy parameter characteristic of the *i*,*j* interaction, and α_{ij} is the non-randomness parameter of the mixture, which is considered to be 0.3 for binary fatty acid mixtures[34,10].

The activity coefficients derived from the NRTL model were as follows:

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right] \tag{11}$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{12}$$

Furthermore, the melting temperature of two equilibrium regions was obtained by inserting Eqs. (11) and (12) into (3) and (4).

Region I

$$T_1 = \frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R\left[\ln(1-x_1) + x_1^2\left\{\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right\}\right]} \tag{13}$$

Region II

$$T_2 = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_{f1}} - R\left[\ln x_1 + x_2^2\left\{\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right\}\right]} \tag{14}$$

Then, eutectic point concentration (x_i) was determined by equalizing the melting temperatures of the above two regions.

$$\frac{\Delta h_{f2}}{\frac{\Delta h_{f2}}{T_{f2}} - R\left[\ln(1-x_1) + x_1^2\left\{\tau_{12}\left(\frac{G_{12}}{(1-x_1)+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+(1-x_1)G_{21})^2}\right\}\right]} = \frac{\Delta h_{f1}}{\frac{\Delta h_{f1}}{T_{f1}} - R\left[\ln x_1 + (1-x_1)^2\left\{\tau_{21}\left(\frac{G_{21}}{x_1+(1-x_1)G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{((1-x_1)+x_1G_{12})^2}\right\}\right]} \quad (15)$$

RESULTS AND DISCUSSION

The eutectic points and corresponding mixing equilibria of (CA+UA): PA, (CA+UA): MA, (CA+UA): SA, (CA+PA): MA, (CA+PA): SA, (CA+MA): SA, (UA+PA): MA, (UA+PA): SA, (UA+MA): SA, and (PA+MA): SA mixtures were obtained by applying the NRTL activity model to the pseudo-binary fatty acid system. Table 3 compares the experimental and theoretical results.

As shown in Table 2, the mass ratio in the eutectic point of the CA-CU binary mixture was obtained at 45.7:54.3. Accordingly, the experimental mass ratio in the eutectic point for a pseudo-binary system of CA-UA (first pseudo-single component) and PA (second component) was 90.0:10:0 (CA+UA: PA), which asserted that the mass ratio of CA:UA:PA was 41.1:48.9:10.0.

To ensure the accuracy of calculated eutectic points, ten ternary mixtures, including (CA+UA): PA, (CA+UA): MA, (CA+UA): SA, (CA+PA): MA, (CA+PA): SA, (CA+MA): SA, (UA+PA): MA, (UA+PA): SA, (UA+MA): SA, and (PA+MA): SA, were prepared with the same combination ratios obtained from theoretical calculations, and their eutectic temperatures were obtained by the DSC method. Based on the preceding analysis, the properties of ternary mixtures were similar to those of pseudo-binary ones. Thus, the NRTL activity model was considered suitable for the ternary (pseudo-binary) fatty acid system. The experimental results showed that the NRTL activity model could reliably estimate solid-liquid equilibrium phase transition. The constant parameters of the NRTL model that were obtained by curve fitting with the interpolation and extrapolation of experimental data are presented in Table 4.

Figures 2a to 2j, in which red markers illustrate experimental data and black curves indicate the NRTL model, depict the calculated melting temperature versus the mole fraction of the second component estimated by the NRTL model.

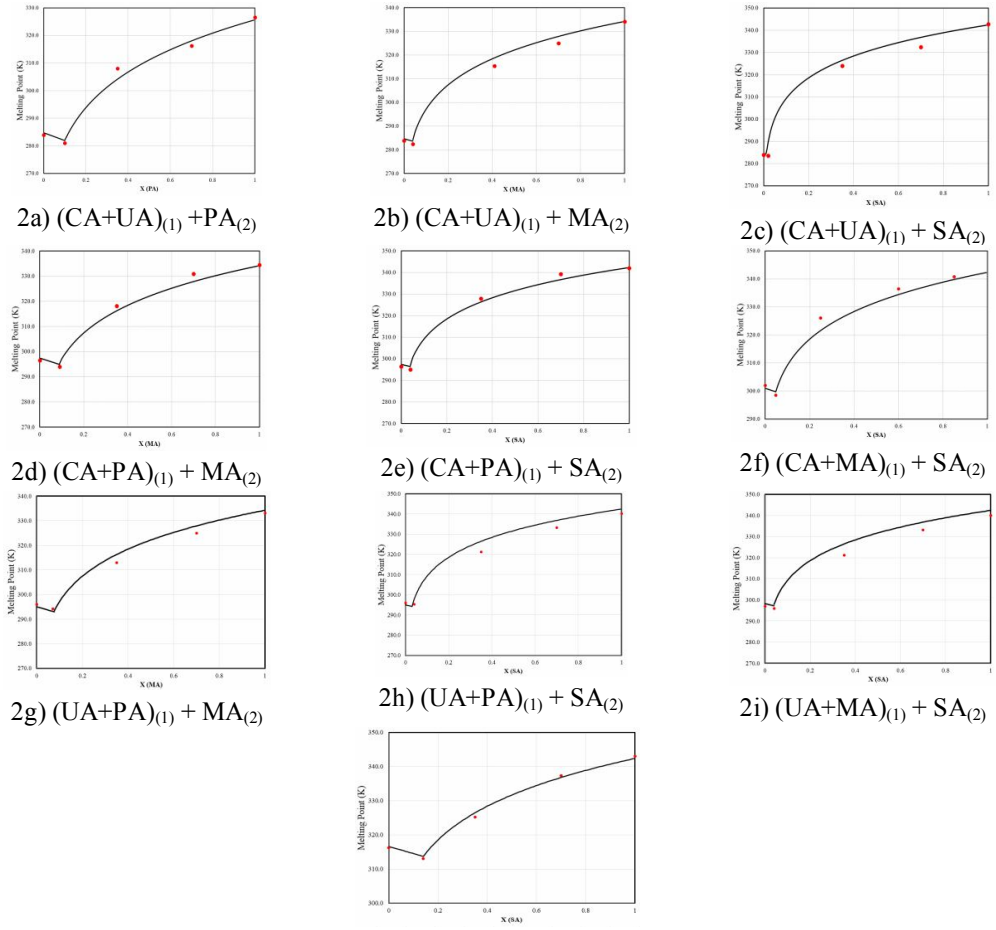
As demonstrated, the NRTL activity model estimated mole fractions at the eutectic point for all ternary mixtures using the same values, showing a good compromise for all ten case studies.

Table 3. Theoretical (Based on the NRTL Model) and Experimental Eutectic Points of Ternary Fatty Acid Systems

Pseudo-binary mixture	Pseudo-binary mass ratio (%)	Ternary mass ratio (%)	NRTL-based eutectic point (K)	Experimental eutectic point (K)	Eutectic latent heat (kJ mol^{-1})
(CA+UA): PA	90.0:10.0	41.1:48.9:10	281.5	281.0	26.65
(CA+UA): MA	96.3:3.7	44.0:52.3:3.7	282.9	282.4	26.09
(CA+UA): SA	98.0:2.0	44.8:53.2:2.0	284.3	283.5	26.36
(CA+PA): MA	91.4:8.6	69.8:21.7:8.6	294.9	294.0	28.75
(CA+PA): SA	95.5:0.045	72.9:22.9:4.5	296.2	295.1	27.81
(CA+MA): SA	94.3:5.7	82.0:12.4:5.7	299.2	298.5	31.30
(UA+PA): MA	92.6:7.4	73.9:18.7:7.4	293.8	295.3	29.57
(UA+PA): SA	96.2:3.8	76.8:19.4:3.8	293.9	296.2	28.77
(UA+MA): SA	95.3:4.7	85.2:10.1:4.7	297.1	298.5	28.93
(PA+MA): SA	84.5:15.5	54.8:29.7:15.5	312.7	315.1	45.74

Table 4. NRTL Adjustable Parameters of Ten Pseudo-Binary Fatty Acid Mixtures under Study

Pseudo-binary mixture	Eq. (13)		Eq. (14)	
	τ_{12}	τ_{21}	τ_{12}	τ_{21}
(CA+UA): PA	0.0278	-0.028	-0.0279	0.0277
(CA+UA): MA	0.0281	-0.0282	-0.0278	0.0279
(CA+UA): SA	0.0276	-0.0279	-0.0275	0.0274
(CA+ PA): MA	0.0281	-0.0282	-0.0278	0.0277
(CA+ PA): SA	0.0271	-0.0279	-0.0269	0.0268
(CA+MA): SA	0.0291	-0.0281	-0.0293	0.0283
(UA+ PA): MA	0.0279	-0.0283	-0.0291	0.0285
(UA+ PA): SA	0.0278	-0.0286	-0.0289	0.0281
(UA+ MA): SA	0.0288	-0.0279	-0.0283	0.0278
(PA+ MA): SA	0.0285	-0.0281	-0.0290	0.0275



2a) $(CA+UA)_{(1)}$ +$PA_{(2)}$ 2b) $(CA+UA)_{(1)}$ + $MA_{(2)}$ 2c) $(CA+UA)_{(1)}$ + $SA_{(2)}$

2d) $(CA+PA)_{(1)}$ + $MA_{(2)}$ 2e) $(CA+PA)_{(1)}$ + $SA_{(2)}$ 2f) $(CA+MA)_{(1)}$ + $SA_{(2)}$

2g) $(UA+PA)_{(1)}$ + $MA_{(2)}$ 2h) $(UA+PA)_{(1)}$ + $SA_{(2)}$ 2i) $(UA+MA)_{(1)}$ + $SA_{(2)}$

2j) $(PA+ MA)_{(1)}$ + $SA_{(2)}$

Fig. 2. Solid-liquid equilibrium diagram for pseudo-binary mixtures.

The average absolute relative deviations (AARD) of the melting temperatures of pseudo-binary mixtures obtained from the models with the experimental data were determined by the following equation:

$$AARD\% = \sum_{i=1}^{N} \frac{\left|T_{\exp,i} - T_{calc,i}\right|}{T_{\exp,i}} \Big/ N \times 100 \quad (16)$$

where N refers to the number of experimental data, and T_{exp} and T_{calc} are the experimental and calculated temperatures, respectively. The AARD% between the experimental melting temperatures for ten ternaries (pseudo-binary) mixtures and those calculated by the NRTL activity model is summarized in Table 5.

Table 5. The Deviation between the T-x Results Obtained by the NRTL Activity Model and Experimental Data

T_{exp} (K)	X	T_{calc} (K)	AARD%	T_{exp} (K)	X	T_{calc} (K)	AARD%
(CA: UA) + PA				(CA: UA) + MA			
283.9	0	284.5	0.21	283.9	0	284.5	0.21
281	0.1	281.5	0.18	282.4	0.04	282.9	0.18
308	0.35	305.2	0.91	315.4	0.41	308.6	2.16
316.2	0.7	318.1	0.60	325	0.7	319.7	1.63
326.5	1	325.6	0.28	334.2	1	334.5	0.09
Average AARD% = 0.43				Average AARD% = 0.85			
(CA: UA) + SA				(CA: PA) + MA			
283.9	0	284.5	0.21	296.5	0	297.2	0.24
283.5	0.02	284.3	0.28	294	0.09	294.9	0.31
324	0.35	326.5	0.77	318.2	0.35	316.3	0.60
332.5	0.7	336.8	1.29	331	0.7	327.9	0.94
342.8	1	342.4	0.12	334.5	1	334.1	0.12
Average AARD% = 0.54				Average AARD% = 0.44			
(CA: PA) + SA				(CA: MA) + SA			
296.5	0	297.2	0.24	302	0	300.4	0.53
295.1	0.04	296.2	0.37	298.5	0.05	299.2	0.23
328	0.35	326.5	0.46	326	0.25	321.5	1.38
339.3	0.7	336.8	0.74	336.4	0.6	334.6	0.54
342.1	1	342.4	0.09	340.8	0.85	342.3	0.44
Average AARD% = 0.38				Average AARD% = 0.62			
(UA: PA) + MA				(UA: PA) + SA			
296	0	295.1	0.30	296	0	295.1	0.30
294.2	0.075	293.8	0.14	295.3	0.03	293.9	0.47
313	0.35	316.3	1.05	321.2	0.35	326.5	1.65
325	0.7	327.6	0.80	333.2	0.7	336.8	1.08
333.2	1	334.4	0.36	340.1	1	342.3	0.65
Average AARD% = 0.53				Average AARD% = 0.83			
(UA: MA) + SA				(PA: MA) + SA			
297	0	298.2	0.40	316.2	0	316.5	0.09
296	0.04	297.1	0.37	313	0.14	312.7	0.10
321.2	0.35	326.5	1.65	325.2	0.35	326.5	0.40
333.2	0.7	337.3	1.23	337.4	0.7	337	0.12
340.1	1	342.3	0.65	343	1	342.3	0.20
Average AARD% = 0.86				Average AARD% = 0.18			

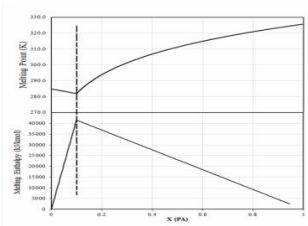
Based on the results in Table 5, the highest AARD% was obtained was 0.86%, which belonged to the ternary mixture of (UA:MA) + SA.

The study of eutectic mixtures requires the creation of the so-called Tammann diagram [32-34]. Therefore, eutectic mixture x_{eut} can be represented by the lever rule as follows:

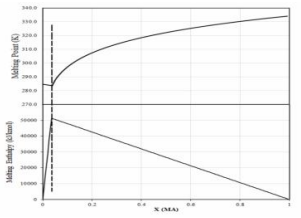
$$\text{For } x \leq x_{eut} x_{eut} = (x - 0)/x_{eut} \quad (17)$$

$$\text{For } x \geq x_{eut} x_{eut} = (1 - x)/(1 - x_{eut}) \quad (18)$$

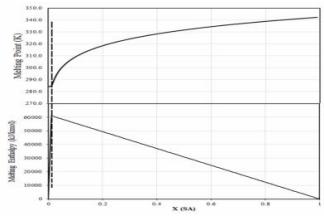
Figures 3a to 3j display the Tammann diagrams of the eutectic mixtures as a function of the third component mole fraction. The results showed that the mixtures were suitable for PCMs and that they could be used for energy storage applications.



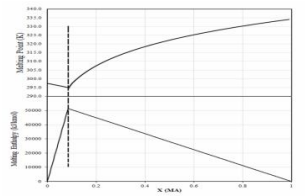
3a) $(CA+UA)_{(1)} + PA_{(2)}$



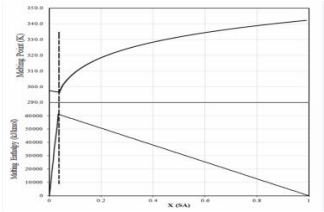
3b) $(CA+UA)_{(1)} + MA_{(2)}$



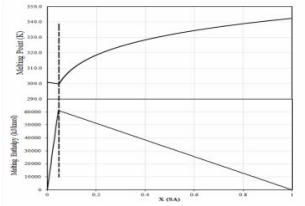
3c) $(CA+UA)_{(1)} + SA_{(2)}$



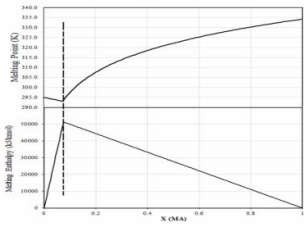
3d) $(CA+PA)_{(1)} + MA_{(2)}$



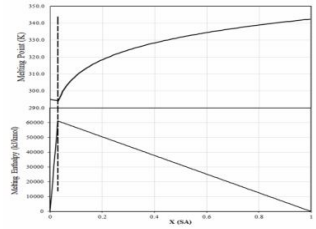
3e) $(CA+PA)_{(1)} + SA_{(2)}$



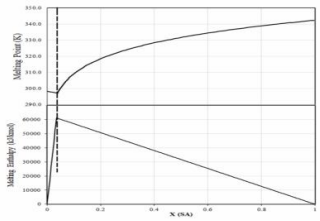
3f) $(CA+MA)_{(1)} + SA_{(2)}$



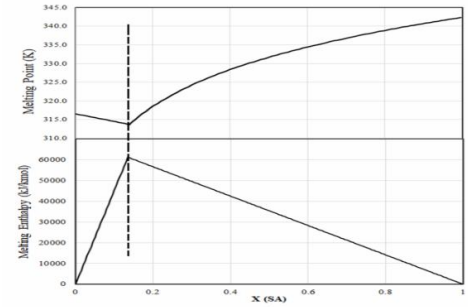
3g) $(UA+PA)_{(1)} + MA_{(2)}$



3h) $(UA+PA)_{(1)} + SA_{(2)}$



3j) $(UA+MA)_{(1)} + SA_{(2)}$



3j) $(PA+ MA)_{(1)} + SA_{(2)}$

Fig. 3. The Tammann plot of mixtures as a function of the third component mole fraction.

CONCLUSIONS

The present study examined the experimental and thermodynamic aspects of solid-liquid phase equilibrium for ten ternary fatty acid mixtures. Due to the high melting temperature of pure PCMs in TES applications, the binary and ternary mixtures of these materials were developed and investigated with different weight ratios percentages. Additionally, the phase transition of the ternary mixtures of CA, UA, PA, MA, and SA was experimentally assessed by the DSC method. The melting temperature of the eutectic point of the studied mixtures was as follows: (CA+UA): PA = 281.0, (CA+UA): MA = 282.4, (CA+UA): SA = 283.5, (CA+PA): MA = 294.0, (CA+PA): SA = 295.1, (CA+MA): SA = 298.5, (UA+PA): MA = 295.3, (UA+PA): SA = 296.2, (UA+MA): SA = 298.5, and (PA+MA): SA = 315.1. Also, the obtained curves were applied to estimate the melting and eutectic temperatures. The adjustable parameters of the NRTL activity model were determined considering the experimental results of the ternary mixtures applying a newly developed mixing rule. Furthermore, the eutectic points of ternary fatty acid mixtures were theoretically calculated by the derived activity models, which supported the validity of the model. It was found that the maximum (0.86%) and minimum (0.18%) deviation between the experimental and calculated melting temperature belonged to the (UA: MA) + SA and (PA: MA) + SA mixtures, respectively. Thus, it can be concluded that the NRTL equation can be utilized for the pseudo-binary fatty acid mixtures and that the method proposed for determining ternary eutectic points is reliable, viable, and efficient.

Nomenclature

T_m = Melting temperature of the mixture
T_i = Melting temperature of component i
R = gas constant
$G_{i,ex}$ = External Gibbs energy for component i
H_m = Latent heat of the mixture
x_i = Mole fraction of component i
H_i = Latent heat of component i
Δh_{fi} = Latent heat of fusion of component i
γ_i = Activity coefficient of component i
C_{PSi} = Specific heat at constant pressure for component iat solid-state
C_{PLi} = Specific heat at constant pressure for component i at liquid-state
g_{ij} = Energy parameter characteristic of the i,j interaction
α_{ij} = Non-randomness parameter
g^E = Excess Gibbs free energy
τ_{ij} = *NRTL* coefficient

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