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Eutectic Mixture of Myristyl Alcohol - Eicosane and the Thermal Reliability of this Binary System as Phase Change Material

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Abstract

Myristyl alcohol (L14), eicosane and their binary mixtures as phase change materials (PCM) were investigated by differential scanning calorimetry (DSC). The eutectic mixture was determined to be 65% L14- 35% eicosane with melting temperature 29.79 ºC and latent heat 225.5 J/g which makes it suitable for solar applications. A (0-360) cycles of heating and cooling (to approximate one year duration) were conducted to study the thermal reliability of the eutectic mixture . (DSC) analysis showed approximately constant melting temperature with fluctuation no more than (0.16 ºC) and the change in latent heat after 360 cycle of heating and cooling was less than (2.2%).

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

1. Introduction

Global warming as a result of increasing rates of CO_2 emissions from combustion of fossil fuels, in addition to the fact that all these fuels are going to diminish as a result of world great demand of energy make scientists working very hard to produce renewable sources of energy.

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Phase change materials PCM'S have been heavily studied by scientists in the last two decades as thermal energy storage [1-7]. PCM'S can benefit from solar energy that can be stored or released as latent heat for heating and cooling of buildings, warming greenhouses for agricultural crops, producing hot water for home uses[8].

Although paraffines have been widely investigated [9-11] as an organic PCM which have many good properties (chemical stability large latent heat, abundant supply,….) there were few articles concerning eicosane [12,13] which is an alkane hydrocarbon with high latent heat, narrow temperatures range of melting and crystallization, no or a little degree of supercooling in addition to chemical stability and non-toxicity. Myristyl alcohol which is classified as a saturated fattyalcohol and derived from natural fats and oils, with high molecular straight chain is a good candidate as PCM for its chemical stability and its large latent heat. A.Aydin and H. Okutan investigated myristyl alcohol: a fatty acid ester as phase change material for thermal energy storage [14] .Yamamoto and his colleagues .[15] studied the heating and cooling phase diagrams of a fatty alcohol binary system (*n*-heptadecanol/*n*-octadecanol) with detailed descriptions of the transitions. The solid – liquid phase diagrams of binary mixtures of fatty acids were investigated by many researchers [16-18] and they found that the melting temperatures of the binary systems are lower than those of the single acids. The phase behavior of mixtures of stearic acid and stearyl alcohol was studied by F. G. Gandolfo and his colleagues [19]. Thermal stability for a phase change material after many cycles of heating and cooling is very important for passive solar storage. Zhang and his colleagues [18] studied thermal properties of binary mixtures of lauric- palmatic acids after (0-100) cycles of heating-cooling and he found nearly constant behavior of phase transition of this system. 120,240 and 360 accelerated thermal cycle tests were conducted by Shilie and his colleagues [20] to study the changes in latent heat of fusion and melting temperature of phase change wallboards combined with the eutectic mixtures of capric acid (CA) and lauric acid (LA). The results showed that the melting temperature and latent heat of these phase change wallboards with eutectic mixtures have not obvious variations after repeated 360 thermal cycles. Eutectic mixtures of some fatty acids (lauric LA, stearic SA, myristic MA and palmitic acid (PA) were subjected to 360 repeated melt/freeze Cycles by Sari and his colleagues [16], and their thermal properties were measured after 0, 90,180 and 360 thermal cycles by the technique of DSC analysis and they showed good thermal reliability in terms of the change in their thermal properties with respect tothermal cycling. This work aims to investigate the thermal properties of binary mixtures of eicosane and myristyl alcohol to determine the eutectic mixture as well as the effect of thermal cycling on the latent heat of fusion and melting temperature of this system.

2. Experimental

2.1 Materials

Eicosane 99% ($C_{20}H_{42}$) with molecular weight of 282.54 and with density of (0.788) g/cm^3 and myristyl alcohol ($C_{14}H_{30}O$) with molecular weight of 214.39 and a density of 0.824 g/cm^3 were obtained from Fisher Scientific (Suwanee, GA) and used without modification .

2.2 Preparation of eicosane and myristyl alcohol binary mixtures

The appropriate weighs of eicosane and myristyl alcohol were placed in a glass tube and placed on a stirring hotplate from Fisher Scientific until the mix was melt, then the melt was stirred for 15 minutes on the hot plate by a small magnet to ensure good mixing of the two substances, after that the mixture was allowed to cool down to room temperature.

2.3 Differential Scanning Calorimetry (DSC)

The thermal properties of the binary mixture of eicosane and myristyl alcohol was determined by differential scanning calorimetry (DSC). The DSC measurements were performed using a TA instrument DSC 200 under nitrogen atmosphere with a sample purge flow 50 mL /min. (5-6) mg of the sample was used each time in a sealed aluminum pan to measure the melting temperature and latent heat capacity of the binary mixture. The samples were heated to 80°C at a rate of 10°C/min to eliminate the heat history. Then they were cooled to 0°C at a rate of 10°C/min and heated again at the same rate to the temperature 80°C. The melting temperature of the binary mixture was determined by the intersection of a tangent line drawn at the point of maximum slope of the leading edge of the peak (in the second heating) with the extrapolated base line and latent heat was taken as the numerical integration of area under the peak of melting.

3 Results and Discussion

3.1 Eutectic model

Figure (1) and figure (2) represent the melting endothermic curves of eicosane and myristyl alcohol obtained from the second heating scans after cooling. The melting temperatures (T_m) of eicosane and myristyl alcohol were 35.67 ºC, 34.97 ºC respectively and both materials had high latent heat compared to other PCM'S.

The solid-liquid phase transition of the binary systems obtained by mixing the above two materials were measured by DSC and the melting temperatures and latent heat of the investigated systems are tabulated in Table(1). From the Table we can notice that the melting temperature of the binary mixture was lower than its components and by using the data in the Table (1) and according to the method of references [20,21] an eutectic transition temperature of the mixture of eicosane and myristyl alcohol can be calculated by Schroder's equation:

$$ln x_A = -\frac{\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right) \qquad (1)$$

Where

x_A : the molar fraction of the main compound A of the mixture.

ΔH_A : latent heat of fusion for pure compound A (J/mole).

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

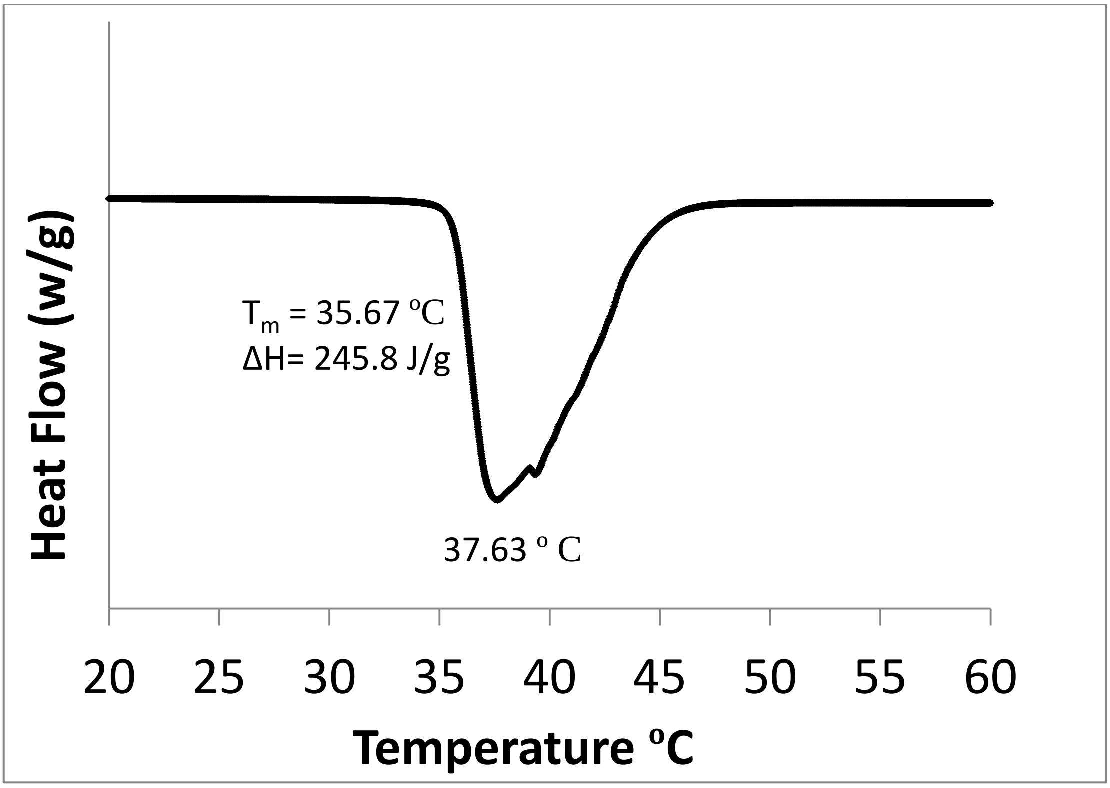

Figure 1: The DSC melting endothermic curve of eicosane

The latent heat of eicosane (ΔH) was 245.8 J/g and 232.6 J/g for myristyl alcohol.

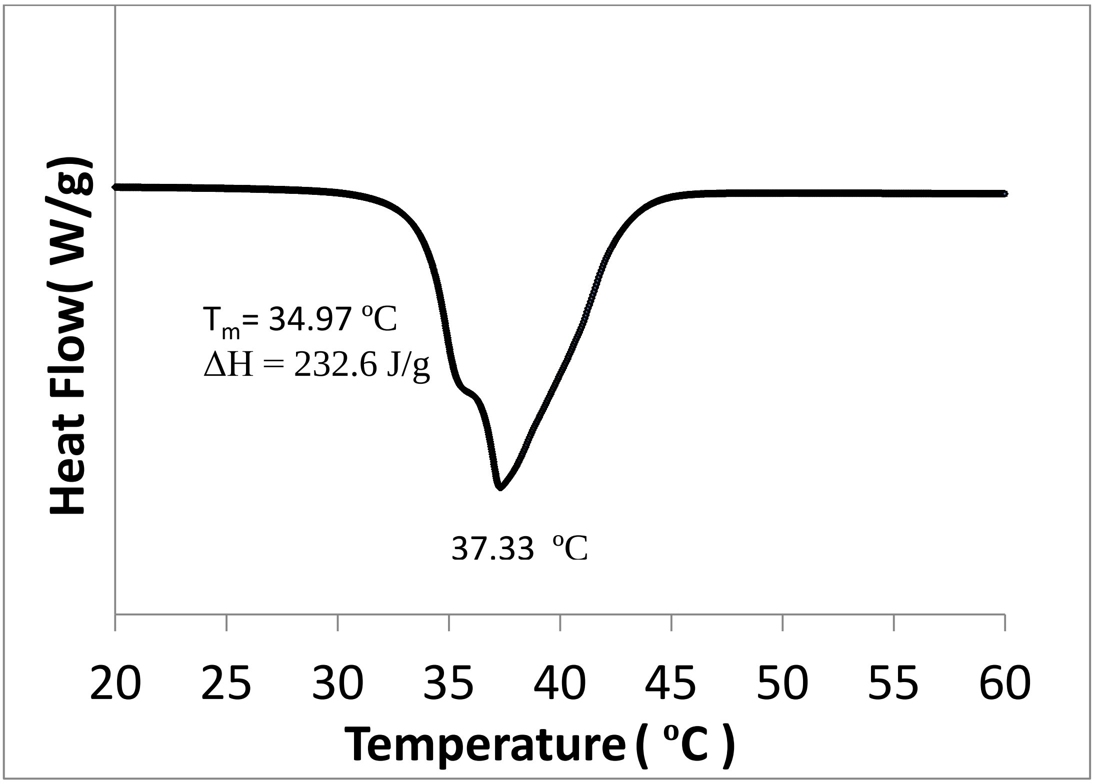

Figure 2: The DSC melting endothermic curve of myristyl alcohol (L14)

Table 1: The melting temperatures and latent heat of myristyl alcohol (L14) – eicosane binary systems measured by DSC analysis.

Sample myristyl alcohol – eicosane(wt%)	T_m(ºC)	ΔH (J/g)
0 - 100	35.67	245.8
10 - 90	34.24	267.2
20 - 80	33.43	250.2
25 - 75	30.36	248.4
30 - 70	30.43	246.2
35 - 65	30.58	248.8
40 - 60	30.49	242.8
45 - 55	30.51	242.1
50 - 50	30.52	228.5
55 - 45	30.44	241.0
60 - 40	30.07	224.4
65 - 35	29.79	225.5
70 - 30	29.80	211.6
75 - 25	29.85	226.1
80 - 20	29.99	214.7
90 - 10	31.91	216.0
100- 0	34.97	232.6

R : the gas constant which has the value of 8.314 J.mole $^{-1}$.K^{-1} .

The calculated eutectic transition temperature of mixtures of myristyl alcohol and eicosane was 29.64 ºC at a ratio of 65% myristyl alcohol to 35% eicosane and by DSC analysis(experimentally) and at the above ratio of myristyl alcohol to eicosane (65% : 35%) both components melted simultaneously at a constant temperature of 29.79ºC known as the eutectic transition temperature as shown in figure 3.

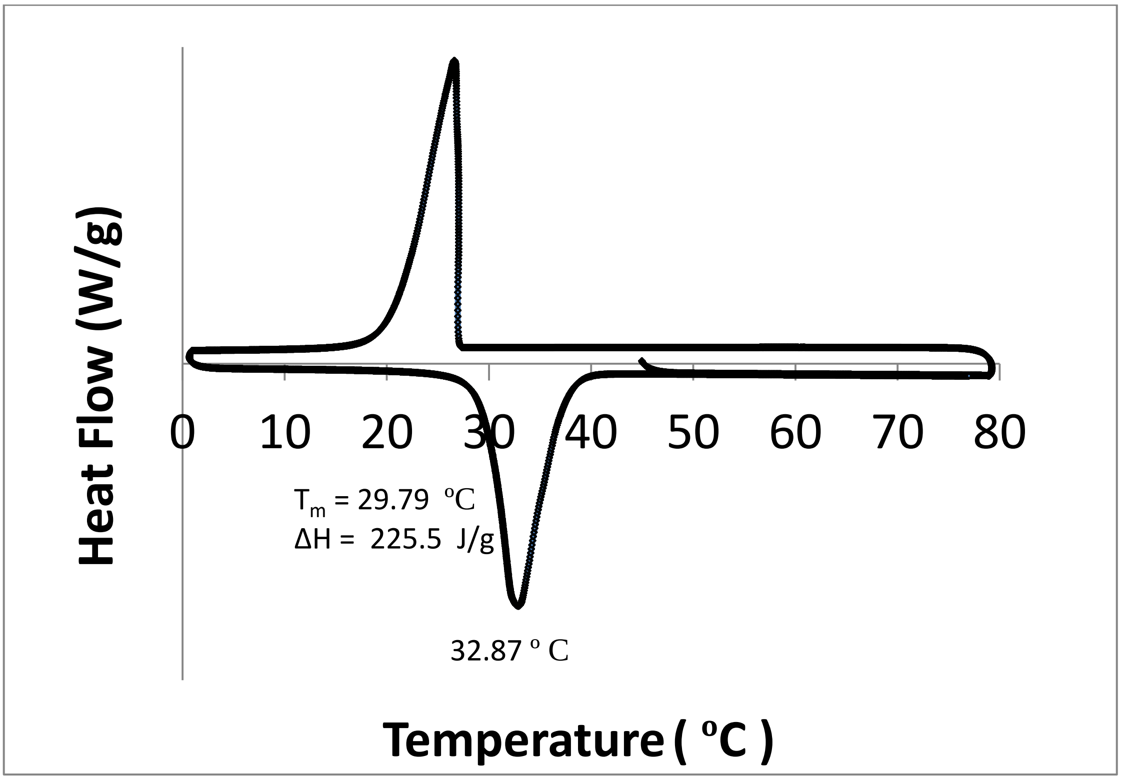

Figure 3: The DSC heat-cool-heat cycle for 65% myristyl alcohol - 35% eicosane binary mixture.

3.2 Supercooling of eutectic mixture

Figure 3 represents the heat-cool-heat cycle for 65% myristyl alcohol - 35% eicosane binary mixture. It is clear that the extrapolated temperatures of the beginning of the melting process and the beginning of the crystallization process approximately coincide which indicates that there is no supercooling in this system in addition to the high latent heat obtained by numerical integration of the area under the melting peak and the suitable melting temperature of the system which was lowered by the mixing process. All these factors make this binary system suitable for solar storage system.

3.3Thermal cycles test

The thermal properties of the eutectic binary mixture (65% L14- 35% eicosane) were determined after conducting cycles of heating and cooling and are summarized in Table (2). It can be seen from Table 2 that the maximum change in the melting temperature was (-0.23ºC) after 200 cycles and it was less than that for 40,80,280,360 cycles .These results indicate that the change in melting temperature is not increased with the increase of the number of cycles and even the maximum change was very small. The latent heat of this system and as it is shown in Table 3 was increased by 0.8% after 40 cycles and then decreased by 2.2% , 0.6% and 0.8% after 120,200 and 280 cycles respectively then a slight increase of 0.35% was detected after 360 cycles of heating. These results of melting temperature and latent heat of this binary eutectic mixture after 360 cycles of heating and cooling (nearly one year) and the negligible changes in these thermal properties indicate the good thermal stability and reliability of this system.

Table 2: The thermal properties of (65% L14- 35% eicosane) after conducting cycles of heating and cooling.

Cycle times (n)	T_m (ºC)	ΔH (J/g)
0	29.79	225.5
40	29.89	227.3
120	29.61	220.5
200	29.56	224.0
280	29.63	223.5
360	29.73	226.3

4. Conclusion

The high latent heat, the absence of super cooling and the moderate melting temperature of an eutectic binary mixture consisting of 65% by weight of myristyl alcohol and 35% of eicosane in addition to the negligible changes in these good thermal properties of this system after 360 cycles of heating and cooling (nearly one year) all these strongly nominate this binary mixture as good candidate of a phase change material suitable for solar storage applications.

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