3.014 MATERIALS LABORATORY
MODULE - γ1
September 18 – 22, 2006
GEETHA P. BERERA

THERMAL ENERGY STORAGE SYSTEMS – STEARIC / LAURIC ACID MIXTURES AS PHASE CHANGE MATERIALS

OBJECTIVES:

•   Prepare stearic acid and lauric acid mixtures of varying composition.

•   Measure the thermal characteristics **[Heat Capacity, Latent Heat of Fusion, and Melting Temperature]** of stearic / lauric acid mixtures using Differential Scanning Calorimetry.

•   Plot a graph of Melting Temperature vs. % Composition of acid components in the mixture. Such a plot illustrates the **Phase Diagram** for the acid mixture.

•   Identify the % composition of the acid mixture that yields the lowest melting temperature. This defines the **Eutectic Point** for the acid mixture.

•   Appreciate the practical application of these materials as thermal storage materials.

INTRODUCTION:

Thermal Energy Storage systems (TES) play an important role in energy conservation. They have the capacity to store energy which can be utilized at a later time.[1] For example, the solar energy can be stored for overnight heating, the summer heat stored for winter use, etc. Thus, these systems have potential applications in solar heating, water heating, air conditioning etc., and is regarded as an economical and safe energy storage technology. TES systems are attractive means for meeting the energy needs at all times.[2] For example, in solar applications, the Sun is available only during the daylight hours or when it is not cloudy, but the demand for energy usually arises at other times, such as at night. This disparity between the availability of energy source and the demand for energy, may be offset with the use of thermal storage materials.

Some of the physical properties that determine the thermal energy storage capacity of materials are:

(1)	The Specific Heat Capacity (C_p)

(2)	The Melting Point (T_m)

(3)	The Latent Heat of Fusion (ΔH_m or L_f)

In this experiment, the above listed thermal properties of fatty acids such as stearic acid, lauric acid, and their binary mixtures[3] will be experimentally determined from the Heat Flow vs. Temperature measurement, using Differential Scanning Calorimetry (DSC).

The TES systems may be classified into three types, (1) Sensible Heat Storage (2) Latent Heat Storage and (3) Thermochemical Storage. [1, 2]

SENSIBLE HEAT STORAGE: In the sensible heat storage, energy is stored by changing the temperature of a storage medium. The thermal property of material that is relevant here, is the **SPECIFIC HEAT CAPACITY** of the material. Examples of this type of storage material are, water, air, rock, sand or soil etc. Water, in particular is a favorable candidate because of its high specific heat(4.186 kJ/kg ˚C). Water is used in solar energy applications where solar energy is collected during the day to heat water which can store more energy than other materials without overheating. At night, the warm water may be circulated for home heating.

THERMOCHEMICAL STORAGE: This type of storage technique involves chemical reactions, typically reversible thermal decomposition reactions where the energy is stored in the products indefinitely at room temperature with no loss of heat capacity. When the energy is required, these products are recombined in a chemical reaction that is exothermic, i.e., releases energy. Examples of thermochemical storage materials are, NH_4HSO_4, $Ca(OH)_2$, $CaCO_3$ etc.

LATENT HEAT STORAGE: In this type of heat storage, energy is stored as latent heat in suitable substances during a phase change, usually, from a solid to a liquid phase at a desired temperature.[1,4] The energy that is absorbed during the melting (solid --> liquid) process is stored as "latent heat of fusion" and is released during the freezing (liquid ---> solid) process. Hence, these substances are also known as *PHASE CHANGE MATERIALS or HEAT-OF–FUSION* materials. Typical examples of such materials are: water/ice, organic compounds such as, paraffin, fatty acids, salt hydrates such as, Glauber Salt (Na_2SO_4. 10 H_2O), certain polymers etc. The thermal characteristics that are relevant here, are the **LATENT HEAT OF MELTING / FUSION**, and the **MELTING POINT** of the material. The latent heat storage materials have high energy storage capacities than sensible storage materials. [ice: 335 kJ/kg, Glauber salt: 250 kJ/Kg, paraffin wax 200 kJ/Kg, fatty acids > 180 kJ/kg][3,5]. The energy is delivered over a narrow temperature range making some of these materials attractive for smaller

and lighter storage devices with low storage losses. They can be easily integrated into building materials.[6] Other applications include astronaut space suits,[7] clothing, blankets, gloves, footwear, packaging materials etc.[7,8]

- PLEASE REFER TO THE HANDOUTS [1,4,6] FOR A LIST OF THE DESIRABLE PROPERTIES OF PHASE CHANGE MATERIALS RELEVANT TO ENERGY STORAGE]

MATERIALS:

Lauric acid [12-Carbon acid] $C_{11}H_{23}COOH$
Stearic acid [18-Carbon acid] $C_{17}H_{35}COOH$
Binary mixtures of the above acids, ranging from 10 – 90% by mass of lauric acid (time permitting)

These are hydrocarbon derivatives known as Fatty acids or Carboxylic acids with a general formula, R - COOH.
As the number of Carbon atoms in molecules of fatty acids increases, their melting point and fusion enthalpies [latent heats] gradually increase. [9]

SAMPLE PREPARATION:

ACIDS:
Lauric acid (99.5% **purity**) and Stearic acid (95% **purity**) from ALDRICH Chemicals with the following specification:

	LAURIC	STEARIC
Formula mass(g)	200.32	284.48
Density(g/cm^3)	0.883	0.845
Melting point(˚C)	44	69

ACID MIXTURES:

Prepare desired composition of acid mixtures as follows:
1. Weigh appropriate amounts of lauric acid and stearic acid of the desired composition to make 100 mg of the mixture.
2. Transfer the mixture into a vial and heat it on a hotplate to approximately, 100 ˚C until a homogenous solution is formed. Turn off the hotplate and cool the solution to room temperature.

Note:

1. Due to time constraints, deviation from controlled procedure is to be expected:
2. It may not be possible to measure the properties of the material prepared during the lab session. You may be provided with samples that are already prepared as above.

EXPERIMENTAL TECHNIQUE:

DIFFERENTIAL SCANNING CALORIMETRY [DSC] – TA INSTRUMENTS – MODEL Q10

- TA Instruments Q-series Manual on DSC[10]
- "Experimental Evaluation Of Procedures For Heat Capacity Measurements By Differential Scanning Calorimetry", K.L.RamKumar, M.K.Saxena, and S. B. Deb, Journal of Thermal Analysis and Calorimetry, vol. 66 (2001) 387-397]

DSC is a thermal analysis technique useful for measuring thermal and thermodynamic properties of materials such as, the specific heat, melting and boiling points, glass transitions in amorphous/semi-crystalline materials, heats of fusion, reaction kinetics etc. The technique measures the temperature and the heat flow (in desired units, mW, W/g etc.) corresponding to the thermal performance of materials, both as a function of time, and temperature.
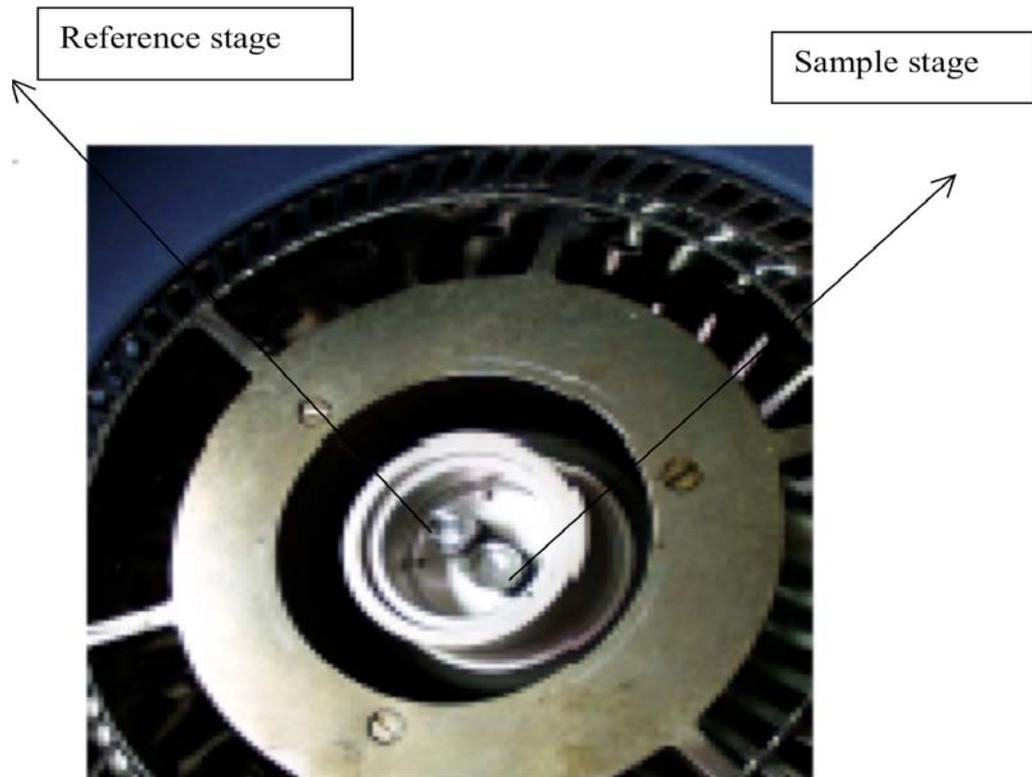
The TA Instruments DSC is a "HEAT FLUX" type system where the differential heat flux between a reference (e.g., sealed empty Aluminum pan) and a sample (encapsulated in a similar pan) is measured. The reference and the sample pans are placed on separate, but identical stages on a thermoelectric sensor platform surrounded by a furnace, as shown in figure 1. As the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric platform. The heat flow difference between the sample and the reference is then measured by measuring the temperature difference between them using thermocouples attached to the respective stages.

The DSC provides qualitative and quantitative information on endothermic / heat absorption (e.g., melting) and exothermic / heat releasing (e.g., solidification or fusion) processes of materials. These processes display sharp deviation from the steady state thermal profile, and exhibit peaks and valleys in a DSC thermogram (Heat flow vs. Temperature profile). The latent heat of melting or fusion can then be obtained from the area enclosed within the peak or valley, as shown in figure 2.

Some factors that may affect the DSC measurements are :
- Sample positioning on the DSC stage
  (variations in baseline)
- Structure and mass of the sample
  (proper thermal contact)
- Heating rate

(Trade-off between sample attaining thermal equilibrium and data acquisition times. A fast heating rate may minimize the data acquisition time compromising salient features of the material property)

Reference stage

Sample stage

Courtesy of TA Instruments. Used with permission.

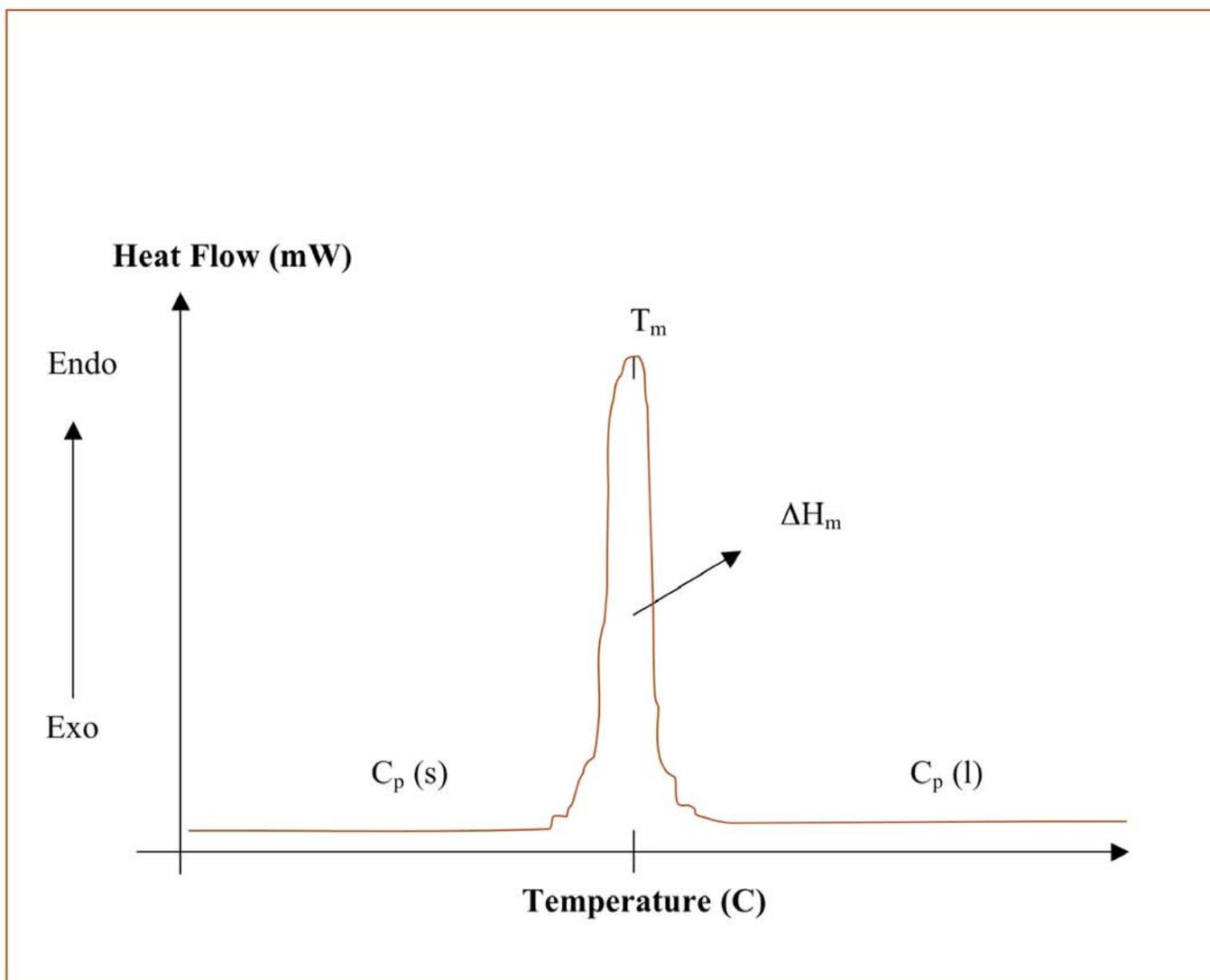Figure 1: The thermal stage in TA instruments DSC. [Figure adopted from TA Instruments Q-series Manual on DSC[10]]

Figure 2: Schematics of a DSC thermogram, where Cp defines the heat capacity in the solid and liquid phase, T_m the melting temperature, ΔH_m the enthalpy of melting or the latent heat of fusion. Note that heat absorbed is chosen positive (endothermic). [symbols as defined in 3.012 lecture notes]

SAMPLE PREPARATION FOR DIFFERENTIAL SCANNING CALORIMETRY [DSC] MEASUREMENTS:

Weigh 5 -10 mg of the acid / mixture samples prepared as above, and spread it uniformly in a NORMAL aluminum pan to ensure proper thermal contact. Crimp the pan with the lid.

EXPERIMENTAL PROCEDURE:

The guidelines for heat capacity measurements provided by TA Instruments (**see handout**)[10] will be followed.

These guidelines are based on ASTM Method, D3947 – 80. [11]
(with modifications* due to time constraints)

1.   Obtain a baseline (zero line) thermal profile (Heat Flow vs. Temperature) with empty, identical (equal mass) aluminum pans placed on the reference and the sample stages, respectively.

The aluminum pan on the reference pan must be **crimped**.
The pan on the sample stage is left uncrimped for later use.

The baseline scan corrects for any asymmetry in the system.

SCAN conditions:

* Set point temperature: 25 ˚C
  (temperature at which the sample is loaded)

* Mass of the sample:
  Input, 0 (ZERO) for the mass of the empty pan in baseline scan

* Scan Mode: RAMP

  Equilibrate at 10 ˚ C
  Heating rate: @ 10˚ C / min scan to 100˚ C

Note: Each scan takes approximately 15 minutes.

* Ideally, an independent baseline profile must be obtained for each sample using the same pan in which it will be placed to subtract the thermal effects of the container. However, in the present study, only one baseline scan will be performed for all

samples, assuming identical mass or volume for all the pans (select pans and lids of similar masses).
Leave the pan on the reference stage undisturbed for the remaining measurements.

2.   Obtain a thermal profile with a calibration standard (e.g. Sapphire) using the same scan conditions as in step 1.
Provides a calibration factor that translates the measured Heat Flow units (in mW) to Heat Capacity units (J/g˚C).

Place the crimped pan containing the calibration standard (sapphire, **mass = 25.68 mg**) on the sample stage.

3.   Obtain thermal profiles for the acid / mixture samples using same scan conditions as in steps 1 and 2.
Enter the weighed amount for each sample in mg (5.00 – 10.00 mg)

Place each crimped pan containing the weighed amounts of sample on the sample stage.

4.   Subtract the baseline data from the sample and the sapphire data, prior to analysis.
[Remember to change the Heat Flow (y-axis) units to mW, before subtracting the data, to ensure identical units for the sample and baseline profiles]

5.   Analyze the data as explained below.

ANALYSIS:

SPECIFIC HEAT:
[see hand out: Quantitative Analysis – TA Instruments] [10]

1.   Calculate the specific heat (C_p) of each sample (acid / mixture) @ 20 ˚ C (solid phase) and @ 80˚C (liquid phase).
Where possible, also include the C_p values @ 40˚C, and 60˚C

$$C_p \text{ (sample)} = \frac{C_p \text{ (sapphire) x m (sapphire) x H (sample)}}{H \text{ (sapphire) x m (sample)}} \qquad (1)$$

Where,

H is the heat flow (in mW) at a given temperature, obtained from the baseline subtracted plot of Heat Flow (mW) vs. Temperature for each sample, and for sapphire, m (mg) is the mass of each sample, and sapphire.

Note:

- Equation 1, is a ratio of the specific heat of the sample with respect to the sapphire standard.

$$\frac{C_p \text{ (sapphire) x m (sapphire)}}{H \text{ (sapphire)}}$$

  is a calibration factor.

- Estimate the C_p value for the sapphire standard at a desired temperature from the table of values provided in the hand-out [10], which translates the measured Heat Flow (in units of mW) to Heat Capacity units (J / g ˚C).

2. Plot a graph of C_p vs. %composition (0 – 100%) of Lauric acid at 20˚ C (solid phase) and at 80˚ C (liquid phase). Where possible, include values at 40 ˚C and 60 ˚C. Discuss these results.

MELTING POINT and LATENT HEAT OF FUSION:

1. Use the Universal Analysis software of the DSC and the peak integration routine to determine from the thermal profile, the latent heat of melting, and the melting temperature for each sample.

2. Plot a graph of **highest melting temperature** (when all components are in the liquid state) vs. percentage composition of lauric acid in the mixture. Such a plot illustrates the Phase Diagram for the Stearic /Lauric acid binary system.
    From the phase diagram thus generated, identify the **EUTECTIC POINT** and the **EUTECTIC MIXTURE COMPOSITION**.
    (The point on the graph yielding the lowest temperature defines the **EUTECTIC POINT**, where the acid components melt homogeneously) [6].
    [You will study phase diagrams and eutectics in 3.012 lectures later]

3. Tabulate the Latent Heat values as a function of % composition of Lauric acid in the mixture. Are these values in the expected range (literature values) for thermal storage applications?

4.   Based on the thermal profiles obtained, discuss the advantage of using an eutectic acid mixture in thermal storage application.

REFERENCES:

1.   "A perspective on thermal energy storage systems for solar energy applications", Ibrahim Dincer and Sadik Dost, International Journal of Energy Research, 20, 547-557 (1996) **[HANDOUT]**

2.   "The viability of thermal energy storage", Kamil Kaygusuz, Energy Sources, 21, 745-755 (1999)

3.   "Thermal Performance of a eutectic mixture of lauric and stearic acids as PCM encapsulated in the annulus of two concentric pipes", Ahmet Sari and Kamil Kaygusuz, Solar energy , vol. 72, #6, p 483-504 (2002)

4.   "Low temperature latent heat thermal energy storage: Heat storage materials", A. Abhat, Solar Energy , 30, 4, 313-332 (1983) **[HANDOUT]**

5.   "Thermal energy storage system using stearic acid as a phase change material", Ahmet Sari and Kamil Kaygusuz, Solar energy , vol. 71, #6, p 365-376 (2000)

6.   "An organic PCM storage system with adjustable melting temperature", P. Kauranen, K. Peippo, and P. D. Lund, Solar Energy, vol. 46, No. 5, P. 275-278 (1991). **[HANDOUT]**

7.   Webarchive: NASA, Scientific and Technical Information (STI), SPINOFF 2004. (accessed, September 18, 2006)

8.   http://www.microteklabs.com/, accessed September 18, 2006

9.   "Thermal studies on the solid-liquid phase transition in binary systems of fatty acids"
Jian-Jun Zhang, Jian-Ling Zhang, Shu-Mei He, Ke-Zhong Wu, Xiao-Di Liu
Thermochimica Acta, 369, 157-160 (2001)

10.   "Guidelines for Quantitative Studies – Heat Capacity Experiments"
TA Instruments Manual DSC 2920, 4-15 – **[HANDOUT]**

11.   D3947- 80. Annual Book of ASTM Standards, Part 25, ASTM, Philadelphia, PA (1980)