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Binary and Ternary Mixtures of Eicosane with Fatty Alcohols and Fatty Acids as Phase Change Material for Building Applications.

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Abstract: Stable phase change materials (PCMS) of binary and ternary mixtures of organic compounds were prepared in this work to be installed in buildings for purposes of heat energy storage. Binary mixtures of PCMS as salt hydrates, paraffins were heavily investigated but most of the mixing was within the same group very few articles deal with mixing PCMS from different organic groups or mixing more than two materials. A preparation and a differential scanning calorimetry (DSC) investigation of binary and ternary mixtures of eicosane with fatty alcohols and fatty acids were performed. The eutectic mixtures of the binary systems were determined to be(70% eicosane – 30% cetyl alcohol) , (50% eicosane – 50% lauric acid) and (25% eicosane – 75% capric acid) with melting temperature and latent heat of (33.77 ºC , 237.6 J/g) , (30.63 ºC , 207.7 J/g) and (24.96 ºC , 200.3 J/g) respectively . The last one is very suitable for building applications. An eutectic mixture of eicosane with myristyl alcohol from previous work was considered as a new material and used to prepare two ternary mixtures(for the first time in literature) with both Cetyl Alcohol and Capric acid . An exciting results of temperatures were obtained : 26.86 ºC for the first ternary mixture and 16.23 ºC for the second one with moderate latent heats of 133.5 J/g and 157.7 J/g. The first one is very suitable for building applications and the second one is suitable for low thermal applications .These results will open the door to try ternary mixtures of common phase change materials to obtain various melting temperatures to suit different applications .

Keywords**:** *phase change material; differential scanning calorimetry; latent heat; eutectic mixture , ternary mixture*

1. INTRODUCTION

A phase change material (PCM) can benefit from solar and environmental energy during melting and solidification , this will occur by releasing heat during the process of melting and absorbing the same amount during solidification at the same temperature and this maintains a regulated temperature (Kürklü,1997) and makes PCMS play the role of heat stores (Pandy et al., 2018; Kenisarin and Mahkamov,2007; Sharma et al. , 2009 ; Sharma and Sagara, 2005,) and can be used in many exciting thermal applications (Wang X and TSO CY, 2017). A very common example of PCMS is pure water. But its 0°C melting temperature makes it unsuitable for most thermal applications .Organic and inorganic PCMs (paraffins, fatty acids, salt hydrates ,……) as main types have been heavily investigated to use across a wide range of melting temperatures . Each type has its own advantages and disadvantages (Abhat, 1983; Zalba et al. 2003; Kaygusuz,1999; Hasnain, 1998). Binary and eutectic mixtures of phase change materials (organic – organic , organic – inorganic , inorganic- inorganic) have been studied by scientists. Mixing a phase change material with another one is used by scientists to modify the melting temperature and in general this process will give a new melting temperature for the eutectic mixture smaller than both components. Feldman et al.(1989) studied the thermal properties of binary eutectic mixtures of fatty acids (capric, lauric, palmitic, stearic) and determined their melting temperatures and their latent heat. A novel binary eutectic mixture of two fatty acids : capric (CA) and myristic (MA) with expanded perlite (EP) is prepared by Karaipekli and Sarı (2008). Mixtures of fatty even saturated acids (caprylic , myristic ,capric , palmitic , lauric and stearic) were prepared in couples that differ by six carbon atoms and the eutectic mixture of each couple of fatty acids was determined by Mariana et.al. (2009) . Most of these studies deal with mixing two substances from the same type i.e mixing of fatty acids together or fatty alcohols or salt hydrates alone . Very few studies in literature investigated the mixing of two PCMs from different groups. Jarrar et al. (2016) studied binary mixtures of eicosane with myristyl alcohol and a 360 cycles of heating and cooling was applied on the eutectic mixture: 65% myristyl alcohol- 35% eicosane with nearly no significant changes on its melting temperature and latent heat .

Rathgeber et al (2013) prepared and characterized mixtures of fatty acids and alcohols with some alkanes, as phase change materials.Because of the chemical stability and good thermal properties of organic PCMS (Genovese et al. , 2006; Sarı , 2004) in comparison with salt hydrates as inorganic ones which showed significant changes in their thermal properties after conducting some cycles of heating and cooling ,while conducting nearly 1000 cycles for organic PCMS has shown small changes in thermal properties (Shukla et al., 2008)) and due to the very few studies on binary mixtures from different organic groups (Jarrar et al. ,2016; Rathgeber et al., 2013) and to the knowledge of authors there is only one study on ternary mixtures of fatty acids only (Kant et al., 2016) . So this research aims to investigate:

Firstly the thermal properties of binary mixtures:
- Eicosane - Cetyl Alcohol (L 16).
- Eicosane - Capric Acid (CA).
- Eicosane - Lauric Acid (LA).

Secondly the thermal properties of ternary mixtures of:
- Cetyl Alcohol (L 16) and an eutectic mixture of (eicosane + myristyl alcohol) from previous work (Jarrar et al. ,2016)
- Capric Acid (CA) and the same eutectic mixture of(eicosane + myristyl alcohol).

2.MATERIAL, METHODS AND DEVICES

2.1 MATERIALS

The used unmodified organic materials from Fisher Scientific (Suwanee, GA) are tabulated in table 1 with their chemical formula and molecular weight .

The main compound used in this research is eicosane which is an alkane with good thermal and chemical properties (high latent heat , little or no supercooling, thermal stability , chemically non-aggressive, non-toxic, non-corrosive) (Genovese et al. , 2006).

Table 1. LIST OF MATERIALS USED

Material	Chemical Formula	Molecular Weight (g/mol)
Eicosane	($C_{20}H_{42}$)	282.54
Myristyl Alcohol L14	($C_{14}H_{30}O$)	214.39
Cetyl Alcohol L16	($C_{16}H_{34}O$)	242.45
Capric Acid (CA)	($CH_3(CH_2)_8COOH$	172.26
Lauric Acid (LA)	$CH_3(CH_2)_{10}COOH$	200.32

Cetyl alcohol and myristyl alcohol are two straight-chain fatty alcohols, derived from natural fats and oils. While capric and lauric acids are two saturated fatty acids.

2.2 PREPARATION of BINARY and TERNARY MIXTURES

2.2.1 BINARY MIXTURE

The appropriate weights of chemicals of binary mixtures of: [Eicosane - Cetyl Alcohol L 16] , [Eicosane - Capric Acid CA] and [Eicosane - Lauric Acid LA] were mixed in a beaker and stirred by a magnet on a hot plate for 15 minutes to melt and to obtain a homogeneous mixture then cooled to room temperature.

2.2.2 TERNARY MIXTURE

The eutectic mixture of (65% myristyl alcohol-35% eicosane) which was determined and prepared in a previous study (Jarrar et al. ,2016) and has a 29.79 ºC melting temperature and 225.5 J/g latent height was considered as a new material and used to mix with cetyl alcohol and capric acid separately to obtain two ternary mixtures as described above.

2.3 DIFFERENTIAL SCANNING CAOLORIMETRY (DSC)

A DSC 200 as a thermal analysis instrument TA was used to obtain the thermal properties (i.e melting temperature and latent heat or heat of fusion) for all mono materials, binary and ternary mixtures of eicosane with other compounds . A small amount of (5-6) mg of the investigated sample is taken in a small sealed aluminum pan and a heat- cool-heat cycle is conducted at a rate of 10°C/min . The first heating to 80°C was to eliminate the heat history of the sample and then the sample is cooled to 0°C and heated again to 80°C .The curves obtained were analyzed to obtain the sample melting temperature from the intersection of the steepest tangent line drawn from the melt peak point with the temperature horizontal axis. The heat of fusion or the latent heat is obtained by calculating the area under the peak of melting.

3.RESULTS AND DISCUSSION

3.1 BINARY MIXTURE

Figure (1-3) represent a part of the heat-cool-heat scan (second heating) for cetyl alcohol L16 , capric acid CA and lauric acid LA .The melting temperatures (T_m) and the latent heat obtained experimentally for all above mentioned materials are tabulated in Table 2.

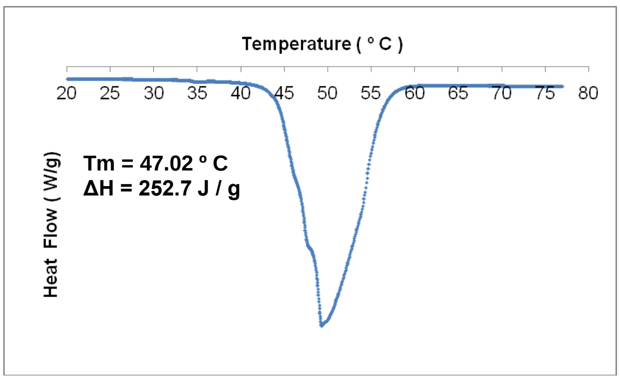

Figure 1. The DSC melting endothermic curve of cetyle alcohol (L16)

Where the melting temperature and latent heat of eicosane and myristyl alcohol are considered to be (35.67°C , 245.8 J/g), (34.97°C , 232.6 J/g) respectively according to (Jarrar et al. ,2016)

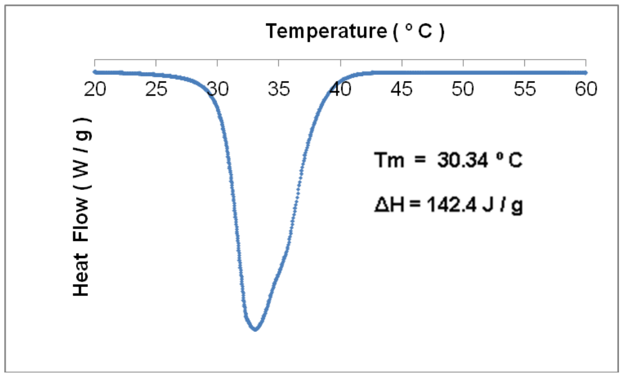

Figure 2. The DSC melting endothermic curve of capric acid.

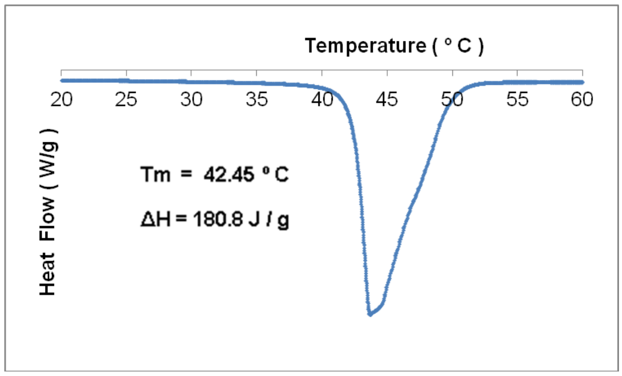

Figure 3. The DSC melting endothermic curve of lauric acid.

Table 2 . The melting temperatures (Tm) and the latent heat obtained from the second heating scans after cooling for materials used.

Substance	Melting Temperature ºC	Latent Heat ΔH (J/g)
Cetyl Alcohol	47.02	252.7
Capric Acid	30.34	142.4
Lauric Acid	42.45	180.8

The melting temperatures and the latent heat of the binary systems : [(Cetyl Alcohol L 16 - Eicosane) , (Capric Acid CA - Eicosane) and (Lauric Acid LA - Eicosane)] with different weight percentage of the components of each binary system were determined from the curves of (heat- cool- heat) as described before (tables 3-5) .By Applying the method of references (Shilei et al., 2006; Kauranen et al.,1991) the theoretical melting temperature for the eutectic mixture of each binary system in this work is calculated using Schroder's equation:

$$\ln X_M = (\Delta H_M/R)(1/T - 1/T_M)$$

Where

X_M : the fraction of moles of the main compound M of the mixture.

ΔH_M : latent heat for pure compound M in (J/mole).

T and T_M : the melting temperature values of the mixture and pure compound M (K), respectively

R : the gas constant (8.314 J. mole $^{-1}$.K^{-1}) .

Table 3. The melting* temperatures and latent heat of cetyl alcohol (L16) – eicosane binary systems measured by DSC analysis

Cetyl Alcohol – Eicosane (wt%)	T_m(ºC)	ΔH (J/g)
100 - 0	47.02	252.7
90 - 10	40.95	165.0
80 - 20	40.61	103.6
70 - 30	35.29	108.8
60 - 40	34.77	222.2
50- 50	33.33	241.9
40 - 60	33.38	237.8
30 - 70	33.77	237.6
25 - 75	33.85	237.6
20 - 80	33.58	225.0
15 - 85	33.93	241.0
10 - 90	32.85	218.7
0 - 100	35.67	245.8

Table 4. The melting temperatures and latent heat of capric acid – eicosane binary systems measured by DSC analysis.

Capric Acid – Eicosane (wt%)	T_m(ºC)	ΔH (J/g)
100 – 0	30.34	142.4
80 -20	24.4	172.7
75 – 25	24.96	200.3
70 – 30	24.73	193.1
65 – 35	25.34	186.4
50 – 50	24.86	210.3
30 – 70	24.57	236.7
0 - 100	35.67	245.8

Table 5. The melting temperatures and latent heat of lauric acid – eicosane binary systems measured by DSC analysis.

Lauric Acid – Eicosane (wt%)	T_m(ºC)	ΔH (J/g)
100 - 0	42.45	180.8
70 – 30	30.93	203.3
50 - 50	30.63	207.7
30 – 70	30.84	221.3
0 - 100	35.67	245.8

The latent heat, the experimental melting transition temperature and the calculated ones by Schroder's equation for the above mentioned binary mixtures with the weight percentage of each eutectic mixture are tabulated in Table 6.

Table 6. The weight percentage of, the experimental melting transition temperature and the calculated ones by Schroder's equation and latent heat for each eutectic mixture

Binary Eutectic Mixture	Weight Percentage	Experimental Melting Temperature (ºC)	Calculated Melting Temperature (ºC)	Latent Heat ΔH (J/g)	ΔT = │Texp– Tcal │ (ºC)
Cetyl Alcohol-Eicosane	30%- 70%	33.77	32.41	237.6	1.36
Capric Acid – Eicosane	75%- 25%	24.96	24.67	200.3	0.29
Lauric Acid –Eicosane	50%- 50%	30.63	30.64	207.7	0.01

Figures (4 - 6) represent the heat-cool-heat cycle for the eutectic mixtures of [(Cetyl Alcohol (L 16)-Eicosane) , (Capric Acid (CA)- Eicosane) and (Lauric Acid (LA)- Eicosane)] which were measured by DSC.

From Figures (4-6) we can notice that both components of each binary mixture melted simultaneously at constant temperature which was very close to the calculated one by Schroder's equation .

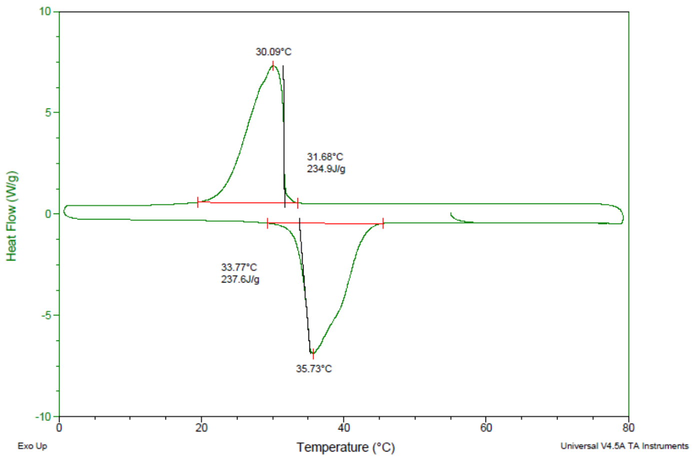

Figure 4. The DSC heat-cool-heat cycle for 30% cetyl alcohol – 70 % eicosane binary mixture.

Figure 5. The DSC heat-cool-heat cycle for 75% Capric Acid – 25 % eicosane binary mixture

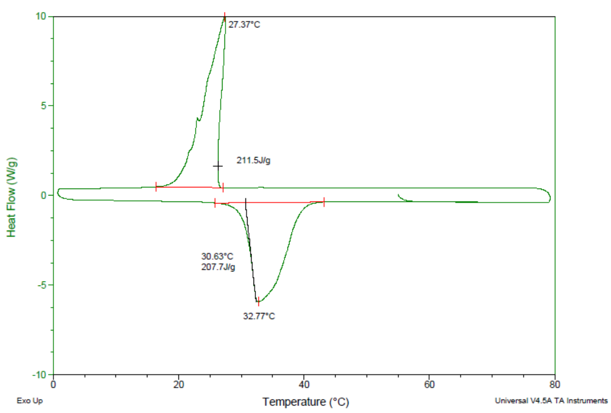

Figure 6. The DSC heat-cool-heat cycle for 50% Lauric Acid – 50 % eicosane binary mixture

The melting transition temperature was lowered for all binary mixtures including the eutectic ones as mentioned by other researchers (Feldman et al. 1989, Karaipekli and Sari 2008, Costa et al. 2009)), a moderate latent heat was obtained for each eutectic binary mixture , a little supercooling was observed in these binary mixtures .

The melting temperature of the binary mixture 75% Capric Acid – 25 % eicosane which was 24.96 ºC with 0.29 ºC deviation from the calculated one by Schroder's equation is very suitable for building and textile applications.

Ternary Mixtures

The eutectic binary mixture of (eicosane –myristyl alcohol) from previous study (Jarrar et al.,2016) and because of its good thermal properties : suitable melting temperature, no supercooling ,large latent heat and thermal reliability after 360 cycle of heating and cooling is used as a new material to mix with Cetyl Alcohol (L16) to prepare the first ternary mixture and Capric acid (CA) to prepare the second ternary mixture.

The melting endothermic curves of the above mentioned ternary mixtures are represented in Figure 7 and Figure 8.

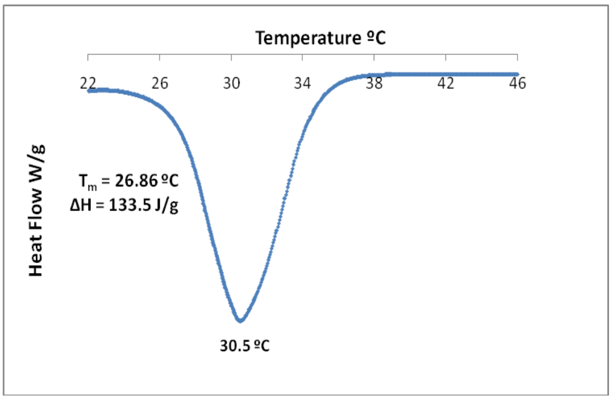

Figure 7. The melting endothermic curves of the first ternary mixture.

Ternary Mixture	Weight Percentage	Experimental Melting Temperature (ºC)	Latent Heat ΔH (J/g)
(Cetyl Alcohol L16) + (65% Myristyl Alcohol – 35% Eicosane)	10% +90%	26.86	133.5
(Capric Acid) + (65% Myristyl Alcohol –35% Eicosane)	50%+50%	16.23	157.7

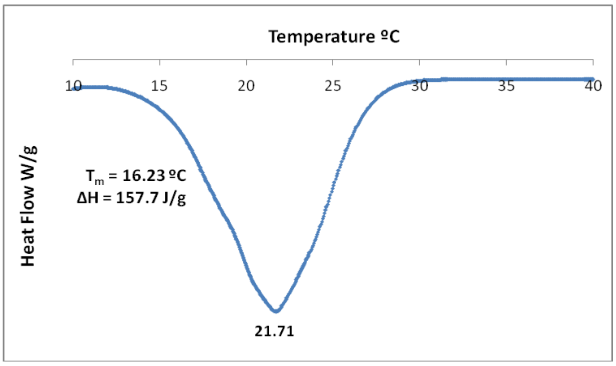

Figure 8. The melting endothermic curves of the second ternary mixture.

An exciting result is obtained for the melting temperature of the second ternary mixture of [50% (Capric Acid) + 50 % (65% Myristyl Alcohol –35% Eicosane)],

it was measured to be 16.23 ºC which was lowered very much by the mixing process this low melting temperature is suitable for thermal applications with low temperatures. The second ternary mixture of [10% (Cetyl Alcohol L16) + 90 % (65% Myristyl Alcohol –35% Eicosane)] with a melting temperature of 26.86 ºC is very suitable for building applications . The latent heat, the experimental melting transition temperature for the above mentioned ternary mixtures with the weight percentage are summarized in Table 7.

Table 7. The latent heat, the experimental melting transition temperature for the ternary mixtures with the weight percentage.

All components of each ternary mixture melted simultaneously at a constant temperature that given in Table 7 and by applying Schroder's equation to the above ternary mixtures and after considering the eutectic mixture of eicosane with myristyl alcohol as a new substance with constant melting transition temperature of 29.79 and with latent heat of 225.5 J/g, the calculated eutectic transition temperatures of ternary mixtures were 28.3 ºC and 17.86 ºC with a difference of 1.47 ºC and 1.64 ºC between experimental melting temperatures and calculated ones.

4. Conclusions

The melting temperature of an eutectic binary mixture of (75% Capric Acid – 25 % eicosane) was determined to be 24.96 ºC with latent heat of 200.3 J/g which is very suitable for building applications . Other exciting results were obtained for ternary mixtures. A low melting temperature of 16.23 ºC for the ternary mixture of [50% (Capric Acid) + 50 % (65% Myristyl Alcohol –35% Eicosane)] which is suitable for low thermal applications and the other one [10% (Cetyl Alcohol L16) + 90 % (65% Myristyl Alcohol –35% Eicosane)] of 26.86 melting temperature is very suitable for building applications. These mixtures were prepared from different organic groups and these results will open the door and encourage other researchers to try ternary mixtures of common phase change materials to obtain various melting temperatures to suit different applications .

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