3.014 MATERIALS LABORATORY
MODULE Beta 3
December 9 – 14, 2005

Eutectic Determination of a Binary Mixture of Rubrene / 5,12- DiPhenylanthracene

OBJECTIVES:

- Prepare rubrene (5,6,11,12 – tetraphenylnaphthacene) and 5,12-diphenylanthracene mixture of varying composition.

- Obtain a thermogram (Heat – Temperature profile) of mixtures using Differential Scanning Calorimetry.

- Generate a Phase Diagram for the rubrene and 5,12- diphenylanthracene binary system, plotting Melting Temperature vs. % Composition of rubrene in the mixture.

- Determine the **eutectic point** and **eutectic composition** for the rubrene and 5,12- diphenylanthracene binary system. i.e., identify the % composition of the component mixture that yields the lowest melting temperature.

EUTECTIC MIXTURES and EUTECTIC POINT:[1,2,3,4,5]

Eutectic mixture is a mixture of two or more substances that melt uniformly and isothermally, at a lowest temperature, defined as the **Eutectic Point** or the **Eutectic Temperature**. The concept of eutectic mixture and eutectic point is clearly understood in terms of a phase diagram. Figure 1 represents a Binary Phase Diagram of two components, A and B at constant Pressure.[1] $\mathbf{T_{mA}}$ and $\mathbf{T_{mB}}$ are the melting temperatures of pure (100%) components A and B, respectively. When the components A and B are mixed in varying proportions, and heated until all the components are completely melted, the melting temperature is found to be lowered compared to the melting temperature of the pure components. If these melting temperatures are plotted against the corresponding composition of the component mixtures, a trajectory, $\mathbf{T_{mA} E\, T_{mB}}$ known as a **Liquidus Curve** is outlined. Above the liquidus curve, both components A and B, are in the liquid phase, and the two substances are soluble in each other. The lowest melting point **E**, of this curve defines the **Eutectic Temperature** or the **Eutectic Point**. The corresponding composition defines the **Eutectic Mixture** or the **Eutectic Composition**. At this point, components A and B, melt uniformly at the same temperature, and the liquid phase exists in equilibrium with the solid phase of A and B. The horizontal line, $\mathbf{T_E}$ passing through the eutectic point **E**, is called the **Solidus Line**. Below this line, the components A and B, are completely in the solid phase, and are insoluble in each other. The non-eutectic compositions of A and B, melt non-uniformly and non-isothermally, starting from the eutectic temperature, $\mathbf{T_E}$ until the maximum melting temperature is reached at the Liquidus Curve [Follow Line **X** in figure 1]. Depending on the mixture composition, in the range of non-uniform melting, the mixture will contain a liquid phase enriched with either a solid phase of A or B.

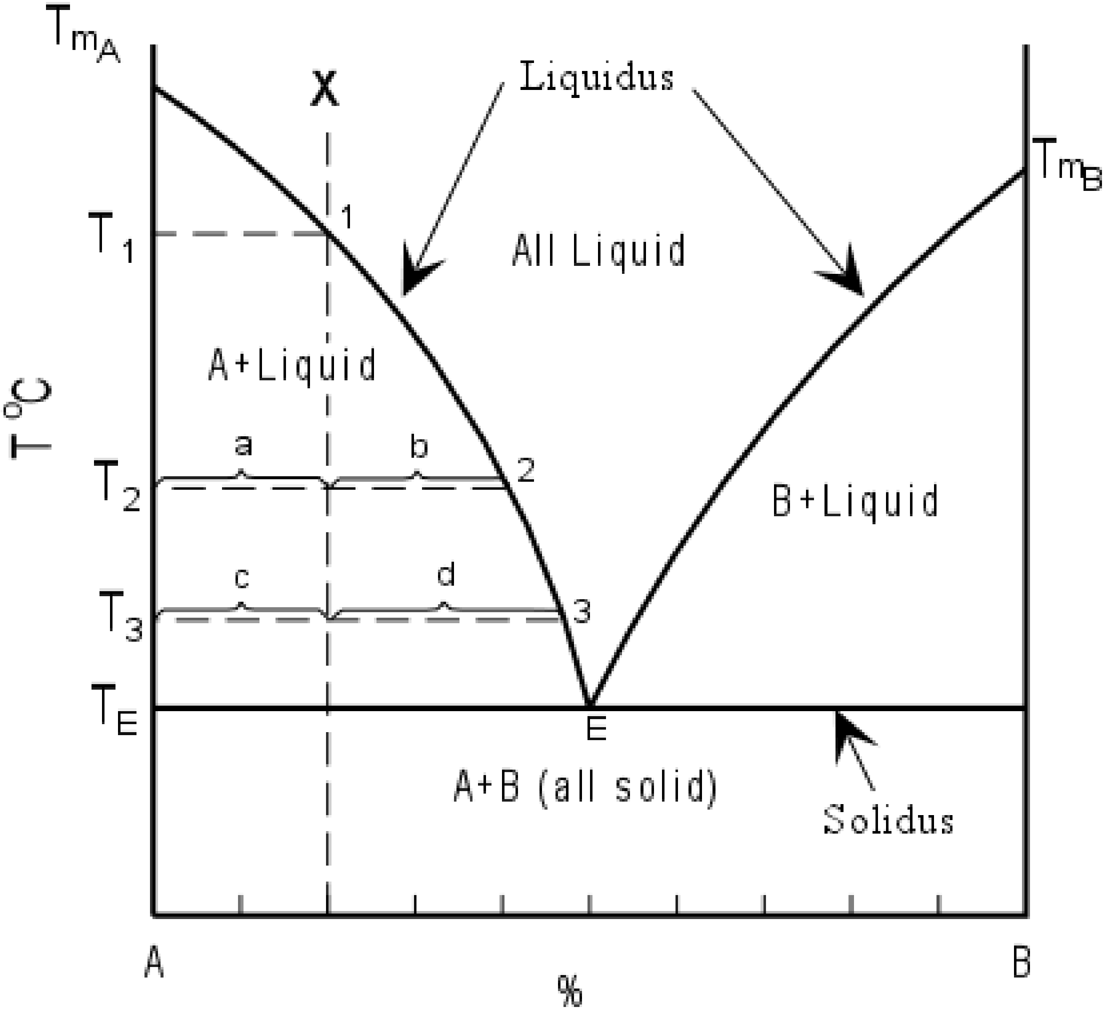

Figure 1

Courtesy of Prof. Stephen A. Nelson. Used with permission.

Figure 1: Phase diagram of a binary mixture of components A and B, depicting the temperature of the system as a function of % composition of the components. The solid **V**-shape curve represents the ***liquidus Line***, above which the two components are completely in the liquid state. The solid horizontal line passing through the point '**E**' represents the ***solidus Line***, below which the two components are in the solid state. The intersection of liquidus curves with the solidus line, defines the ***eutectic*** point, **E**. At the eutectic point in this two component system at constant pressure, the liquid phase exists in equilibrium, with the solid A and solid B phase.

[Figure 1, adopted from http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

A simple example of a eutectic system is the water – salt (NaCl) binary system which has a eutectic temperature at –21.1˚C and a eutectic composition of 23.3 % (mass of anhydrous salt). [5] This explains the use of salts in "de-icing" roads.

Eutectic mixture of phase change materials is exploited in thermal storage applications where large amounts of energy are released at a lower temperature (compared to the mixture components) during a liquid – solid phase transition [Please see MODULE BETA 1 LAB WEEK1 NOTES – THERMAL STORAGE SYSTEMS].

In this experiment, Phase Diagram of a Binary Mixture of Rubrene / 5,12-DiPhenylanthracene will be generated, plotting the highest melting temperature against the corresponding % composition of rubrene in the binary mixture.

MATERIALS:

Rubrene, alias 5,6,11,12 – tetraphenylnaphthacene : obtained from ALDRICH
Sublimed grade,
Molecular Formula: $C_{42}H_{28}$
Formula Mass (g): 532.67
Melting Point (˚C):

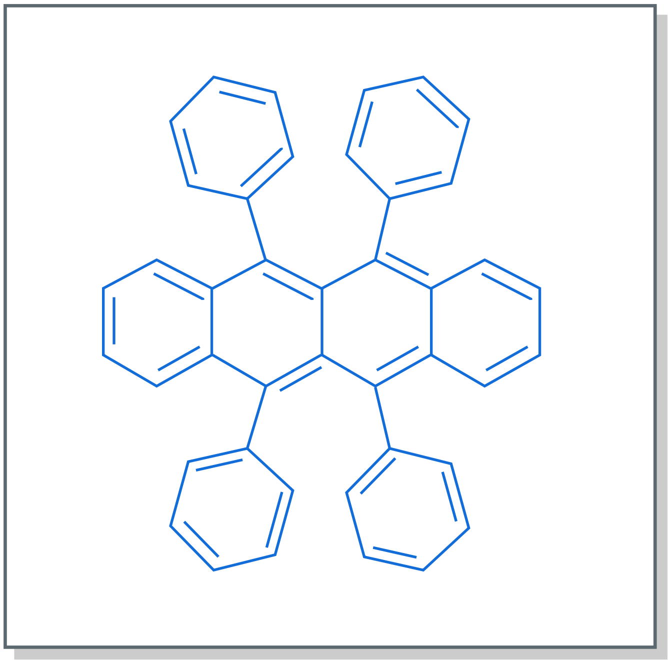

Figure by MIT OCW.

5,12 – diPhenylanthracene, alias 9,10 – diPhenylanthracene: obtained from ACROS 99% pure

Molecular Formula: $C_{26}H_{18}$

Formula Mass (g): 330.42

Melting Point (C): 248 – 252

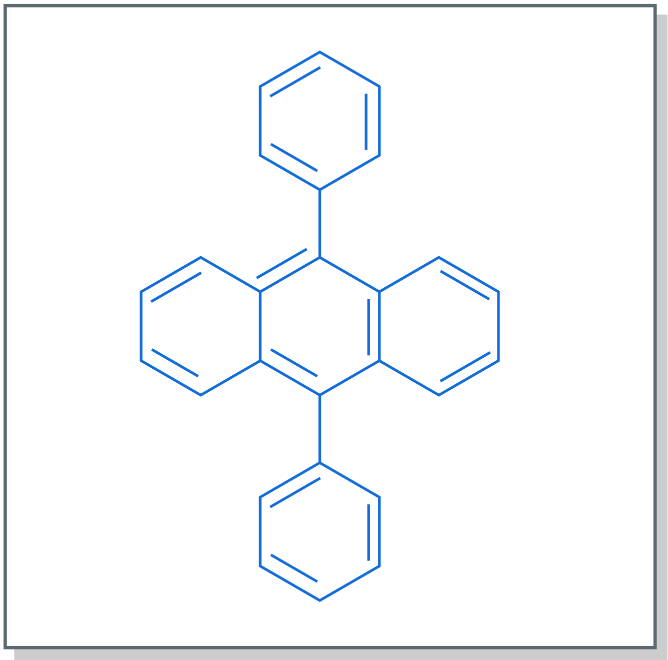

Figure by MIT OCW.

Structural representations adopted from http://www.acros.be

Material Specifications from Aldrich and Acros

Rubrene and 5,12- diphenylanthracene are fluorescent dyes. Rubrene is also a promising semiconductor material with potential application in organic electronics. The binary system, rubrene - 5,12- diphenylanthracene has been explored for the controlled processing of semiconductor thin films for a field-effect transistor (FET) device. [Read reference 6].

SAMPLE PREPARATION:

Binary mixtures of rubrene (5,6,11,12 – tetraphenylnaphthacene) and 5,12-diphenylanthracene, ranging from 10 – 90% by mass of rubrene are prepared as follows:

1. Weigh appropriate amounts of rubrene (5,6,11,12 – tetraphenylnaphthacene) and 5,12- diphenylanthracene, 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 355 ˚C (above the melting temperature of rubrene, 332 C) for at least an hour. 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 Q100

- TA Instruments Q-series Manual on DSC[7]
- "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 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.

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)

SAMPLE PREPARATION FOR DIFFERENTIAL SCANNING CALORIMETRY [DSC] MEASUREMENTS:

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

EXPERIMENTAL PROCEDURE:

These guidelines are based on ASTM Method, D3947 – 80. [7,8]
(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 heat flow of the system.

   SCAN conditions:

   - Set point temperature: 25 ˚C

   - Mass of the sample: enter the weighed amount for each sample in mg (5.00 – 10.00 mg)

     Input, 0 (ZERO) for the mass of the empty pan in baseline scan

   - Scan Mode: RAMP

Equilibrate at 150 C
Heating rate: @ 10˚ C / min scan to 350˚ C

* Ideally, an independent baseline profile must be obtained for each sample using the same pan in which it will be placed. 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.

3. Obtain thermal profiles for the mixture samples using same scan conditions as in step 1.
   Place each crimped pan containing the weighed amounts of sample on the sample stage.

4. Subtract the baseline data from the sample, 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:

MELTING POINT, EUTECTIC POINT and LATENT HEAT OF FUSION:

1. Use the Universal Analysis software of DSC and the peak integration routine to determine the **melting temperature and heat of fusion** for each sample.

2. Plot a graph of **highest melting temperature** (when all components are in the liquid state) vs. **%composition of rubrene** in the mixture.
   From the Phase Diagram thus generated, identify the **eutectic point** and the **eutectic mixture composition.**
   Compare your results with the results presented in reference 5.

REFERENCES:

1. “Two component(Binary) Phase Diagrams”, by Prof. Stephen Nelson, Tulane University.
   < http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html>,
   accessed on 24 November 2004.

2. “Eutectic Alloys”, http://www.ul.ie/~walshem/fyp/Eutectic%20alloys.htm,
   accessed on 24 November 2004.

3. “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). **[HANDED OUT]**

4. “Heterogeneous Systems”, Chapter sixteen in Heat and Thermodynamics by Mark W. Zemansky and Richard H. Dittman, McGraw- Hill Inc., 6th edition (1981).

5. “Physical Chemistry”, 3rd edition by G . W. Castellan, The Benjamin /Cummings Publishing Company, Inc. , P.224 (1983) **[HANDED OUT]**

6. “Organic thin-film electronics from vitreous, solution-processed rubrene hypereutectics”, Natalie Stingelin-Stutzmann, Edsger Smits, Harry Wondergem, Cristina Tanase, Paul Blom, Paul Smith and Dago de Leeuw, Nature Materials, vol.4, 601 – 606, (2005) **[HANDED OUT]**

7. “Guidelines for Quantitative Studies – Heat Capacity Experiments” TA Instruments Manual DSC 2920, 4-15.

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