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CALORIMETRIC INVESTIGATION IN THE FIELDS OF BIOLOGY AND BIOCHEMISTRY

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ABSTRACT

A new calorimeter based on the Calvet heat flux principle is presented. It has been optimized for investigation in the fields of Biology and Biochemistry. Its main feature is a very high sensitivity associated with removable vessels. It offers many possibilities : upwards and downwards temperature scanning, heat capacity measurements, isothermal batch calorimetry and flow calorimetry.

INTRODUCTION

The calorimeter presented in this paper has been developed for the investigation of biochemical and biological systems. It is shown in Figure 1.

Figure 1 - Photograph showing the BIO-DSC "Batch and Flow" calorimeter.

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The instrument is designed on the Calvet principle. The advantages of the heat flux design offers many facilities :

- removable experimental vessels
- any connections (gas or liquid) between the vessels and the outside
- linear temperature scanning up and down
- high sensitivity 0.2 µW isothermal
  2 µW scanning
- temperature range 0 to 100°C
- scanning rates from 0.1°C per hour to 1.2°C per minute
- vessel capacity 1 cm^3

The temperature control is achieved by a loop of thermostated liquid. The liquid is circulated by a pump. The heating and the cooling is performed by an electronic thermostat, as shown in schematic arrangement Figure 2.

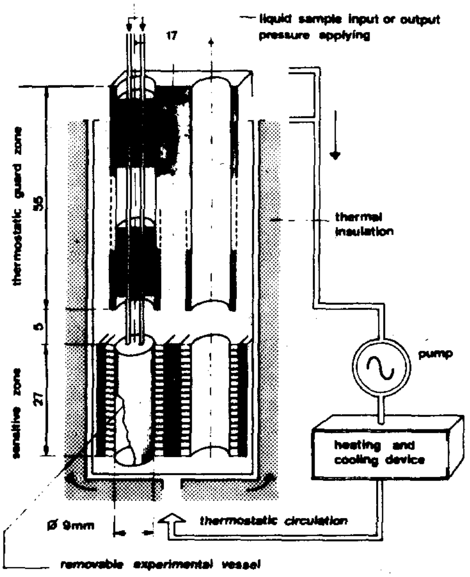

Fig. 2 - Schematic arrangement of the calorimeter.

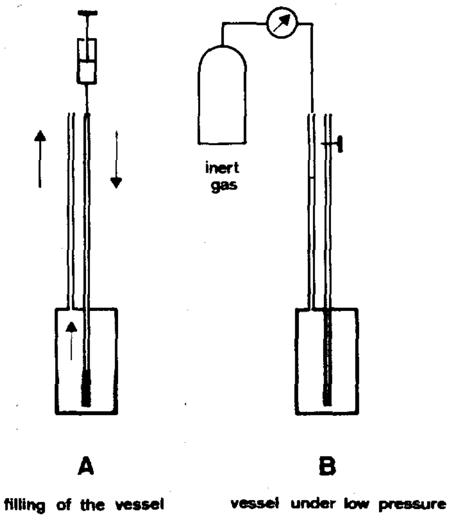

Fig. 3 - Open vessel application.

TEMPERATURE SCANNING (D S C)

The temperature is controlled either upwards or downwards or at a constant value. This control is achieved by a thermostatic loop designed with Peltier effect elements. It allows heating and cooling at scanning rates from 0.1°C h^{-1} to 1.2°C mn^{-1} between 0°C and 100°C.

The sample under investigation is located in a tight and removable vessel.

This technique is used to study for instance :

- denaturation of bio-polymers (proteins)
- conformational transitions (polysaccharides, phospholipids)
- reversibility
- gel forming transition e.g. Figure 4

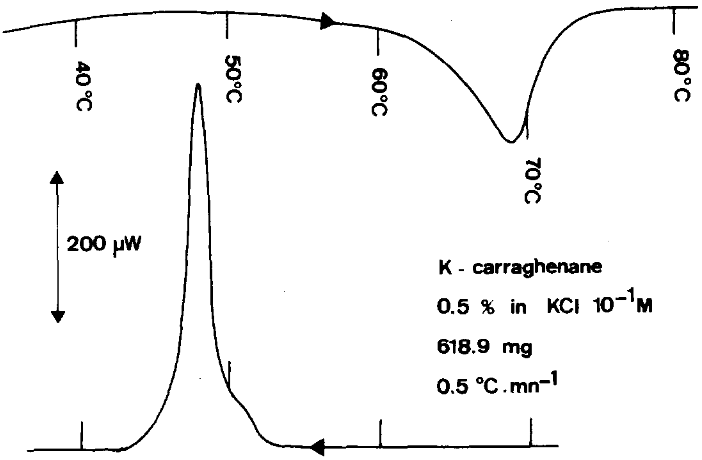

Fig. 4 - Gel forming transition of Kappa-carraghenane.

The BIO-DSC can also be used in other fields of research which require a high sensitivity, a slow scanning rate with the cooling facility. For instance :

- low energetic transitions in metallurgy
- transitions of liquid crystalls
- pore size distribution determination

HEAT CAPACITY MEASUREMENT

For this application an open vessel (Figure 3) is used so that a constant volume of liquid is placed in the sensitive zone of the calorimeter. It allows a control of the pressure of the studied sample and a filling of the vessel without extraction.

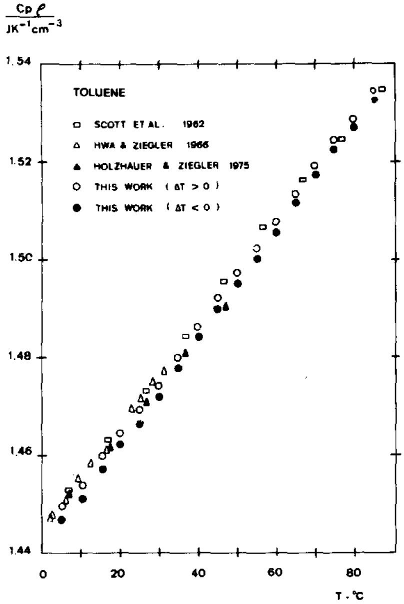

Fig. 5 - Heat capacity of Toluene

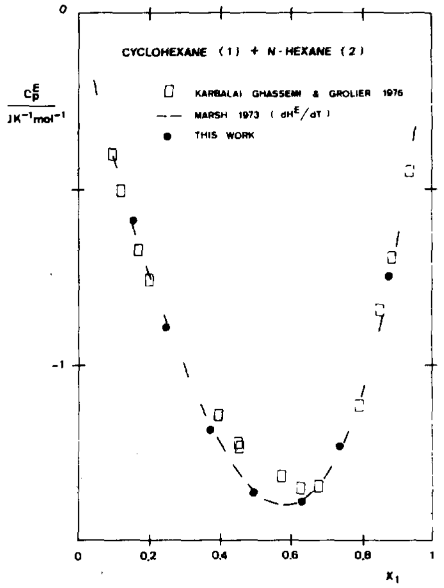

Fig. 6 - Excess heat capacity of (cyclohexane + n -hexane)

(by courtesey of J.P.E. GROLIER and coll.)

Absolute and relative heat capacities can be measured by two methods :

- continuous scanning of the temperature (e.g. the variation of heat capacity) before and after denaturation is monitored during a temperature scan)
- incremental temperature programming : it provides the high accuracy required by thermodynamic determination suchas either excess or apparent heat capacities. This mode is more precise than the previous one because the temperature scanning is a succession of isothermal states. The sample is in thermal equilibrium after the end of each temperature increment even during a transformation of the sample

With this mode the heat capacity threshold is 5 10^{-5} of the absolute value.

Figure 5 (Ref. 1) shows the values of the absolute heat capacity of Toluene between 5°C and 85°C; it shows the good agreement with the values found in the literature (Ref. 2 - 3 - 4).

Figure 6 shows the values of excess heat capacities of Cyclohexane + n hexane. These values (Ref. 1) are in good agreement with the values found by KARBALAI GHASSEMI and GROLIER, which were determined by using the Picker calorimeter (Cp model). The values found by means of the BIO-DSC, however, have a better correlation than with the derivative values of the heat of mixing of Cyclohexane + n hexane obtained by MARSH (Ref. 5).

FLOW CALORIMETRY

Experiments are carried out with continuous introduction of reactive in the isothermal mode. A built in stabilisation of temperature allows to preheat the temperature of the inlet liquids.

The introduction of one or two liquids through a special vessel enables the investigation of liquid-solid and liquid-liquid interactions. For this purpose vessels with one or two inlets and one outlet are available (Figure 3).

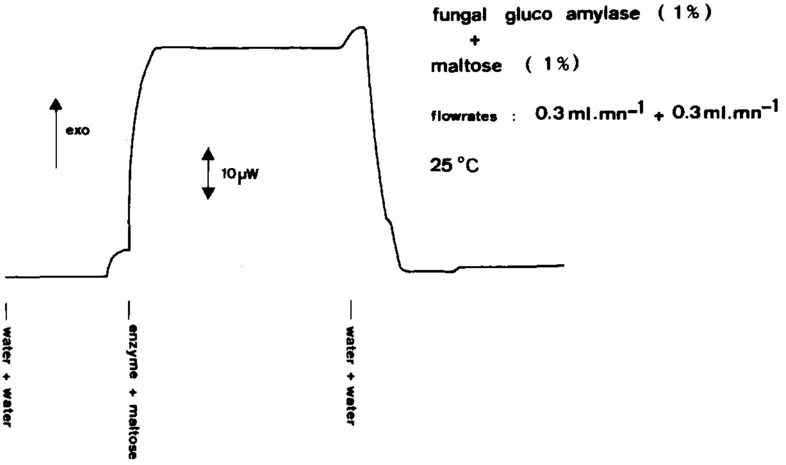

Fig. 7 - Fungal gluco amylase + maltose

Different types of applications are possible depending on the experimental settings :

- a single liquid flows through : own activity of the fluid-control of fermentors, bacterial activity...
- a single liquid flows on a solid : study of sorption, reaction, catalytic decomposition...
- two liquids flow inlet : continuous mixing, chemical or biochemical reactions, heat of dilution, enzyme-substrate reactions....

The Figure 7 shows an enzymatic reaction. A 1 % solution of Fungal-gluco Amylase is mixed with a 1 % solution of maltose at a constant temperature of 25°C.

ISOTHERMAL BATCH CALORIMETRY

The experiment is carried out in a closed vessel at a constant temperature. The activity of the sample is monitored.

Examples of application :

- bacterial growth and metabolism (aerobic and anaerobic)
- decomposition, hazards, safety
- self discharge of batteries

CONCLUSION

The design of this new instrument offers a versatile tool in the field of calorimetric investigations. Just by changing the vessel it is possible to use this instrument for many purposes : upwards and downwards scanning of the temperature (DSC), heat capacity measurement (absolute and relative), continuous introduction of liquids (flow calorimetry), investigation of sample activity (batch calorimetry). These techniques can be combined such as : a slow temperature scanning in a flow experiment, discontinuous introduction of liquids, batch calorimetry associated to a slow temperature scanning.

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