SPECIFIC HEAT CAPACITY OF PURE TRIGLYCERIDES BY DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

This report discusses the methods of measuring specific heat capacity of triglycerides using differential scanning calorimeter, DSC. The optimum operating conditions for specific heat capacity determination of triglycerides using the heat flux differential scanning calorimeter, is first established. Operating conditions such as scanning rate, sample weight and atmospheric condition seemed to affect the specific heat capacity value considerably. The specific heat capacity of pure triglycerides are then determine using these optimum operating conditions. The pure triglycerides used in the experiment are four simple triglycerides and three mixed triglycerides. The four simple triglycerides used are trilaurin, trimyristin, .tripalmitin and tristearin. The mixed triglycerides used are 1,2-dimyristoyl-3-oleoyl, 1,2-dimyristoyl-3-palmitoyl and 1,2-dioleoyl-3-palmitoyl. Comparisons of the specific heat capacity results are made with the reported values and values calculated for triglycerides using estimation methods. The accuracy's of the specific heat capacity results for triglycerides are within 95% using DSC methods.

1. INTRODUCTION

The specific heat capacity of pure triglycerides is an important thermal property but are still not completely understood. The specific heat

capacity of vegetable oils can be estimated if relationships between triglycerides and vegetable oils are developed. The data on specific heat capacity of pure triglycerides is considerably lacking: data on simple triglycerides is available up to about a 100°C, but for mixed triglycerides no data has been reported before. The thermal property up to 250° C is necessary since palm oil refineries involves processes such as deodorisation which operates at that temperature. With this knowledge, the future of the palm oil industry can be further improved; energy conservation within the industry is possible.

Specific heat capacities have been measured with high precision and accuracy over a wide temperature range at atmospheric pressure. In determining the specific heat capacity of substances, the two most important factors are the construction of the adiabatic calorimeter and the method of measurement of the amount of energy supplied. Throughout the years a lot of improvements has been made in constructing calorimeters. Calorimetric methods (using vacuum flask) has been used as far back as 1935 to determine the heats of fusion of triglycerides *(Ram Rao and Jatkar, 1935). Charbonnet and Singleton, 1947* constructed a copper, semi-adiabatic calorimeter to measure a fairly accurate specific heat capacity of triglycerides. A sophisticated adiabatic, high pressure, stainless steel calorimeter for measuring specific heat capacity of liquids and solids has been developed by *Zhi-Cheng et. al., 1991.*

In the more recent years the use of differential scanning calorimeter, DSC in the measurement of specific heat capacity and phase transitions is increasingly favored and fast replacing other methods of measurement. This is due to the ease of handling of the equipment, the numerous number of

data points obtainable in a relatively short period as well as the high accuracy of results.

The present investigation reports attempts to measure specific heat capacity of pure triglycerides using DSC from their melting points up to a temperature of 250°C. The experimental results are to be compared with the specific heat capacity values estimated from the methods of *Sakiadis and Coates, (1956); Bondi, (1968);* and *Phillips and Mattamal, (1976)* as well as the reported values of *Charbonnet and Singleton, (1947); Phillips and Mattamal, (1976)* and *Hampson and Rothbart , (1983).* This enables the evaluation of the reliability of measuring specific heat capacity of pure triglycerides using DSC.

2.0 THE HEAT FLUX DSC

2.1 Instrumentation

In this work the heat capacity measurements were made using the Seiko heat flux DSC. The Seiko SSC5200 thermal analysis system is comprised of the furnace DSC 220, the data processing unit TA station, an output device for recording of hard copy and a visual display unit. *Figure 2.1* shows the block diagram of the Seiko heat-flux DSC model. *Figure 2.2* is the schematic representation of the basic structure of DSC heating chamber.

2.2 Theory of Specific Heat Capacity Measurement By DSC

Specific heat capacity using DSC, is derived from three different measurements. These include empty container data, data from a reference substance with a known specific heat capacity, and the sample data. Data from the empty container gives the baseline. All calculations are made

relative to the baseline *(figure 2.3)*. The specific heat capacity of a substance is given by:

$$Cp_S = \frac{Y_S \, M_r \, Cp_r}{Y_r \, M_S} \qquad (2.6)$$

2.3 Optimum Condition Of DSC

The optimum operating condition in the DSC is to ensure high quality specific heat capacity measurements. If specific heat capacity measurement is taken randomly at any scan rate and sample weight, the chances of reproducibility at a different sample weight and scan rate is nil. It is the operating parameters such as the scan rate, the sample weight and the atmospheric conditions which gives reproducible results. These three parameters are dependent on the sample type as well as the DSC module.

Trilaurin being the simplest triglyceride used in this work is selected to determine the optimum conditions. Four sets of runs were carried out for each operating condition. The procedure to determine the best scan rate requires the measurement of specific heat capacity of trilaurin with fixed sample weight, temperature range of 50 °C to 150 °C with 3 minutes isotherm at the start and limit temperatures without any gas purging.

The best sample weight is determined by carrying out the experiment by varying the sample weight, all other conditions are the same as before.

The effect of nitrogen purging was studied by running at the scan rate and sample weight determined previously. The operating condition is from 50 °C to 250 °C with 3 minutes isotherm at the start and limit temperatures. The nitrogen flow used as purged gas during the experiment is varied.

physical properties are usually available for the four simple triglycerides chosen. These enables comparison between experimental values and reported values. The study of the physical properties of the four simple triglycerides are also important since this reveals any relationship between the property and the carbon number present in the triglycerides. The mixed saturated triglycerides are chosen to see if there is any effect of mixed fatty acid groups has on the property. All the triglycerides except 1,2-dimyristoyl-3-oleoyl, MMO and 1,2-dioleoyl-3-palmitoyl, OOP are in the solid state at room temperature (between 20 °C - 30 °C).

As noted earlier, the specific heat capacity of the samples was observed to drop suddenly above around 150 °C when no purge gas was used in the apparatus *(figure 4.1)*. This point was taken as a rough indicator of onset of degradation.

The specific heat capacity of triglycerides as a function of temperature is shown as a family of straight lines (*figure 4.2)*. It is observed that the specific heat capacity values are higher for larger molecules (high carbon number) from the simple triglycerides in the lower temperature range (50 °C to 160°C). Thus, tristearin with carbon number 54 (C54) has the highest specific heat capacity value followed by tripalmitin, C48, trimyristin, C42 and trilaurin, C36.

For mixed triglycerides, however, the specific heat capacity values are lower than the simple triglycerides. A further reduction in specific heat capacity of 1,2-dimyristoyl-3-oleoyl, MMO, and 1,2-dioleoyl-3-palmitoyl, OOP may be attributed to the presence of double bonds.

The specific heat capacity values in the higher temperature region, from about 160 °C to 250 °C) is shown as the dotted lines in *figure 4.2*. Tristearin (C54) has the highest specific heat capacity value followed by

3.0 EXPERIMENTAL PROCEDURE

The method known as the round robin test, RRT is used in the specific heat capacity measurements using DSC *(Hatakeyama et. al., 1989, Nakamura et. al., 1988)*. The method is also described in the *Seiko Instrumentation Manual, 1989.*

4.0 RESULTS & DISCUSSION

4.1 Determining The Optimum Conditions For Specific Heat Capacity Of Triglycerides by DSC

As mentioned earlier, the specific heat values determined by the DSC were found to depend largely on the conditions of the experiment (e.g. scan rate, purging) and also on the weight of the sample taken. Analysis of data are therefore first carried out to determine the optimum conditions. Various statistical measures are necessary here to establish whether the difference is a real one or a result of random fluctuations.

In this work since experimental precautions are observed strictly and a lot of effort is taken to ensure reproducibility of results. a confidence level of 95% is used on the regressed data.

The optimum conditions are scan rate of 17 °C/min., sample weight of 21mg and purge gas flowrate of 50ml/min. These conditions were used for the determination of specific heat capacity of other triglycerides up to a temperature of 250 °C.

4.2 SPECIFIC HEAT CAPACITY BY DSC

The seven triglycerides studied with carbon number ranging from C36 to C54 are found to be common in most vegetable oils. Experimental data on

tripalmitin (C48), trimyristin (C42) and trilaurin (C36). The specific heat capacity value for the mixed triglycerides are in general lower and the degree of unsaturation decreases the values further as observed earlier.

4.3 COMPARISON OF SPECIFIC HEAT CAPACITY OF TRIGLYCERIDES WITH REPORTED VALUES AND CORRELATION

The use of DSC technique for the determination of specific heat capacity of simple triglycerides was first reported by *Phillips and Mattamal (1976)*, this is followed by *Hampson and Rothbart (1983)*.

The earliest reported value on the specific heat capacity of triglycerides is probably by *Charbonnet and Singleton, (1947)* using calorimetric methods.

All the above three reported experimental specific heat capacity values are only at few selected temperature in a very narrow range. These are the only available experimental values to compare with the results of this work. The results are also compared with the estimated values using the methods of *Bondi, (1968); Phillips and Mattamal, (1976) and Sakiadis and Coates, (1956)* over wider temperature range from melting point to about 250 °C.

Comparison of experimental with reported and estimated values of specific heat capacity are shown in *figures 4.3 to 4.6* for trilaurin (C36), trimyristin (C42), tripalmitin (C48) and tristearin (C54) respectively. The experimental value of this work are closest in agreement to the values reported by *Charbonnet and Singleton (1947)*, the maximum deviation being about 4%.

Comparison with *Hampson and Rothbart, (1983) and Phillips and Mattamal, (1976)* is difficult because of their experimental data being

sporadic in nature. *Phillips and Mattamal, (1976)* themselves gave 5% deviation from the experimental results. The individual data points of *Hampson and Rothbart, (1983)* show 2-4% deviation except for tristearin which is lower by 5 - 10% when compared to the values of this work.

Specific heat capacity of trilaurin, are also compared with the values estimated obtained by *Sakiadis and Coates, (1956)* method. These values seem to be much deviated from the experimental values and also from the reported values of specific heat capacity. Therefore, this method was not used for the estimation of specific heat capacity of the other triglycerides. In fact this method is more suitable for hydrocarbons *(Sakiadis and Coates, 1956)*.

Comparisons are also made with the estimated values of specific heat capacity of triglycerides using the methods of *Bondi, (1968) and Phillips and Mattamal, (1976)* and are shown in the *figures 4.3* to *4.6*. Both of these methods estimate specific heat capacity lower than the experimental values of this work; *Phillips and Mattamal, (1976)* method giving estimates closer to the experimental values. The maximum deviation is 6%. The method, however, gives large deviation in the case of unsaturated triglycerides: 1,2-dimyristoyl-3-oleoyl MMO and 1,2-dioleoyl-3-palmitoyl, OOP. The method may not be used for the estimation of the specific heat capacity of unsaturated triglycerides containing double bonds. This method does not consider the presence of double bonds present in the unsaturated triglycerides (method only takes into account the types and numbers of alkane groups present and the number of carboxyl groups). This might be leading to the large deviation observed.

The method of *Bondi, (1968)* when applied to triglycerides does not give a satisfactory estimate of the specific heat capacity *(figures 4.3* to *4.6)*.

Bondi' s method when used to estimate specific heat capacity of triglycerides gives a linear relationship with temperature with a maximum deviation of 12% . Bondi's method is a group contribution method which is developed based on principles of corresponding state.

5.0 CONCLUSION

1. Reproducible specific heat capacity results of triglycerides by DSC can only be obtained when measured under optimum operating conditions. The optimum operating conditions are scan rate of 17 °C/min., sample weight of 21mg and nitrogen flow of 50ml/min. The confidence level that can be put on all the specific heat capacity of triglycerides measured under this conditions is 95%.

2. Dependence of specific heat capacity of triglycerides on temperature is linear in the experimental range. The specific heat capacity of all the triglycerides determined are graphically illustrated in *figure 4.2*.

3. The measurement of specific heat capacity of triglycerides in a DSC should be done with inert gas purging (nitrogen) because of degradation of samples that take place in the presence of air. Even at lower temperatures a slow deterioration of the samples does occur which affects the thermal properties. this problem can only be overcome by purging gas in the cell.

4. For simple triglycerides. the reported values of *Charbonnet and Singleton, (1947)* give the best agreement within 4% of the experimental results found in this work.

5. The best estimated specific heat capacity of triglycerides was found to be the method developed by *Phillips and Mattamal, (1976)*, however, it only applies to saturated triglycerides. The deviation of the estimated values varies between 1.5-6% from the experimental values.

6. DSC was found to be a satisfactory method of measuring the specific heat capacity. Experiments using DSC gives a large number of data for a given set of run and is especially suitable for expensive samples such as triglycerides since only a small amount of sample is required.

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NOMENCLATURE

C - carbon number - e.g. C36 indicates a carbon number 36

Cp - specific heat capacity at constant pressure in J/mole K

C_V - specific heat capacity at constant volume J/mole K

M - weight of the reference substance/sample in mg

MMO - 1,2-dimyristoyl-3-oleoyl, a triglyceride

MMP - 1,2-dimyristoyl-3-palmitoyl, a triglyceride

N_2 - chemical symbol for nitrogen

OOP - 1,2-dioleoyl-3-palmitoyl, a triglyceride

P - pressure

t - time, s

T - temperature, C

Tm - melting point, C

U_S - velocity of sound in liquid, m/s

Y - DSC curve difference between empty container and sample or reference

Superscript

l - liquid, attached to Cp or Cv

° - ideal gas condition or zero pressure, attached to Cp

s - sample (triglycerides) - attached to M or Y

r - reference substance (sapphire) - attached to M or Y

Greek letters

α - the ustable phase in the triglyceride polymorph

β - the most stable phase in the triglyceride polymorph

β' - the most ustable phase and intermediate phase in the triglyceride polymorph

Glossary

degradation - physical and chemical changes observed in the triglycerides during heating, might be cause by breakdown, polymerisation and isomerisation.

deodorisation - a treatment process for oils and fats at high temperature (200 °C - 250 °C) and low pressure (0.1 - 1mmHg). It is important step in the refining of oils and fats resulting in the removal of volatile and odorous compounds including fatty acids, monoacylglycerols and oxidation products.

DSC - Differential Scanning Calorimeter

DTA - Differential Thermal Analysis

oil refining - industrial technology to obtain edible oils from crude palm oils through processing steps such as degumming, neutralization, bleaching and deodorization.

palm oil - the oil palm produces two major vegetables oils. One comes from its fleshy endosperm (palm oil) and the second, of different character, from the kernels (palm oil kernel). The former is rich in palmitic and oleic acids (each about 40%) whilst the latter is a lauric oil with over 50% of lauric acid.

polymorphism - alternative crystal structures in the solid state which give complex melting behavior with multiple melting points. Fats and triglycerides occur in any one of three basic polymorphs designated α alpha), β' beta prime) and β (beta). α is the least stable and

the lowest melting point; β is the most stable and highest melting point. Transformation from α to β' to β take place in that order and are irreversible.

RRT - round robin test, a technique for measuring specific heat capacities on DSC.

triglycerides - lipid class based on glycerol esterified to three fatty acids. The major compounds in all fats and oils and the most abundant type of lipid structures. They serve as a source of energy, but are also needed for insulation and protection purposes.

unsaturation- generally used to describe 4-electron (double bond) and 6-electron (triple bond) linkages between carbon atoms.

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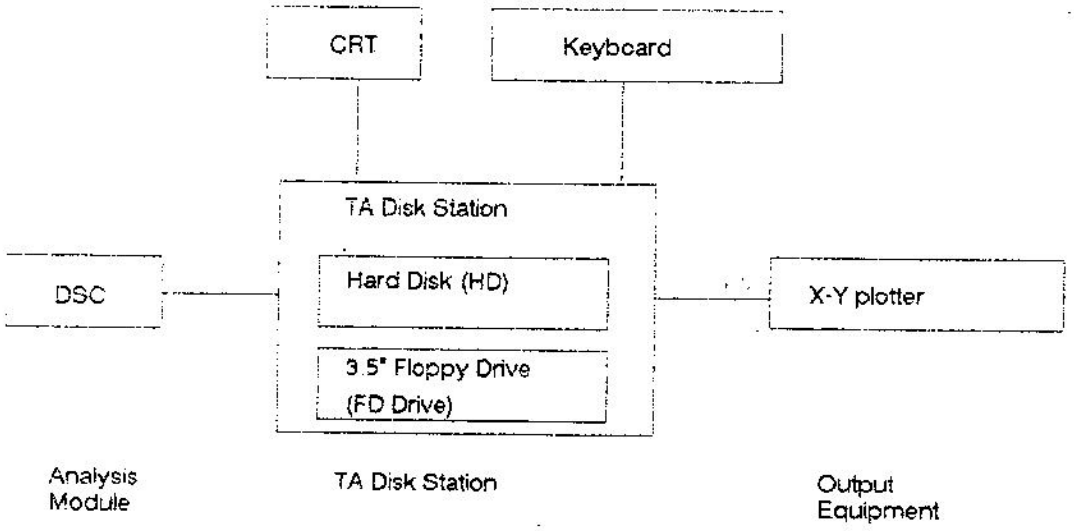


Figure 2.1 The block diagram of the Seiko heat-flux DSC system

(The three main units in the Seiko DSC system is the analysis module (DSC 220), the TA disk station (SSC 5200) and the Seiko X-Y plotter (Seiko Instrumentation Manual (1989)).

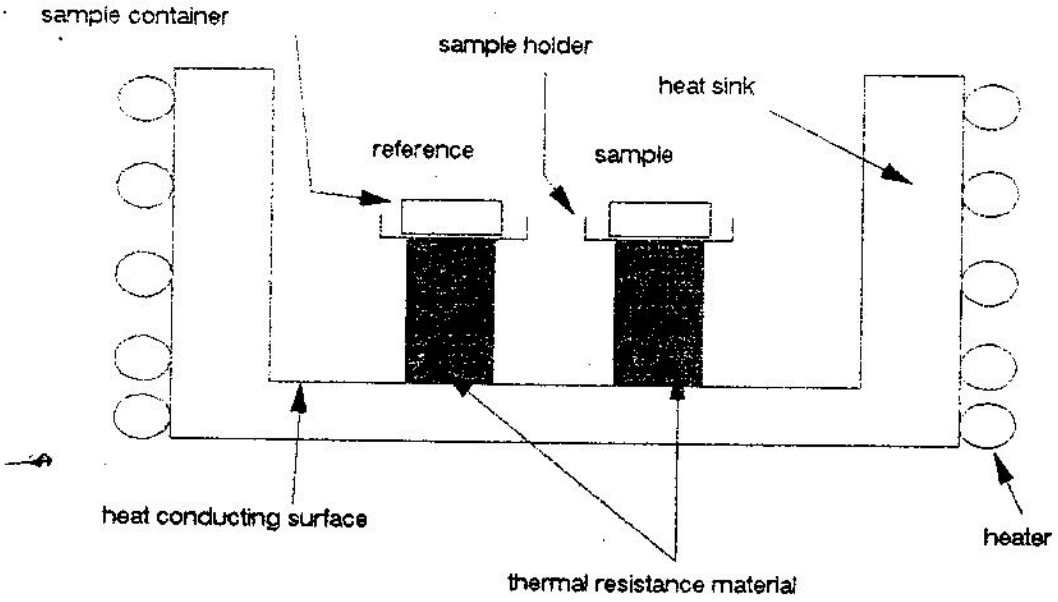


Figure 2.2 Schematic representation of the basic structure of the DSC heating chamber

(Details of the heating cell is shown, Seiko Instrumentation Manual (1989)).

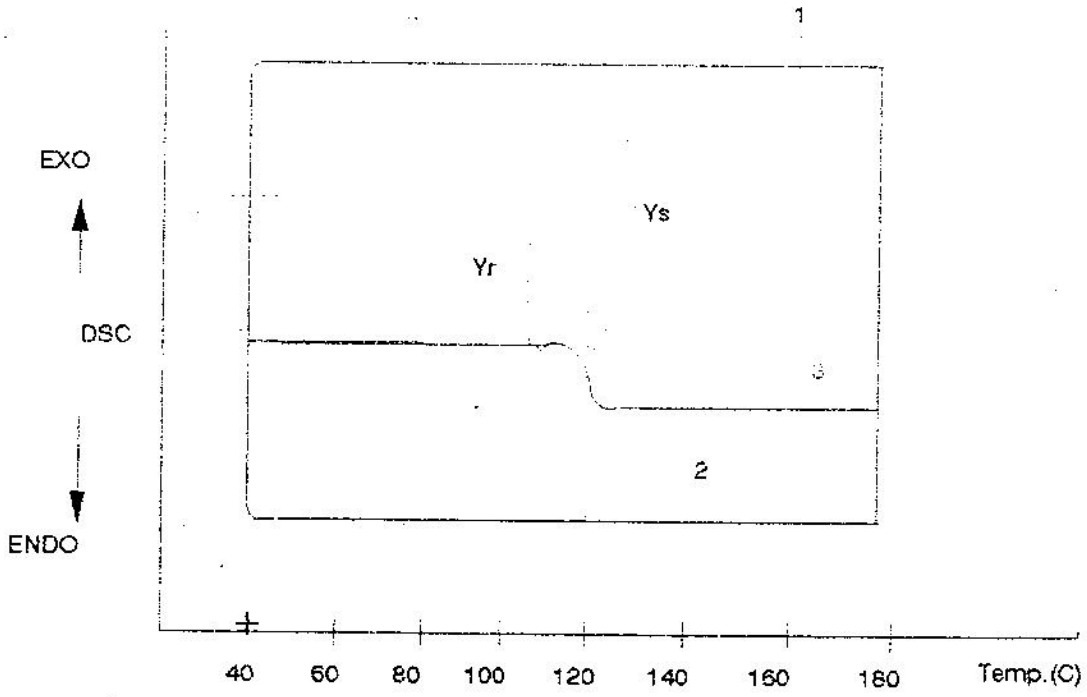


Figure 2.3 Typical specific heat capacity calculation in a DSC

(1 - baseline curve, 2 - reference DSC curve, 3 - sample DSC curve
Yr - the difference between reference and baseline DSC output,
Ys - the difference between sample and baseline DSC output,
Seiko Instrumentation Manual (1989)).

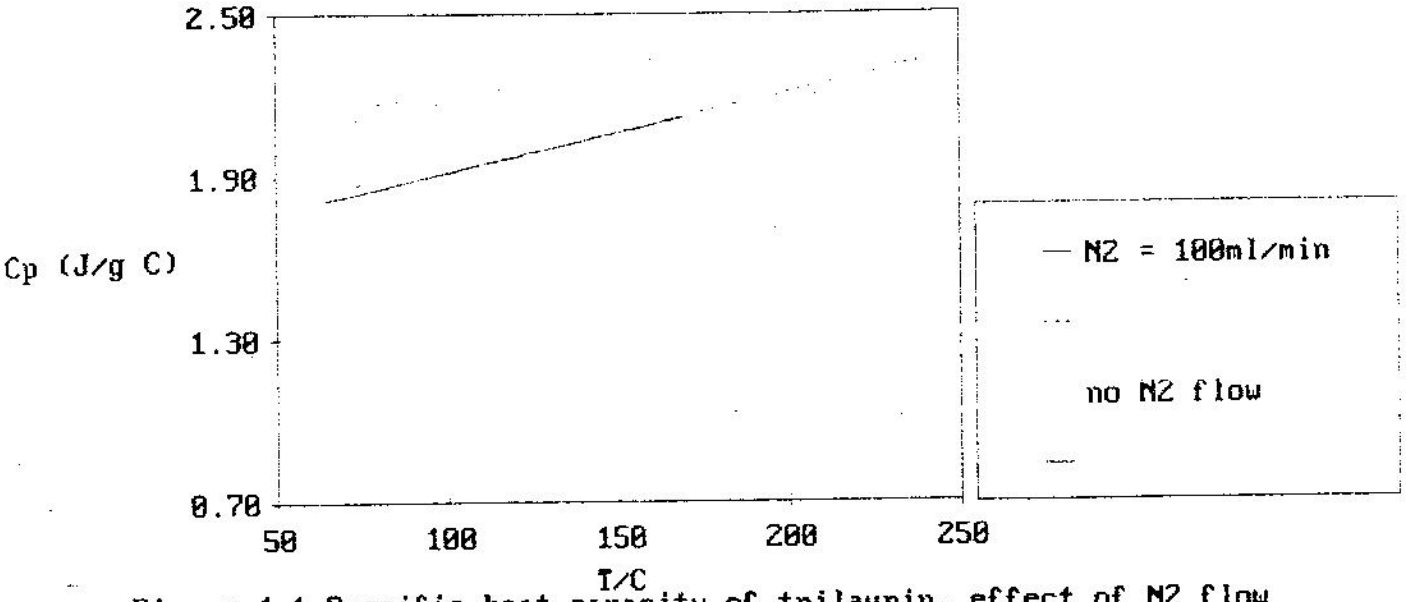


Figure 4.1 Specific heat capacity of trilaurin, effect of N2 flow in the cell: Indicate degradation with no flow of N2.

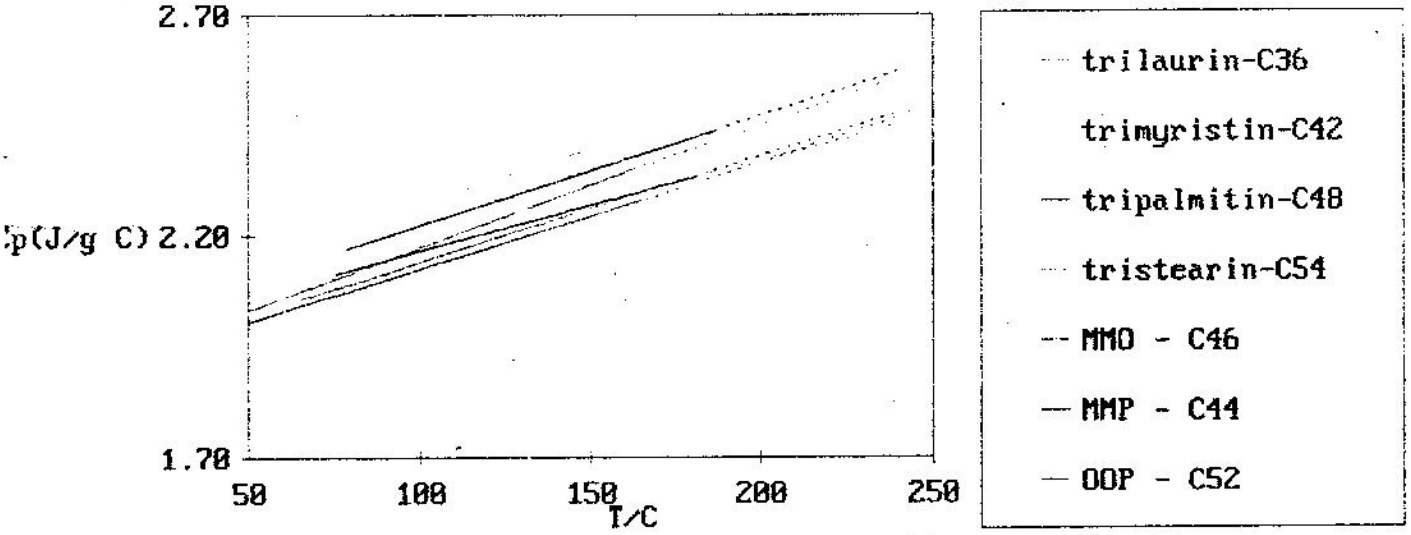


Figure 4.2 Specific heat capacity of triglycerides as a function of temperature with gas purging. (Scan rate = 17 K/min., sample weight = 21mg. Temperature range is wider. - solid lines - lower T range, dotted lines - higher T range).

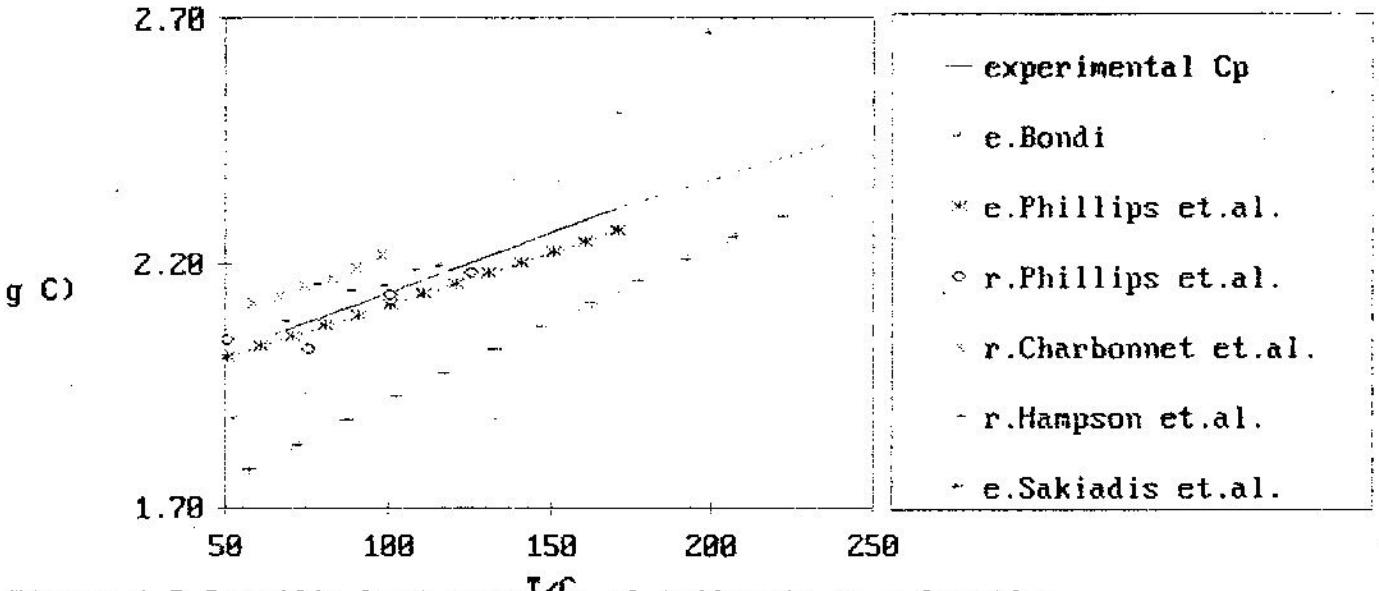
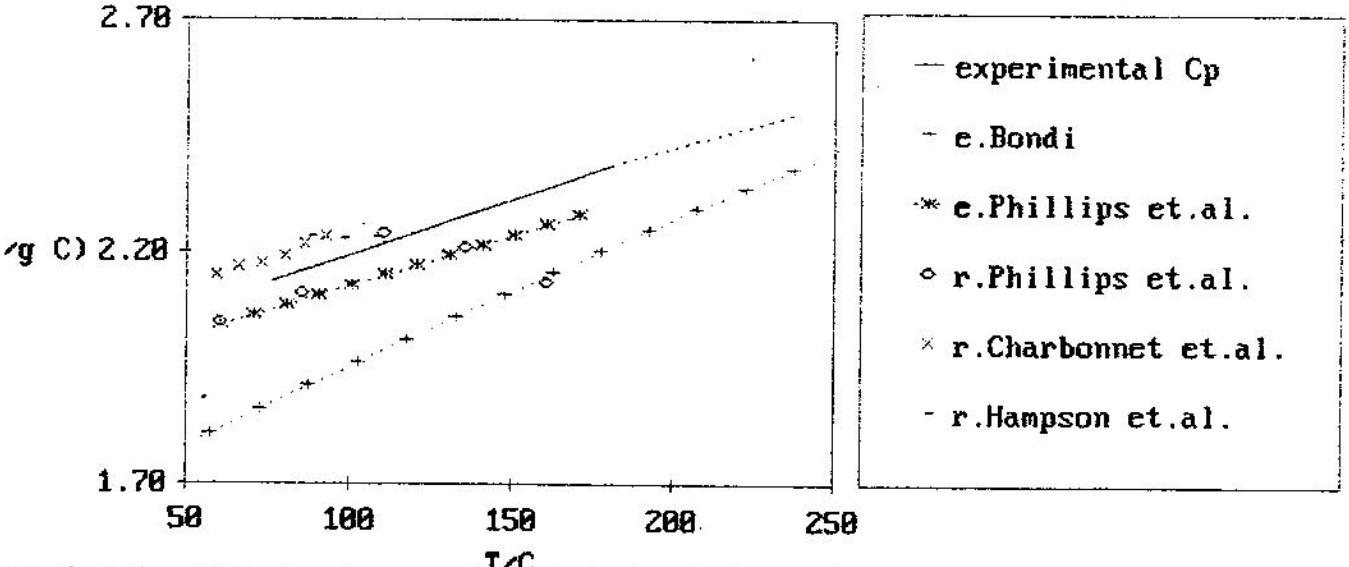


Figure 4.3 Specific heat capacity of trilaurin as a function of temperature. (Scan rate = 17 K/min., sample weight = 21mg, purge gas=50ml/min. Comparison with e - estimated, r - reported values).



re 4.4 Specific heat capacity of trimyristin as a function temperature. (Scan rate=17K/min., sample weight=21mg, purge gas=50ml/min. Comparison with e - estimated values, r -reported Cp values).

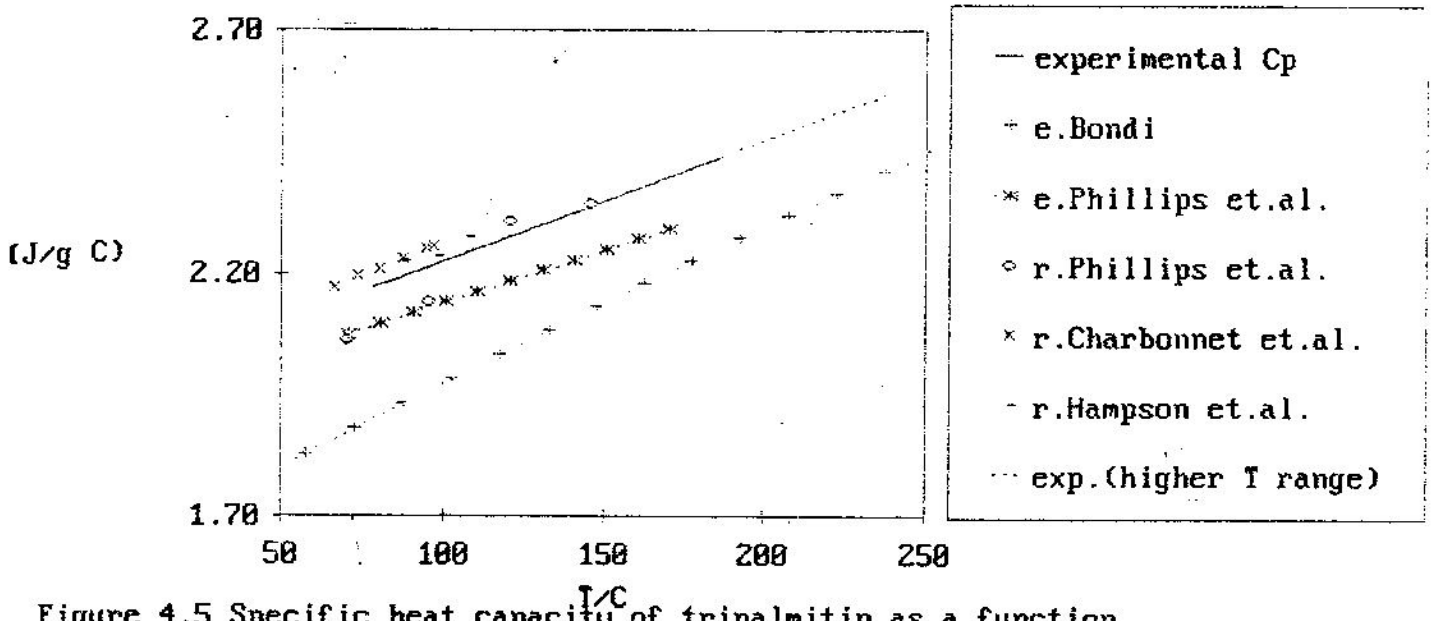


Figure 4.5 Specific heat capacity of tripalmitin as a function of temperature. (Scan rate=17K/min., sample weight=21mg, purge gas=50ml/min. Comparison with e-estimated and r-reported Cp values).

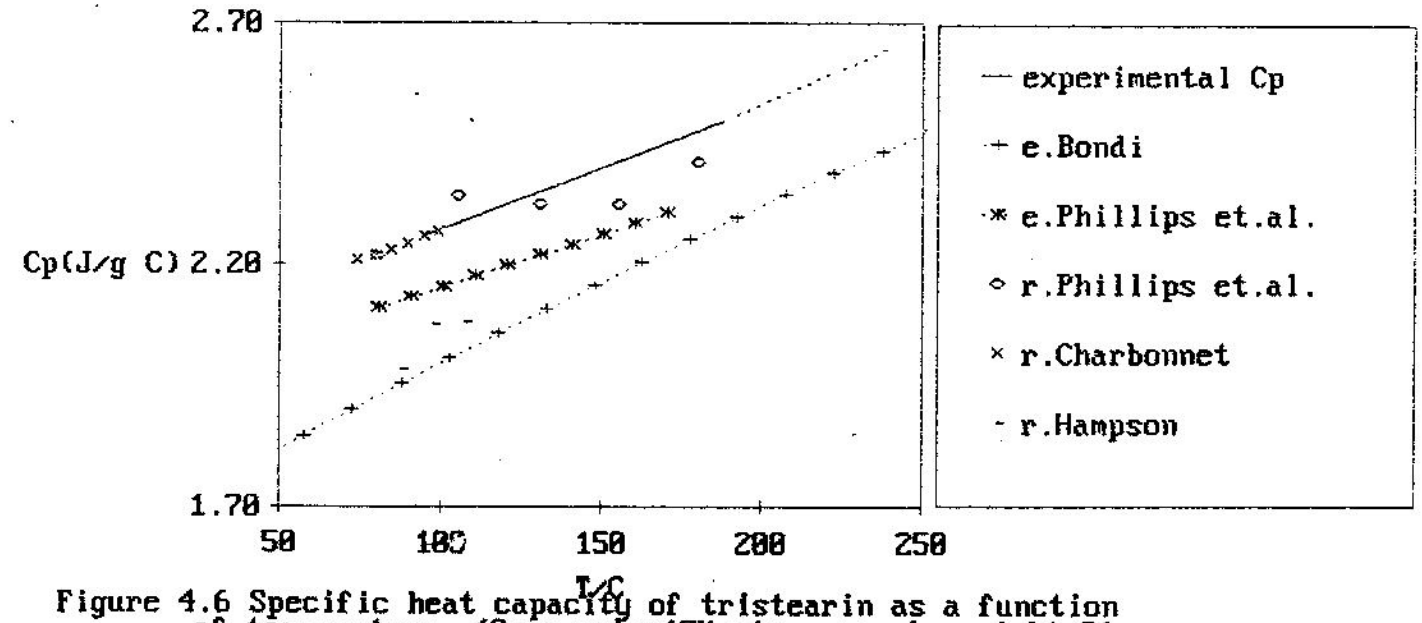


Figure 4.6 Specific heat capacity of tristearin as a function of temperature. (Scan rate=17K/min., sample weight=21mg, purge gas=50ml/min. Comparison with e-estimated and r-reported Cp values).