

## Experimental Investigation of Isobaric specific heat capacity ( $C_p$ ) of 9-ethylcarbazole in liquid and solid state

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### ABSTRACT

Liquid organic hydrides, e.g. 9-ethylcarbazole, are potentially interesting hydrogen storage materials because of their reversible hydrogen sorption properties. In this study, the isobaric specific heat capacity of 9-ethylcarbazole in solid and liquid phases was investigated using adiabatic calorimeter. The experimental setup consisting of two basic components adiabatic calorimeter and pressure unit was developed. To calibrate the apparatus the specific heat of the water was measured. The experimental data points were obtained at 0.1 MPa to 0.88 MPa pressure range and 353 K to 480 K temperature range. The specific heat dependence on pressure and temperature was presented. The increase in specific heat of 9-ethylcarbazole was observed with increasing pressure and temperature for solid phase, while for liquid phase decrease in trend was observed for increasing pressure.

**Keywords:** 9-ethylcarbazole, Adiabatic Calorimeter, Specific Heat, Nitrogen Gas Cylinder

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### 1. INTRODUCTION

Aromatic compounds can reversibly take up a large amount of hydrogen in chemical forms, which may offer a potential solution for storing hydrogen as a lightweight energy carrier. For instance, hydrogen gas can be supplied from these carriers on demand for mobile applications as a result of a change in pressure or temperature within a vehicle or device system. Interestingly, the organic based liquid-phase hydrogen carriers when assembled with fuel cells have been recently shown to deliver substantially higher energy density packages than those of lithium ion batteries. Furthermore, hydrogen is thought to be one of the most promising clean energy due to its many advantages such as pollution free, higher energy density, rich in quantity and highly efficient. Hydrogen energy is also being accepted as a fuel for many vehicles and portable devices within the near future [1], [2]. However, there are many problems to use hydrogen in daily life, out of which hydrogen storage is a major bottleneck. Due to these reasons, tremendous efforts have been made to search hydrogen storage materials which can hold hydrogen reversibly with high energy density [3], [4]. Hydrogen storage using organic heterocyclic liquid compound as a media is one of the most promising method for automotive applications. These storage materials are liquids at near ambient conditions and can be catalytically hydrogenated and dehydrogenated at relatively moderate temperatures [5]. This process is reversible by which reactant and products can be recycled between hydrogenation and dehydrogenation [6]. During hydrogenation and dehydrogenation, a surplus amount of heat is required to complete the process for hydrogen storage due to which thermodynamic properties are very important to be known and these are also affected by pressure.

Among different organic liquid compounds, 9-ethylcarbazole is the most suitable material for hydrogen storage because of its 5.8 wt. % gravimetric storage capacity [7]. Several studies have been reported on the kinetics of 9-ethylcarbazole hydrogenation and dehydrogenation. It was found that the hydrogenation and dehydrogenation of 9-ethylcarbazole are highly dependent on the temperature, pressure,

specific heat etc. [8]–[10]. The adiabatic calorimetry is the appropriate method for the measurement of specific heat at low temperatures [11], [12]. This method is preferable for specific heat measurement at low temperature due to the adiabatic control during the process and also use of a small amount of sample. An automated adiabatic calorimeter is used for precise specific heat measurement [13]. Isobaric heat capacities of R245fa and R236fa have been measured by using Calvet calorimeter and pressure balance unit [14]. The specific heat and other combustion properties of several carbazole compounds have been determined [15]–[19]. Previously, static bomb calorimeter has been used to measure the thermochemical properties of 9-ethylcarbazole at atmospheric conditions [20]. 9-ethylcarbazole in liquid form was investigated in this experiment. Moreover, 9-ethylcarbazole originally exists in solid form and it converts into liquid form at 67 °C. Therefore, in the present study, isobaric specific heat capacity in liquid and solid state was measured for the development of reliable thermodynamic property models. Applying the idea of automated adiabatic calorimeter with some modifications and pressure unit, the adiabatic calorimeter was constructed to determine the specific heat of 9-ethylcarbazole. The heat capacities were measured in solid and liquid phases at temperatures ranging from 294 K to 480 K and pressure up to 0.8 MPa in the adiabatic calorimeter. This temperature range was selected because the hydrogenation and dehydrogenation processes occur in this temperature range. Nitrogen gas cylinder was used to supply the required pressure for the experiment.

## 2. MATERIALS AND METHODS

### 2.1 Sample

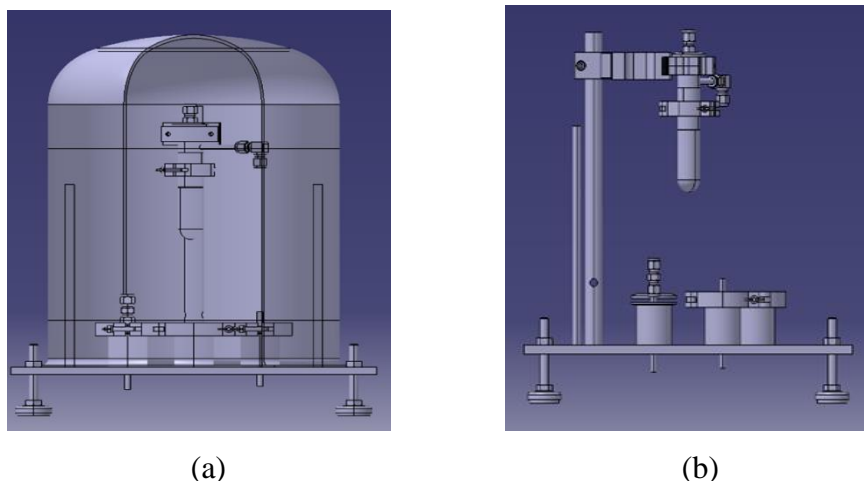
The sample for the present study was purchased from Sigma-Aldrich Company. The purity of the sample was 97%. The adiabatic calorimeter was constructed to measure heat capacity.

### 2.2 Adiabatic Calorimeter

An adiabatic calorimeter is a calorimeter used to examine a runaway reaction. Since the calorimeter runs in an adiabatic environment, any heat generated by the material sample under test causes the sample to increase in temperature, thus fueling the reaction. No adiabatic calorimeter is fully adiabatic - some heat will be lost by the sample to the sample holder. In addition, Adiabatic calorimetry is a technique that has also been introduced as an important approach to hazard evaluation of exothermically reactive systems.

In this manuscript, the adiabatic calorimeter consisted of a vacuum can and sample cell was constructed. The sample cell was attached to a metallic rod fixed to the base as shown in Fig. 1. The sample cell of 27.2 mm in diameter with 2.1 mm thickness, 70 mm long and 30 cm<sup>3</sup> volume was made of stainless steel. The sample cell was fully wrapped from outside with an insulation material of aluminum sheets to make sure that all the heat is absorbed by the sample in it. An electric heater was coiled around the sample uniformly to provide enough heat to the sample. The electric heater was also made of stainless steel with a wire thickness of 1 mm.

Three thermocouples (K-type) purchased from OMEGA Engineering were installed at different locations of the sample cell i.e. first at the bottom of the cell, second inside the heating wires and last one was installed inside of the sample cell. The vacuum can was made of stainless steel which was internally covered with the aluminum sheets to avoid any heat loss. Vacuum pump was attached to this vacuum can to remove the air. The system also comprised of programmable AC power supply, pressure regulator, and nitrogen gas cylinder and data acquisition system. Programmable AC power supply was used to provide the electric energy to electric heating wires coiled around the sample cell. Vacuum can insulated from inside was used to maintain the adiabatic conditions. The vacuum pump was connected to the vacuum can to perform the experiment under strict adiabatic conditions. The pressure was applied using nitrogen cylinder and the pressure regulator was installed to control the constant pressure continuously during the experiment. Moreover, a check valve was installed in order to avoid any leakage to the atmosphere.



**Figure:** Pictorial views of adiabatic calorimeter (a) Full view (b) Iso view

The actual diagram of the built in adiabatic calorimeter is shown in Fig. S1 (supplementary data).

### 2.3 Experimental Procedure

Specific heat measurement was conducted by taking 14 g of 9-ethylcarbazole in the sample cell and the vacuum pump was operated for making vacuum can and the pressure was maintained constant under strict adiabatic conditions. AC power supply was used to input electric energy for a short interval of time i.e. 90 sec which was used to raise the temperature during heating intervals. The specific heat was calculated by a transient change in temperature. The recorded temperature data in the data acquisition system was used to plot the graph and then this data was fitted using the following equation.

$$mC \frac{dT}{dt} = Q - k(T - T_{\infty}) \quad (1)$$

Multiplying and dividing by k on right side of the equation gives:

$$= k \times \frac{Q}{k} - k(T - T_{\infty})$$

$$= k \left( -\frac{Q}{k} - T + T_{\infty} \right)$$

By rearranging the above equation

$$mC \frac{dT}{dt} = -k \left( T - T_{\infty} - \frac{Q}{k} \right) \quad (2)$$

In the above equation, mC is the specific heat, Q is the heat supplied, T is the final temperature,  $T_{\infty}$  is the initial temperature and k is the heat transfer coefficient.

Let another well-known equation,

$$mC = \alpha + \beta(T - T_a) \quad (3)$$

where  $\alpha$  and  $\beta$  are constants and  $T_a$  is the atmospheric temperature.

Adding and subtracting  $T_{\infty} + \frac{Q}{k}$  on right side of equ.3

$$mC = \alpha + \beta \left( T - T_{\infty} - \frac{Q}{k} + T_{\infty} + \frac{Q}{k} - T_a \right)$$

$$mC = \alpha + \beta \left( T - T_{\infty} - \frac{Q}{k} + T_{\infty} + \frac{Q}{k} - T_a \right)$$

$$mC = \alpha + \beta \left( T_{\infty} + \frac{Q}{k} - T_a \right) + \beta \left( T - T_{\infty} - \frac{Q}{k} \right) \quad (4)$$

Comparing equ.3 & 4, we have

$$[\alpha + \beta(T_{\infty} + \frac{Q}{k} - T_a) + \beta(T - T_{\infty} - \frac{Q}{k})] \frac{dT}{dt} = -k(T - T_{\infty} - \frac{Q}{k})$$

Dividing both sides by  $(T - T_{\infty} - \frac{Q}{k})$ ; we get:

$$\frac{\alpha + \beta(T_{\infty} + \frac{Q}{k} - T_a)}{(T - T_{\infty} - \frac{Q}{k})} dT + \beta dT = -kdT \quad (5)$$

Let  $T_a = T_{\infty} + \frac{Q}{k}$

Hence, equ.5 can be rewritten as;

$$\frac{\alpha}{(T - T_{\infty} - \frac{Q}{k})} dT + \beta dT = -kdT \quad (6)$$

By integrating equ.6,

$$\alpha \times \ln(T - T_{\infty} - \frac{Q}{k}) + \beta T = -kT + ka \quad (7)$$

Where  $ka$  is the integration constant.

After rearranging equ.7,

$$kt = ka - \alpha \times \ln(T - T_{\infty} - \frac{Q}{k}) - \beta T$$

$$t = a - \frac{\alpha}{k} \times \ln(T - T_{\infty} - \frac{Q}{k}) - \frac{\beta}{k} \times T \quad (8)$$

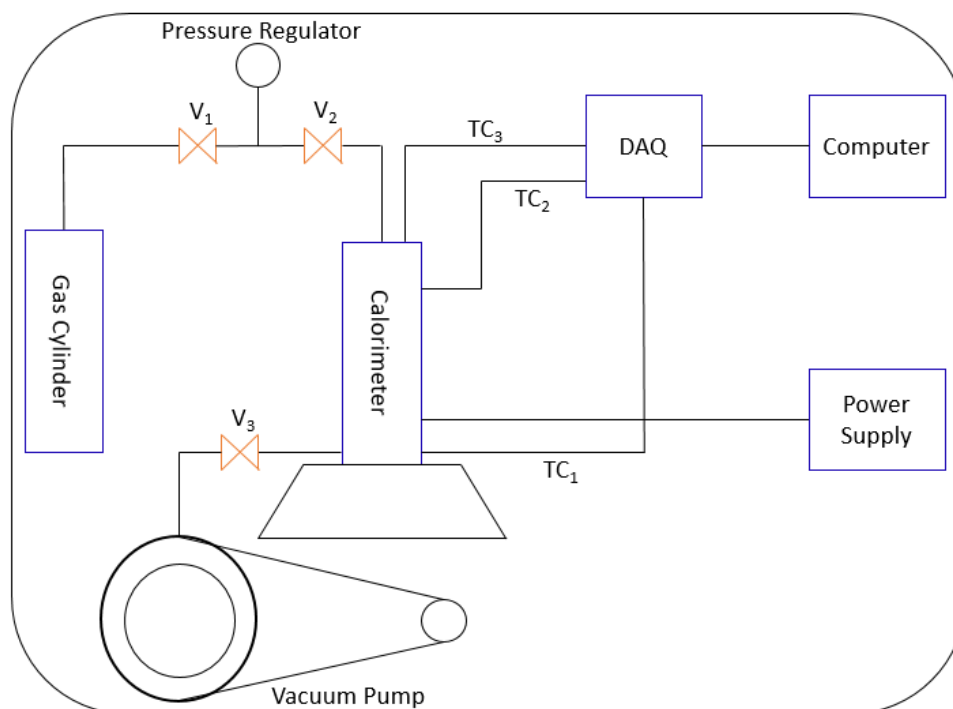
The equ.8 was applied to find out the unknown constant values  $\alpha$ ,  $\beta$  and  $k$  w.r.t. to time ( $t$ ) in origin 8 software. These values were used to calculate the specific heat of system and water. Later, the same procedure was done to measure the specific heat of 9-ethylcarbazole.

$$mC)_{sys} = \alpha + \beta(T - T_{\infty} - \frac{Q}{k}) \quad (9)$$

$mC)_{sys}$  represents the specific heat of the system. This was achieved by supplying heat to the empty sample cell. For  $mC)_{sys+water}$  the water was put in the sample cell.

$$mC)_{water} = mC)_{sys+water} - mC)_{sys} \quad (10)$$

For the case of higher pressure, the procedure was the same except, the sample was pressurized by using nitrogen gas. The pressure regulator was used for controlling the pressure from the nitrogen cylinder and pressure gauge was used to measure the pressure applied to the sample cell. At some phases of the experiment when the pressure was increased, fluctuation in trend was observed. The same procedure was then applied to obtain the average temperature rise. The schematic flow chart of experimental setup is shown in Fig. 2. The actual diagram of the experimental setup for the calculation of Isobaric specific heat capacity ( $C_p$ ) of 9-ethylcarbazole in liquid and solid state is shown in Fig. S2 (supplementary data).



**Figure 2:** Schematic of Experimental Setup

### 3. RESULTS AND DISCUSSION

#### 3.1 Validation of Apparatus

The specific heat of the water was measured to calibrate the accuracy of the apparatus. The 27 g of water was taken in the sample cell and the specific heat was measured by following the same procedure as discussed above. Numerical data for water heat capacity at 0.2 MPa and 0.5 MPa is listed in table S1 (supplementary data). The obtained experimental results were then compared with NIST data. In Fig. 3, the trend line of water heat capacity is shown which is quite like NIST data. The error was found up to 5 %. Our experimental calculations for water revealed that this apparatus can be used to measure the specific heat of 9-ethylcarbazole.

#### 3.2 Specific heat of 9-ethylcarbazole in the solid phase

Specific heat capacity is a measure of the amount of heat energy required to change the temperature of 1 kg of a material by 1 K. Hence it is important as it will give an indication of how much energy will be required to heat or cool an object of a given mass by a given amount. This will give information as to how long the heating or cooling process will take under a given supply, as well as the cost implications thereof. The specific heat of 9-ethylcarbazole in solid phase was measured at pressures ranging from 0.2 MPa to 0.8 MPa when the temperature was varied from 293 K to 325 K. This temperature was selected to make sure that the 9-ethylcarbazole remained in the solid phase within this temperature range and after 333K it changes its phase to liquid having a melting point of 340 K. The specific heat values increased from 1.4 J/g.K to 2.34 J/g.K. The trend in Fig. 4 showed that the specific heat of 9-ethylcarbazole increased with increment in pressure and temperature. Initially, at pressures 0.2 MPa and 0.3 MPa and lower temperatures up to 303 K, there is not a big difference in the values of specific heat. Anyhow, when the temperature inclined a certain increment in specific heat values can be seen for lower pressures. On increasing the pressure from 0.4 MPa to 0.8 MPa, higher values of specific heat were achieved as compared to lower pressures while on the higher temperature the calculated values were closed enough. Table S2 (supplementary data) listed the specific heat of 9-ethylcarbazole in the solid phase.

### 3.3 Specific heat of 9-ethylcarbazole in the liquid phase

The 9-ethylcarbazole changes its phase to liquid at almost 343 K. We conducted our experiment beyond 353 K to make it sure that all the sample was in liquid form. The temperature was increased from 365 K to 380 K when the pressure was varied from 0.2 MPa to 0.8 MPa. The specific heat of 9-ethylcarbazole was found to be lower than that of water which suggested that it absorbed the thermal energy more rapidly as compared to water. Moreover, it also elucidated that it might have higher thermal conductivity. It can be seen from Fig. 5 that the pressure had a significant effect on the specific heat of 9-ethylcarbazole, increasing pressure lowered the specific heat value while it was opposite for the temperature. At lower temperatures, of 9-ethylcarbazole was decreased while after 450 K, there was not much difference among the specific heat values irrespective of the pressure. It seemed like that at higher temperatures, pressure had a negligible effect on the specific heat calculations. A similar trend was found for the specific heat of 9-ethylcarbazole in the solid phase. Moreover, there was a sudden increase in the specific heat value after the temperature was passed over 440 K. This sudden increment needs to be explained in later studies. All the measured data is listed in Table S3 (supplementary data). The specific heat behavior with temperature was compared with published data [14], [21]. The increasing trend with temperature and deviation with pressure was previously observed in literature [22]. In addition the many basic ideas have already been published in our published materials

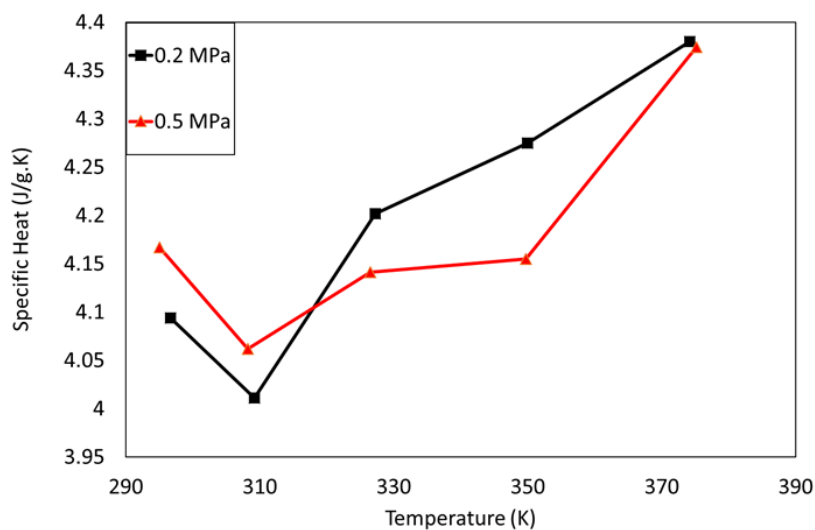


Figure 3: Specific water of water at pressures 0.2 MPa and 0.5 MPa

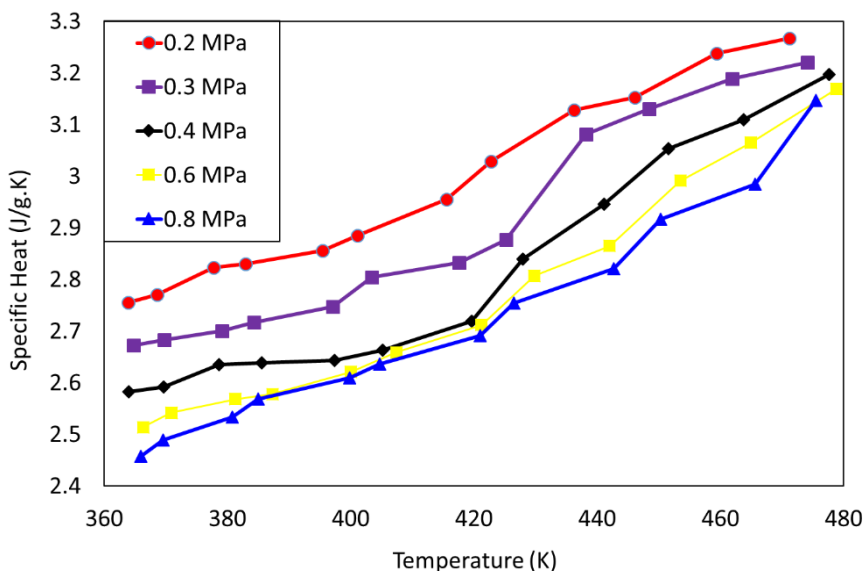
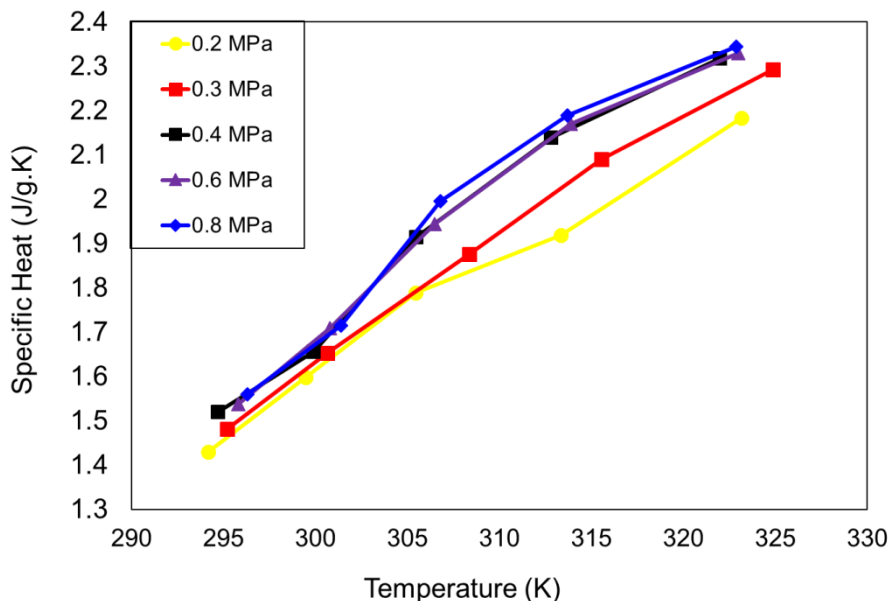


Figure 4: Specific heat of 9-ethylcarbazole from 0.2 MPa to 0.8 MPa



**Figure 5:** Specific water of 9-ethylcarbazole in liquid phase from 0.2 MPa to 0.8 MPa

#### 4. CONCLUSIONS

An adiabatic calorimeter for measurement of specific heat in liquid and solid was constructed and tested. The experimental setup was consisted of two basic components which were adiabatic calorimeter and pressure unit. Apparatus was calibrated by measuring specific heat of water with an error of 5 %. The experiment was conducted in a temperature range of 353 K to 453 K keeping the pressure constant. The pressure was increased from 0.2 MPa to 0.8 MPa to investigate its effect on specific heat. The specific heat of 9-ethylcarbazole elucidated distinct trends for both phases w.r.t various pressure and temperature ranges. For solid phase, specific heat of 9-ethylcarbazole increased with increment in pressure from 0.2 MPa to 0.8 MPa and temperature. The specific heat values increased from 2.183 J/g.K at 0.2 MPa to 2.34 J/g.K at 0.8 MPa. Anyhow, the values of the specific heat in liquid phase showed declination at higher pressures and presented opposite behavior with increment in temperature. At 0.2 MPa, the specific heat has a maximum value of 3.267 J/g.K which was decreased to 3.147 J/g.K at 0.8 MPa. The results showed that the 9-ethylcarbazole absorbs heat rapidly as it goes into the liquid phase. Moreover, the pressure has a direct effect on lowering the amount of heat required for raising the temperature of 9-ethylcarbazole in liquid phase.

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