

# Design and Development of Low Temperature Organic Eutectic PCMs

## 5.1 INTRODUCTION

The major portion of the energy production is disbursed for building heating and cooling applications for improving thermal comfort by curtailing the temperature variations [Henze, 2005; Wyse, 2011]. The use of space heating systems and air conditioners are major causes for electricity load variation in cold and hot climatic regions. Therefore, efficient heating and cooling methods based on renewable energies are required to lessen the energy and climatic snags. Renewable energy sources, such as solar, sea, geothermal and wind energies are intermittent and thus, prone to the energy demand and supply gap [Amar *et al.*, 2004]. The problem of intermittency, associated with such renewable energy sources can be reduced by integrating thermal energy storage systems (TESSs) with renewable energy production systems. The usage of TESSs in combination with renewable energy sources will also support in the augmentation of energy efficiencies of building heating and cooling systems [Hausmann *et al.* 2002; Mehling *et al.*, 2002].

The use of LHTESS is relatively beneficial over sensible heat thermal energy storage system (SHTESS) because of their large energy storage density and storage/liberation of heat at nearly constant temperature [Abhar, 1983; Lane, 1983; Lane, 1986; Dincer, 2002]. The phase change materials (PCMs) based TES devices are considered for their potential use in building floor, ceiling, and walls to augment thermal mass of buildings for comfort applications. Various reports have been published on Inorganic, organic and eutectic PCMs developed for such potential applications [Sharma *et al.*, 2009]. Inorganic PCMs such as hydrated salts offer high latent heat of fusion and high energy storage density as compared to the organic PCMs [Al-Abidi *et al.*, 2012]. However, these PCMs suffer from low thermal stability during charging and discharging cycles, large supercooling requirement, incongruent melting etc. [Zalba *et al.*, 2003; Mohamed *et al.*, 2017]. The thermophysical properties, such as long term thermal stability in conjunction with relatively good latent heat of fusion of organic fatty acids make them suitable candidates for above mentioned applications [Feldman *et al.*, 1986; Hasan *et al.*, 1994; Sari and Kaygusuz, 2003; Farid *et al.*, 2004; Inoue, 2004, Murat, 2004; Sari and Karaipeki, 2009; Sari *et al.* 2011a]. However, the melting temperature range of these fatty acids PCMs is relatively higher than the desired temperature range for practical solar thermal applications, especially for building comforts. In addition, these fatty acids also suffer from relatively low latent heat of fusion.

The eutectic compositions, which are specific compositions of two or more materials with different melting temperatures, at which material has sharp melting and solidification without any phase segregation, may provide the desired thermophysical properties for required applications [Mehling and Cabeza, 2008]. The melting temperature of eutectic mixture is the lowest in the entire composition range of mixtures of individual phase change materials. Thus, eutectic compositions of fatty acids may provide low melting temperature range PCMs and thus, making them suitable for building heating and cooling applications. Zhang *et al.*, 2001 investigated capric acid (CA) and lauric acid (LA) based eutectic mixture consisting 65 wt% CA and 35 wt% LA, showing 18 °C melting

temperature and 141 kJ kg<sup>-1</sup> latent heat of fusion. Kauranen *et al.*, 1991 and Peippo *et al.*, 1991 explored numerous fatty acids eutectic mixtures with melting temperature ranging from 10.2 to 18.5°C and latent of heat ranging from 138 to 185 kJ kg<sup>-1</sup> for TES applications. Other binary and ternary eutectic compositions have been reported by researchers across the globe for probable solar thermal applications [Feldman *et al.*, 1989; Cedeno, 2001; Baran and Sari, 2003; Sari, 2003; Rozanna *et al.*, 2004; Sari, 2005; Alkan, 2006; Akgun *et al.* 2007; Oret *et al.*, 2010; Yan, 2011; Zhang, 2013; Pielichowski and Pielichowski, 2014; Yuan, 2014; Kant *et al.* 2016].

There are other developments on different kinds of fatty acid such as esters via esterification of fatty acids using alcohols for enhanced phase change temperature and to reduce the bad odor problem of fatty acids [Feldman *et al.*; 1986; Saria *et al.*, 2009, 2011a & 2011b, Agafonova *et al.*, 2011; Costa *et al.*, 2012, Aydin, 2012 & 2013]. Sari *et al.*, 2009 produced butyl and isopropyl stearate based phase change materials for buildings related TES applications. The phase change temperature and latent heat of fusion of these PCMs are 23.67, 22.12 °C and 121, 113.1 kJ kg<sup>-1</sup> respectively.

The latent heat of fusion of fatty acids eutectic systems is relatively low, which leads to the poor thermal energy storage density. Thermal energy storage system with such materials will be quite bulky to compensate the low energy storage density. Thus, there is a need to design and develop PCMs with considerably higher latent heat of fusion, desired melting temperature ~ 20 °C, showing stability against thermal cycling, low supercooling, congruent melting, non-toxic and lower cost with ease of availability. Therefore, new eutectic compositions of LA, MA and PA fatty acids with 1-deodecanol are developed for low temperature solar thermal applications. In this work, the eutectic compositions based on these compounds are designed and their melting point and latent heat of fusion are computed. Further, experimental validation of computed results is carried out using DSC measurements. The designed eutectic systems exhibit reasonably higher latent heat of fusion and suitable melting temperatures in the desired for low temperature thermal energy storage applications such as building heating and cooling, cool clothings etc.

## 5.2 COMPUTATIONAL AND EXPERIMENTAL METHODS

### 5.2.1 Computational Details

New PCMs with preferred thermophysical properties can be developed by mixing two or more materials in particular ratios i.e. by designing their eutectics. The Gibbs excess energy approach can be used to model solid-liquid regions of mixtures of two or more materials [Smith and Ness, 1987]. If a homogeneous liquid system comprising two or more chemical substances at constant pressure P and does not form a solid solution, then correlation among solidified mole fraction of *i*<sup>th</sup> substance (A or B) during cooling and corresponding enthalpy change with their melting temperature can be defined as Eq. (5.1)

$$\ln(x_i^l \gamma_i^l) = \int_{T_{mi}}^{T_i} \frac{[\Delta H_i(T, P)]}{R \cdot T^2} \cdot dT \quad (5.1)$$

Here,  $x_i^l$  denotes the mole fraction of substance *i* in liquid phase;  $\gamma_i^l$  is the activity coefficient of substance *i* in liquid phase at temperature T and pressure P;  $\Delta H_i(T, P)$  is enthalpy change at temperature T and pressure P;  $T_{mi}$  represents the pure substance melting temperature;  $T_i$  is the system temperature and R is the ideal gas constant (8.315 J mol<sup>-1</sup> K<sup>-1</sup>).

If  $\Delta H_i(T, P)$  is temperature independent, the Eq. (5.1) will be converted to the Eq. (5.2) after integration

$$\ln(x_i^l \gamma_i^l) = \frac{\Delta H_i(T, P)}{R} \left( \frac{1}{T_{mi}} - \frac{1}{T_i} \right) \quad (5.2)$$

For ideal solutions,  $\gamma_i^l=1$  and Eq. (5.2) converts to

$$\ln x_i = \frac{\Delta H_i(T, P)}{R} \left( \frac{1}{T_{mi}} - \frac{1}{T_i} \right) \quad (5.3)$$

Eq. (5.3) is known as the Schroder-Van Laar Eq.. For liquid to solid phase change process,  $\Delta H_i(T, P)$  is known as molar enthalpy of fusion for  $i^{\text{th}}$  substance, at temperature T and pressure P [Smith and Ness, 1987]. The compositions for A and B substances at different liquidus temperatures can be computed using Eq. (5.3) and used to estimate eutectic compositions and corresponding temperature from the intersection point of the respective liquidus lines.

The enthalpy of fusion for a system comprising several constituents can be estimated using following Eq. (5.4)

$$H_m = T_{e,m} \sum_{i=1}^n \left[ \frac{x_i \Delta H_{i,m}}{T_{i,m}} + x_i \{C_{PLi} - C_{PSi}\} \ln \frac{T_{e,m}}{T_{i,m}} \right] \quad (5.4)$$

Here,  $C_{PLi}$  and  $C_{PSi}$  are specific heat capacity of solid and liquid phases at constant pressure for  $i^{\text{th}}$  constituent respectively.  $T_{e,m}$  and  $T_{i,m}$  are the melting temperatures of eutectic composition and pure  $i^{\text{th}}$  constituent respectively [Kumar *et al.*, 2016]. The estimated enthalpy of fusion for eutectic composition involves the contribution of solid and liquid specific heat capacities of the original constituents. As the organic molecules are relatively large and the difference between solid and liquid phase specific heats is very small as compared to the molar enthalpy, the contribution of liquid and solid specific heats in total enthalpy is not significant (and is less than 4%) as compared to molar enthalpy of fusion part [Diarce *et al.*, 2015]. Therefore, the second term containing specific heat contributions in Eq. (5.4) can be dropped and thus, enthalpy of fusion becomes

$$H_m = T_{m,e} \sum_{i=1}^n \left[ \frac{x_i \Delta H_{i,m}}{T_i} \right] \quad (5.5)$$

We utilized simplified Schroder-Van Laar model to compute solid-liquid phase diagrams for lauric acid (LA) - 1-dodecanol (DE), myristic acid (MA) - 1-dodecanol (DE), and Palmatic acid (PA) - 1-dodecanol (DE) binary systems. The computed phase diagrams are utilized to derive the eutectic composition and respective melting temperature. The latent heat of fusion is calculated using Eq. (5.5) for these binary eutectic mixtures.

### 5.2.2 Experimental Details

The LA (purity 98%), MA (purity 98%), PA (purity 95%) fatty acids and DE (purity 98%) are procured from Alfa Assar and utilized for experimental investigations without any further purification.

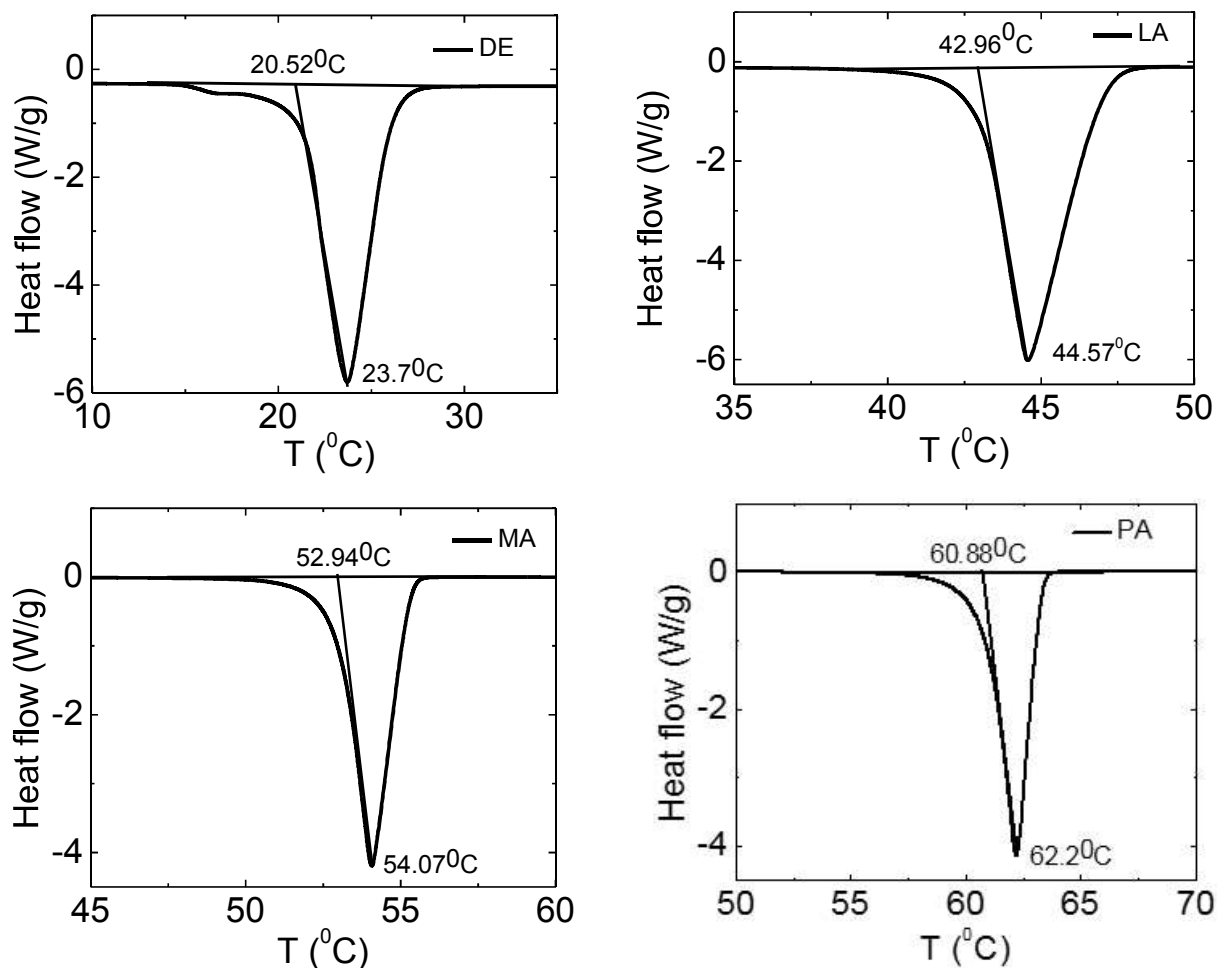
The LA, MA, PA and DE materials are used to prepare eutectic mixtures using the computed molar fractions of individual compounds. The thermal properties of these pristine materials and

eutectic mixtures are determined using differential scanning calorimeter (DSC), model Q10 (TA Instruments, USA make). The detailed procedure is explained in chapter 4 under section 4.4.2.2. The thermal conductivity of pristine and eutectic mixtures are investigated using TPS 2500S (Hot disk AB Sweden) thermal constant analyzer.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Differential Scanning Calorimetric Analysis of Pure Materials

DSC measurements are carried out to measure the latent heat and melting point of pristine fatty acids LA, MA, PA and DE samples. The melting profile of these pristine materials is presented as endothermic peaks in Figure 5.1. The melting point and latent heat of fusion are extracted from these DSC thermographs, using the methodology as explained in Chapter 3. The extracted melting point and latent heat of fusion with corresponding molecular weights values are tabulated in Table 5.1 for DE, LA, MA, and PA samples.



**Figure 5.1:** DSC thermographs of (a) 1-deodecanol, (b) lauric acid, (c) myristic acid, and (d) palmitic acid

**Table 5.1:** The melting point, latent heat and molecular weight of pristine 1-dodecanol, lauric acid, myristic acid and palmitic acid PCMs

<b>Name of sample</b>	<b>Melting point (°C)</b>	<b>Latent heat of fusion (kJ/kg)</b>	<b>Molecular weight (kg/mole)</b>
<i>1-Dodecanol</i>	20.52	191	186.334
<i>Lauric acid</i>	42.96	174.8	200.317
<i>Myristic acid</i>	52.94	184.8	228.37
<i>Palmitic acid</i>	60.88	199.1	256.42

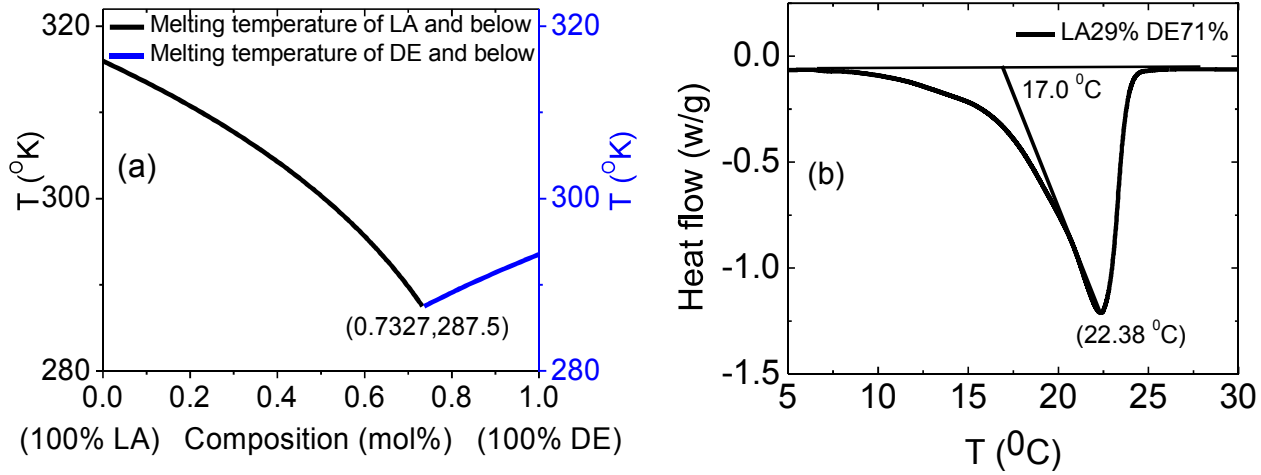
### 5.3.2 Development of 1-Dodecanol and Fatty Acids Binary Eutectic PCMs

#### 5.3.2.1 1-Dodecanol and Lauric Acid Eutectic PCM

Thermophysical properties of pristine 1-dodecanol and lauric acid, listed in Table 5.1, are used in simplified Schroder-Van Laar model, Eq. (5.2), to compute the temperature versus composition thermal phase diagram. The computed thermal phase diagram of DE-LE binary system is plotted in Figure 5.2(a). This diagram suggests that the LA liquidus temperature decreases with increasing mole fraction ratio of DE to LA. Similarly, the DE liquidus temperature also reduces with increasing LA mole fraction. The liquidus lines of LA and DE intersects each other at 73.27 mol% DE and 26.73 mol% LA. The equivalent mass fractions for DE and LA are 71.83 wt% and 28.17 wt%, respectively. The intersecting point represents the eutectic composition and the corresponding temperature 287.5 K (15.5°C) is the eutectic melting point for DE and LA binary eutectic system. The computed enthalpy, Eq. (5.3), is 183.02 kJ kg<sup>-1</sup> for DE and LA eutectic mixture.

The melting point and enthalpy of fusion for DE-LA binary eutectic mixture are also measured experimentally using DSC. The binary mixtures of DE and LA are prepared near computed eutectic composition by varying weight fraction of DE and LA. These binary samples are homogenized by heating under continuous 15 minutes magnetic stirring above melting temperature of pristine materials. The samples are cooled slowly to the ambient temperature after homogenization and the weight of individual sample was kept same (2g) for DSC measurements. The DE and LA eutectic composition DSC thermograph is shown in Figure 5.2 (b).

The experimentally determined weight fractions of DE and LA for eutectic system are ~ 71 and ~ 29 wt%, respectively, Figure 5.2 (b). The measured eutectic melting point and latent heat of fusion are 17 °C and 175.3 kJ kg<sup>-1</sup> for DE-LA binary eutectic system, Figure 5.2(b). The computed and experimental results are summarized in Table 5.2 for DE and LA system with their relative and absolute errors.



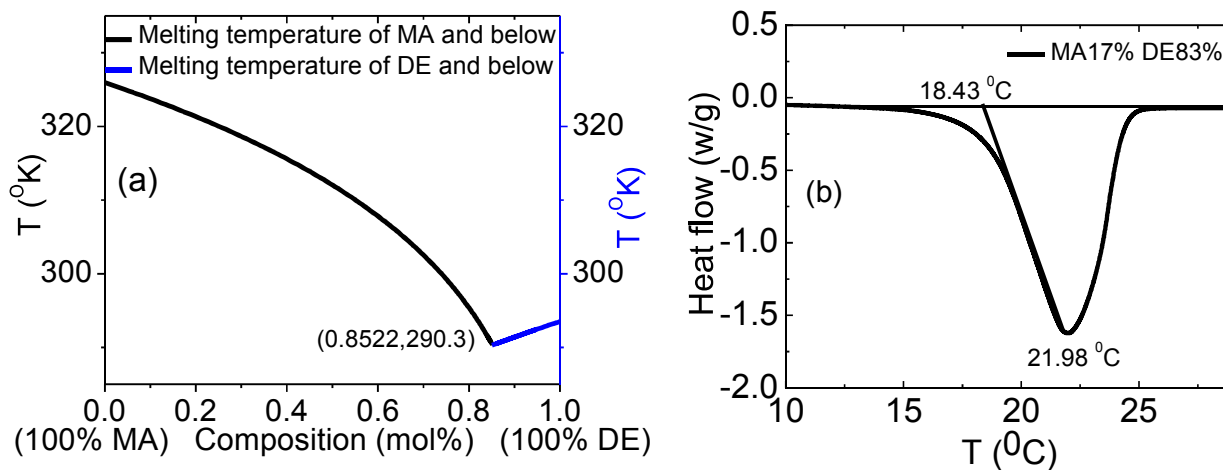
**Figure 5.2:** (a) Computed thermal phase diagram for 1-dodecanol and lauric acid binary system, and (b) DSC thermograph of 1-dodecanol and lauric acid binary eutectic system

**Table 5.2:** Comparison between computed and experimental results for DE-LA eutectic mixture

	<b>DE- LA composition (wt%)</b>	<b>Melting point (°C)</b>	<b>Latent heat of fusion (kJ.kg<sup>-1</sup>)</b>
Computed	71.83:28.17	15.5	183.02
Experimental	71:29	17.0	175.3
Absolute error	0.83	1.5	7.72
Relative error	1.17%/2.86%	8.82%	4.4%
#1.17%/2.86%, the 1.17% is relative to 71, whereas 2.86% computed error is relative to 29.			

### 5.3.2.2 1-Dodecanol and Myristic Acid Eutectic PCM

The MA liquidus temperature with different DE mol% and DE liquidus temperature with different MA mol% are computed by substituting MA and DE thermophysical properties, as listed in Table 5.1 in simplified Schroder-Van Laar Eq. (Eq. (5.2)), as described under section 5.2.1. The computed results are plotted in Figure 5.3(a), suggesting that the MA 14.78 mol% (17.53 wt%) and DE 85.22 mol% (82.47 wt%) form eutectic composition with 290.3 K (17.3 °C) melting point. The DSC measurements are carried out for binary systems containing different MA and DE wt% near computed eutectic composition to validate DE-MA eutectic compositions, eutectic melting point and latent heat of fusion. The measured DSC thermograph is plotted in Figure 5.3(b) for of DE and MA eutectic composition. The computed and experimental results for MA and DE eutectic mixture are summarized in Table 5.3 with relative and absolute errors and are in good agreement.



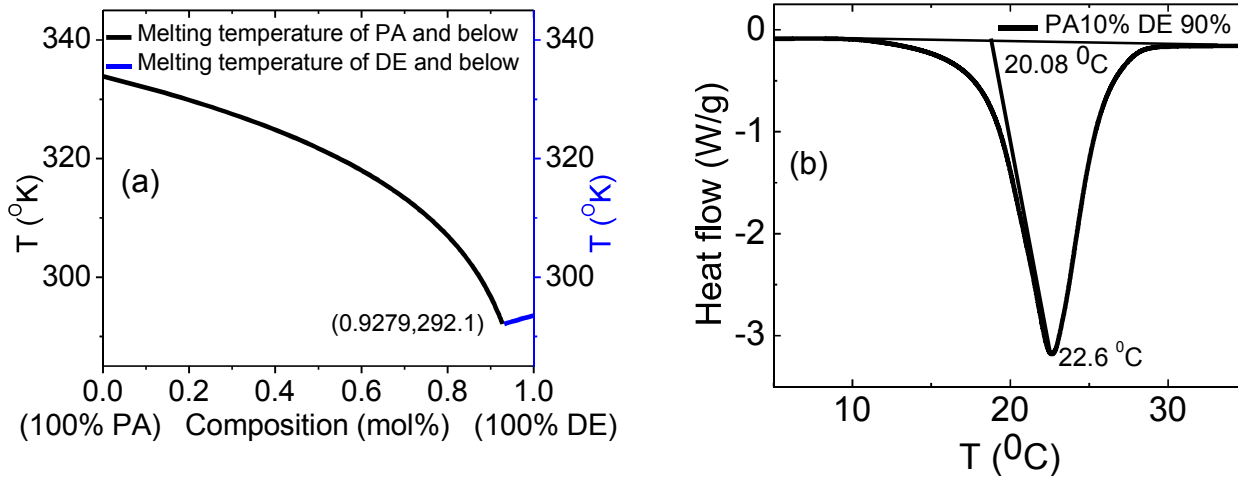
**Figure 5.3:** (a) Computed phase diagram for 1-dodecanol and myristic acid binary system and (b) DSC thermograph of eutectic composition of 1-dodecanol and myristic acid binary system

**Table 5.3:** Comparison on computed and experimental results for DE-MA eutectic mixture

	DE-MA composition (wt%)	Melting point ( $^{\circ}\text{C}$ )	Latent heat of fusion ( $\text{kJ kg}^{-1}$ )
Computed value	82.47:17.53	17.3	185.25
Experimental value	83:17	18.43	180.8
Absolute error	0.53	1.13	4.45
Relative error	0.64%/3.12%	6.13%	2.46%
#0.64%/3.12% , 0.64% is relative to 83, whereas the 3.12% computed error is relative to 17,			

### 5.3.2.3 1-Dodecanol and Palmitic Acid Eutectic PCM

The compositions, melting point and latent heat of fusion for DE and PA binary eutectic system were computed and validated experimentally using DSC with similar approach as described in earlier sections. The computed results are plotted in Figure 5.4(a). Figure 5.4(a) suggests that 92.79 mol% (90.34 wt%) DE and 7.21 mol% (9.66 wt%) PA form the eutectic composition with 292.1 K ( $19.1^{\circ}\text{C}$ ) melting temperature. The DSC measurements were carried out on different binary mixtures comprising different DE and PA mass fractions near the computed compositions to estimate eutectic composition of DE and PA experimentally. The measured DSC thermograph is shown in Figure 5.4(b) for DE and PA eutectic mixture. The computed and experimental results are summarized in Table 5.4 with relative and absolute errors. The measured and computed results are fairly in agreement.



**Figure 5.4:** (a) Computed phase diagram for 1-dodecanol and palmitic acid binary system, and (b) DSC thermograph of 1-dodecanol and palmitic acid eutectic mixture

**Table 5.4:** Comparison on computed and experimental results for DE-PA eutectic mixture

	<b>DE-PA composition (wt%)</b>	<b>Melting point (°C)</b>	<b>Latent heat of fusion (kJ kg<sup>-1</sup>)</b>
Computed value	90.34:9.66:	19.1	188.15
Experimental value	90:10	20.08	191.1
Absolute error	0.34	0.98	2.95
Relative error	0.38%/3.4%	4.88%	1.54%
#0.38%/3.4%, the 0.38% computed error is relative to 90, whereas 3.4% is relative to 10.			

#### 5.3.2.4 Analysis of Computational and Experimental Results

The computed thermophysical properties are listed in Tables 5.2 - 5.4 for DE-LA, DE-MA and DE-PA eutectic systems considering the ideal solution conditions. The experimental eutectic compositions are investigated for these binary eutectic systems using DSC measurements. The computed results for eutectic compositions are found in good agreement with the experimentally investigated compositions. The absolute and relative errors are summarized in respective Tables 5.2 - 5.4 for individually eutectic mixture. The maximum relative and absolute errors observed for eutectic compositions are 3.4% and 0.83 wt% respectively. The maximum observed relative and absolute errors for eutectic melting temperature and latent heat of fusion are 8.82%, 1.5 °C and 4.4%, 7.72 kJ kg<sup>-1</sup> respectively. Therefore, the activity coefficient of fatty acids and 1- dodecanol in liquid phase does not exhibit any significant contribution, while computing eutectic compositions and eutectic melting point for 1-dodecanol and fatty acids based eutectic mixtures. Similarly, the solid and liquid phase specific heat terms also do not affect significantly the latent heat of fusion results for these eutectic systems. Thus, simplified Schorder-Van Laar model can be applied for computing the eutectic compositions, their melting points and latent heat of fusion without any significant deviation from experimental results.

#### 5.3.2.5 Thermal Conductivity Measurements

Thermal conductivity of pure and 1- dodecanol-fatty acids based eutectic mixtures was investigated using Hot Disk AB, Sweden make TPS 2500S thermal constant analyzer system. The

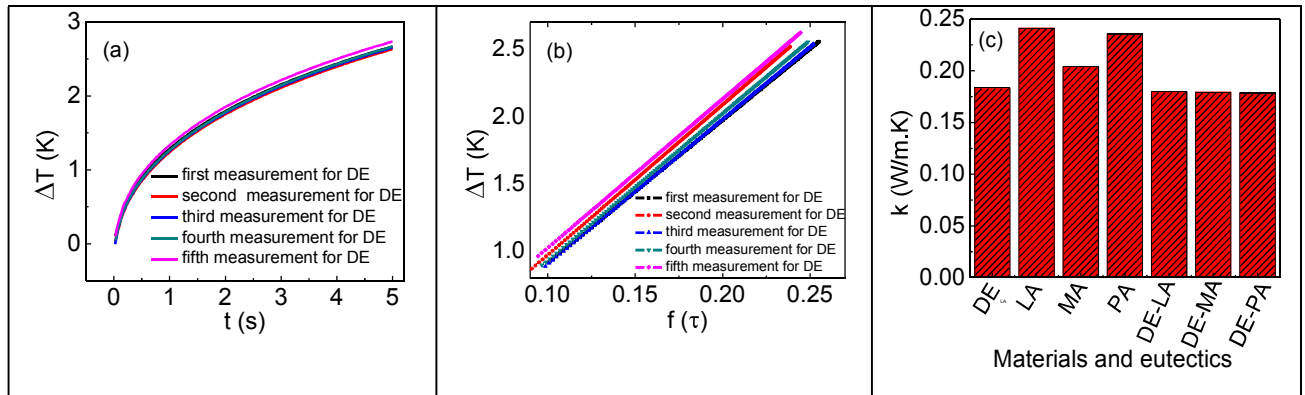


instrument works on transient plane source (TPS) technique, where plane sensor temperature variation is measured as a function of time [Gustafsson, 1991; Gustavsson *et al.*, 1994; He, 2005, Gustafsson, 2014; Harish *et al.*, 2015]. The Hot Disk sensor 7577 (radius  $\sim 2$  mm) was used to measure liquid samples thermal conductivity and sensor 5501 (radius  $\sim 6.4$  mm) was used to measure solid samples thermal conductivity. These sensors contain a thin double spiral Ni metal sensor, fixed between two thin insulating layers made of Kapton polyimide material for mechanical strength and electrical insulation while measuring thermal constants of conducting materials. The heat is delivered to the sample through resistive heating by passing electric current through the sensor and the average temperature as a function of time is measured by sensor itself simultaneously. The heat propagation rate inside the material depends on thermal conductivity of sample under investigation. It suggests that the selection of total measuring time and input power parameters relies on materials thermal conductivity and are key input factors for these measurements. Considering such restrictions, the total measurement time interval and input power were selected cautiously for both solid and liquid PCMs. The temperature variation as a function of time data were recorded for small time intervals and utilized further for estimating the materials' thermal conductivity. The temperature change against total measurement time for 1-dodecanol PCM is plotted in Figure 5.5(a). The measurements were repeated for five times to ensure the measurements reproducibility and are plotted in Figure 5.5(a).

The total measurement time used in temperature difference measurements are used to calculate dimensionless time function  $f(\tau)$ , which is defined as

$$f(\tau) = \frac{1}{(n(n+1))^2} \int_0^\tau \frac{d\sigma}{\sigma^2} \left[ \sum_{l=1}^n l \left\{ \sum_{p=1}^n p \cdot \exp\left(\frac{-(l^2 + p^2)}{2\sigma^2 n^2}\right) \cdot I_0\left(\frac{lp}{2\sigma^2 n^2}\right) \right\} \right] \quad (5.6)$$

Where  $n$  is total number of sensor spirals,  $I_0$  is a modified Bessel function and characteristic time ratio  $\tau = \sqrt{\alpha \cdot t}/r_s = \sqrt{t/\Theta}$ , characteristic time of measurement  $\Theta = r_s^2/\alpha$ ;  $\alpha$  is thermal diffusivity of the sample and  $t$  is total measurement of time for experiment. The measured temperature change is plotted against function  $f(\tau)$  in Figure 5.5(b).



**Figure 5.5:** (a) Temperature change Versus time response for liquid 1-dodecanol at ambient temperature 25°C (b) temperature change of Versus function  $f(\tau)$  for liquid 1-dodecanol corresponding to results  $\Delta T$  versus  $t$  and (c) average thermal conductivity of pristine fatty acids, 1-dodecanol and fatty acid/1-dodecanol eutectic PCMs

The increase in average temperature at the sensor surface, while passing a constant current through it is given as

$$\overline{\Delta T (t)} = \frac{P_0}{\pi^2 r_s k} f(\tau) \quad (5.7)$$

Here,  $P_0$  is the output power at the sensor,  $r_s$  sensor outer radius, and  $k$  is thermal conductivity of substance under investigation. This relationship suggests that the slope of  $\overline{\Delta T (t)}$  versus  $f(\tau)$  curve can be utilized for estimating the thermal conductivity of the materials of interest [Gustafsson, 1991; He, 2005]. The best straight line fits was used for estimation of the thermal conductivity of 1-dodecanol and the value is  $0.183 \pm 0.0033 \text{ W m}^{-1} \text{ K}^{-1}$ . The similar methodology was used to estimate thermal conductivity of other pure and eutectic compositions, where measurements were reiterated for five times to get the statistically averaged thermal conductivities and the results are summarized in Figure 5.5(c). The averaged thermal conductivity values with standard deviation are also listed in Table 5.5.

**Table 5.5:** Thermal conductivity of 1-dodecanol, lauric acid, myristic acid, palmitic acid and eutectic compositions with respective standard deviation at room temperature (25 °C)

Materials	Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> )	Standard Deviation	Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> )*
1-Dodecanol	0.183	3.309x10 <sup>-3</sup>	0.15
Lauric acid	0.241	4.1787 x10 <sup>-3</sup>	0.22
Myristic acid	0.203	1.0216x10 <sup>-3</sup>	0.15
Palmitic acid	0.235	7.6299 x10 <sup>-3</sup>	0.22
LA-DE eutectic	0.180	1.57558 x10 <sup>-3</sup>	NA
MA-DE eutectic	0.180	5.778 x10 <sup>-3</sup>	NA
PA-DE eutectic	0.180	1.0331 x10 <sup>-3</sup>	NA

\*Thermal conductivity from literature (Wang et al., 2010, Harish et al., 2015; Ince et. al., 2015)

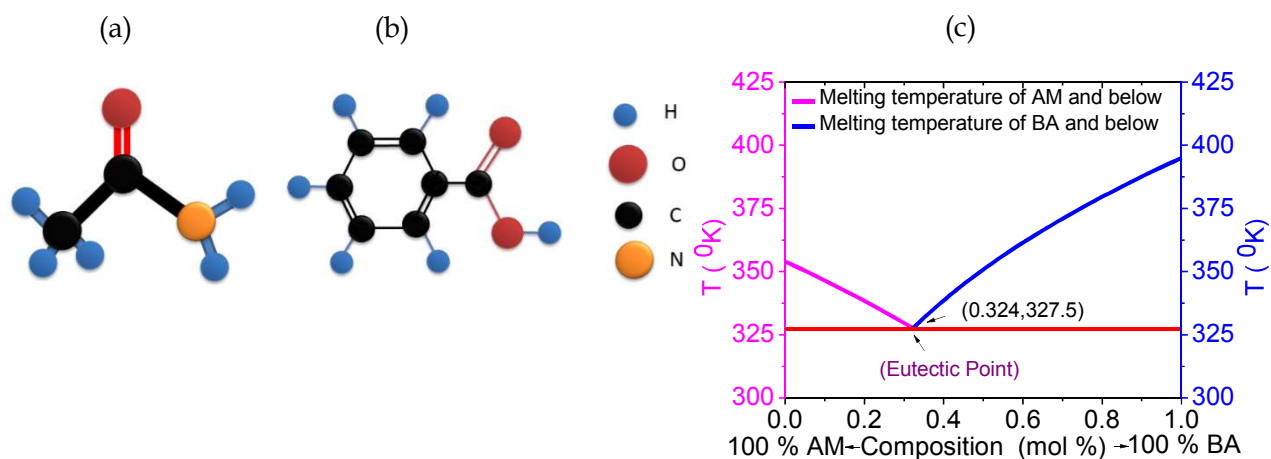
### 5.3.3 Benzoic Acid and Acetamide Binary Eutectic PCM

The optimal PCMs melting temperature range is 50 – 70 °C for their uses in thermal energy storage systems such as solar water heating system [Hasan et al., 1994]. This necessitates the development of suitable PCMs with melting point in this range and significantly higher latent heat of fusion. Considering the same, we considered acetamide and benzoic acid to design new eutectic PCM for such applications. Thermal properties of these materials are summarized in Table 5.6 [Rozanna et al., 2004].

**Table 5.6:** Melting point, latent heat of fusion and molecular weight of AM and BA substances

Sl. No.	PCM	Melting Temperature (°C)	Latent heat of fusion (kJ kg <sup>-1</sup> )	Molecular Weight (kg kmole <sup>-1</sup> )
1.	Acetamide	81	241.6	58
2.	Benzoic Acid	122	148.18	121

The demonstrative molecular structures of these organic materials are shown in Figure 5.6. The pure acetamide and benzoic acid materials are not appropriate for such application, due to relatively higher melting points. Therefore, eutectic mixture of these binary system was computed using Schorder-Van Laar model as explained above. The liquidus temperature of AM and BA were computed using same approach as explained in section 5.3. The computed thermal phase diagram is plotted in Figure 5.6 (c). The BA-AM and AM-BA liquidus curves intersect each other at 67.6 and 32.6 molar fraction of AM and BA, respectively. This unique AM and BA composition mixture forms eutectic mixture for these binary systems with 54.5 °C melting temperature, much lower as compared to AM and BA pristine compounds. The latent heat of fusion for this eutectic composition is calculated using Eq. (5.5) and is ~191 kJ kg<sup>-1</sup>. The lower melting temperature and relatively large latent heat make this eutectic very suitable for the said applications.



**Figure 5.6:** Molecular structure of (a) acetamide, (b) benzoic acid; and (c) thermal phase diagram of acetamide-benzoic acid binary system, with eutectic point

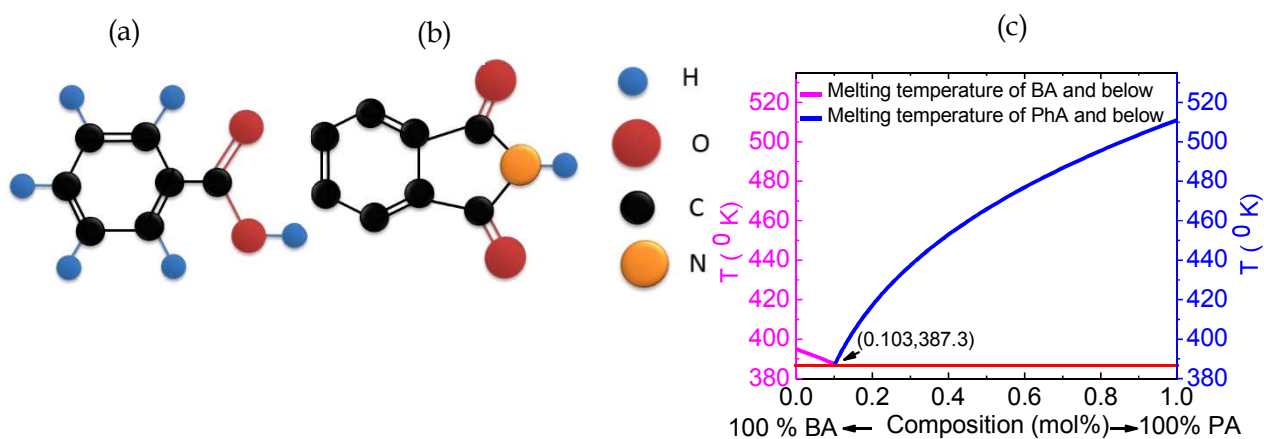
#### 5.3.4 Benzoic Acid and Phthalimide Binary Eutectic PCM

We also explored benzoic acid (BA) and phthalimide (PhA) binary system for solar cooking applications, where suggested optimal melting temperature range for PCM is 105 – 110 °C [Hausmann *et al.*, 2002]. The molecular structure of these organic compounds is shown in Fig 5.7 (a and b). These pristine organic compounds have higher melting temperature and their respective thermal properties are listed in Table 2 [Rozanna *et al.*, 2004].

**Table 5.7:** Melting point, latent heat of fusion and molecular weight of BA and PM system

Sl. No	PCM	Melting Point (°C)	Latent heat of Fusion (kJ.kg <sup>-1</sup> )	Molecular weight (kg. kmole <sup>-1</sup> )
1.	Benzoic Acid	122	148.18	121
2.	Phthalimide	238	206.66	147.12

The mixing of these organic compounds may possibly result into a suitable eutectic composition with desired melting temperature and heat of fusion. The PhA-BA and BA-PhA liquidus lines are calculated and are plotted in Figure 5.7 (c). The intersection point of these lines is at 114.3 °C, representing the eutectic point for this binary system. The molar composition of this eutectic point is 89.7 and 10.3 molar fraction of BA and PhA, respectively. The calculated latent heat of fusion for this eutectic composition is 146.5 kJ kg<sup>-1</sup>. These values of melting point and latent heat make it suitable for solar cooking application.



**Figure 5.7:** Molecular structure of (a) benzoic acid, (b) Phthalimide, and (c) thermal phase diagram of benzoic acid-phthalimide binary system, with eutectic point

## 5.4 CONCLUDING REMARKS

This chapter presents a simplified approach to design and develop organic eutectic phase change materials with desired melting temperature and latent heat of fusion for low temperature solar thermal applications. The eutectic systems based on 1-dodecanol and different fatty acids, benzoic acid and acetamide/phthalimide are investigated computationally. The experimental validation is carried out for 1-dodecanol-fatty acids eutectic mixtures and these experimental results are fairly in agreement with theoretical results. The thermal conductivity is measured for these newly developed eutectic phase change materials and values are relatively low  $\sim 0.2 \text{ Wm}^{-1}\text{K}^{-1}$ . The issue of thermal conductivity is discussed in Chapter 8.

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