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HEAT CAPACITY UNCERTAINTY CALCULATION FOR THE EUTECTIC MIXTURE OF BIPHENYL/DIPHENYL ETHER USED AS HEAT TRANSFER FLUID

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Abstract

The main objective of this study was to calculate the uncertainty at 95% confidence for the experimental values of heat capacity of the eutectic mixture of biphenyl/diphenyl ether (Therminol VP-1) determined from 300 to 370 °C. Twenty-five samples were evaluated using differential scanning calorimetry (DSC) to obtain the sample heat flow as a function of temperature. The ASTM E-1269-05 standard was used to determine the heat capacity using DSC evaluations. High-pressure crucibles were employed to contain the sample in the liquid state without vaporizing. Sample handling has a significant impact on the random uncertainty. It was determined that the fluid is difficult to handle, and a high variability of the data was produced. The heat capacity of Therminol VP-1 between 300 and 370 °C was measured to be equal to 0.0025T+0.8672 with an uncertainty of ± 0.074 J/g.K (3.09%) at 95% confidence with T (temperature) in Kelvin.

Keywords: biphenyl/diphenyl ether, heat capacity, uncertainty, differential scanning calorimetry.

1. Introduction

The heat transfer characteristics of large-scale solar parabolic trough power plants rely on the thermal properties of a high-temperature synthetic oil (eutectic mixture of biphenyl/diphenyl ether) also known by the commercial names Therminol VP-1 [1–3] and Dowtherm A. Accurate knowledge of the oil's properties, in particular heat capacity, is important for the efficient operation of concentrating solar power (CSP) plants and thus reduces their operating costs. This eutectic mixture has a low melting point of 12 °C, a boiling point of 257 °C, and a maximum operating temperature of 400 °C at elevated pressure [3]. For the oil to be in the liquid phase at the current operating temperatures (293 – 393 °C), the plants need to operate at high pressure (approximately 1.2–1.5 MPa).

The experimental evaluation of the thermal properties of liquid biphenyl/diphenyl ether is extremely difficult under the plant operating conditions. Cabaleiro et al. experimentally measured the density, viscosity, and thermal conductivity of pure diphenyl ether and three different binary mixtures of diphenyl ether and biphenyl, including the eutectic mixture, from 288.15 K (15 °C) to 343.15 K (70 °C) [1]. The density was measured at 45 MPa of pressure, but viscosity and thermal conductivity were measured at atmospheric pressure.

Just a few articles have reported the experimental heat capacity of this eutectic synthetic oil [4]. The liquid heat capacity values reported in the literature [3] are an extrapolation from low temperatures, below its boiling point of 257 °C. Knowledge of a more accurate value of its heat capacity at high temperatures is extremely important for calculating the thermal energy absorbed by the solar collector field at parabolic trough plants. Total uncertainty of heat capacity has been reported in the literature for different calorimeter techniques [5–8].

2. Measurement procedure

The heat capacity was measured using a differential scanning calorimeter DSC1 STARe System from Mettler-Toledo. The instrument measures the difference between heat flows from the sample and reference (empty crucible) sides of a sensor as a function of temperature or time. The sensor has 120 thermocouples, which guarantee excellent sensitivity.

The specific heat capacity (C) measurements were performed following the standard ASTM E-1269-05. This method consists of heating a blank (baseline), the sample, and a sapphire disk (reference material for C measurements) through the same temperature range at a fixed rate in a controlled atmosphere (nitrogen flow as protective gas at 80 cm^3/min). The difference in heat flow between the blank (reference) and the sample or the sapphire, due to energy changes, is continuously recorded. The system provides corrected heat flows for the sapphire (HF_{Ref}) and for the sample (HF_{Sample}). This information is obtained after subtracting the heat flow of the blank (baseline) from the sample or sapphire. The software STARe from Mettler-Toledo was used to determine the heat capacities of the samples in which the corrected heat flow values are used to calculate the unknown heat capacity of the sample (C_{Sample}) by using the known values for the heat capacity of the sapphire reference material (C_{Ref}) and the weights of the reference sapphire (W_{Ref}) and the sample (W_{Sample}) following the equation:

$$C_{Sample} = C_{Ref} \times \frac{HF_{Sample}}{HF_{Ref}} \times \frac{W_{Ref}}{W_{Sample}} \quad (1)$$

Uncertainty calculations for DSC measurements have been a subject of some controversy. Different articles have discussed the ways to minimize errors associated with recording data. They have identified that DSC can perform thermal properties measurements (phase transition temperatures and their latent heats, heat capacities, etc.) with low uncertainty if the calibration of the instrument is carefully performed [5]. This analytical calibration must be executed by using high-purity reference materials with well-known melting temperatures and heats of fusion. We performed temperature and heat flow calibrations for the DSC by melting indium and zinc and recording the onsets and their respective heats of fusion. This calibration was carried out prior to running the heat capacity method for the blanks, samples, and sapphires.

As stated by Rudtsch (2002), the repeatability of DSC measurements is in most cases the major source of uncertainty. The factors that influence achieving good repeatability are the thermal contact and thus the heat transfer conditions between the sample, crucible, sensor/furnace, and the surroundings [6,7]. Therefore, control of the atmosphere, sensor cleanliness, and crucible positioning play important roles on the uncertainty. To minimize these effects, positioning of the crucibles in the measuring cell was executed by an autosampler; the sensor was cleaned carefully using dry air before performing the tests; vibrations and gas flow fluctuations were avoided; and three runs per sample were recorded to report the average of the runs per sample. The uncertainty associated with the mass of the samples and sapphires was minimized using a balance with a resolution of 0.001 mg.

3. Heat capacity uncertainty

Nowadays it is commonly accepted that the statement of quantitative results obtained from measurements should contain both the values attributed to the measuring process and the associated uncertainty [6]. Uncertainty is the preferred term, instead of precision, trueness, etc., used to define the level of confidence or the accuracy of a measurement. Uncertainty considers both the random error (precision) and the systematic error (bias). Those errors define the band in which the true value of the measurement can be expected to lie with a stated confidence level. Error is defined as “the true difference between the true value of the parameter being measured and the measurement obtained (measurand)” [9]. As the true value is never known, the error cannot be calculated.

Knowing the error will allow us to correct the data. Because of this, we need to calibrate the instrument to trade the large unknown error we would have without calibration for the expected small errors resulting from the calibration process.

Uncertainty is "an estimate of the limits in which we can expect an error to go, under a given set of conditions as part of the measurement process" [9]. Random uncertainty sources are those that cause scatter in the data. Random uncertainty is obtained using the standard deviation ($S_{X,i}$) of the elemental random source *i*, as follows:

$$S_{X,i} = \left[\frac{\sum_{k=1}^{N_i}\left(X_{i,k} - \bar{X}_i\right)^2}{N_i - 1}\right]^{\frac{1}{2}} \tag{2}$$

The sum is over *k* where there are N_i (number of data points averaged for error source *i*) values of $X_{i,k}$with its average $\bar{X}_i$.

What matters the most about an error source is its average effect for a particular experimental error. This represents the random standard uncertainty for an error source ($S_{\bar{X},i}$) or standard error of the mean for error source *i*, and it is calculated as follows:

$$S_{\bar{X},i} = \frac{S_{X,i}}{\sqrt{N_i}} \tag{3}$$

The combined effect of the several random uncertainties on the average for the test result that needs evaluation will define the total random standard uncertainty ($S_{\bar{X},R}$), which is determined by:

$$S_{\bar{X},R} = \left[\sum_{i=1}^{N_i}\left(S_{\bar{X},i}\right)^2\right]^{\frac{1}{2}} \tag{4}$$

Those sources that do not produce scatter in the results will produce systematic uncertainties (b_i) that are constant for the duration of the test and are associated with the instrument itself. They will affect every measurement equally and are not observable in the test data. It is a common approach for DSC manufacturers to report the systematic uncertainty of their instruments (b_R) as that associated with the measured heat capacity of stable samples in which their heat capacities are well reported in the literature. The manufacturers usually use single-crystal sapphire disks to report the systematic uncertainty.

The total uncertainty with 95% confidence (U_{95}) is then calculated using the systematic uncertainty (b_R), the total random standard uncertainty ($S_{\bar{X},R}$) with the Student's *t* at 95% confidence (t_{95}) as follows:

$$U_{95} = \pm t_{95}\left[(b_R)^2 + \left(S_{\bar{X},R}\right)^2\right]^{\frac{1}{2}} \tag{5}$$

The Student's *t* is determined using the degrees of freedom for the sample (*v*), which is the number of data points used to calculate the standard deviation minus one (*N-1*). With the degree of freedom, the following table is employed to determine the value of t_{95}.

ν	t_{95}	ν	t_{95}	ν	t_{95}
1	12.706	11	2.201	21	2.080
2	4.303	12	2.179	22	2.074
3	3.182	13	2.160	23	2.069
4	2.776	14	2.145	24	2.064
5	2.571	15	2.131	25	2.060
6	2.447	16	2.120	26	2.056
7	2.365	17	2.110	27	2.052
8	2.306	18	2.101	28	2.048
9	2.262	19	2.093	29	2.045
10	2.228	20	2.086	≥ 30	2

Table 1: Student's *t* for 95% confidence [9].

The systematic uncertainty for the DSC1 used in this investigation was determined by performing several heat capacity calculations using a sapphire disk as the sample as well as the reference material. The known values of heat capacity of sapphire as a function of temperature reported in the standard ASTM E-1269-05 are included in the database of STARe software. Those values were considered as the "true" value for that particular sample (sapphire).

The heat flow of seven sapphire samples was measured from 300 to 380 °C at 20 K/min. Isothermals of 10 minutes were employed before and after the dynamic region. High-pressure crucibles made of stainless steel were employed. The heat capacity of these sapphire samples was indirectly measured by STARe software using equation 1. The error of the measurement was then determined by subtracting the expected heat capacity value (reference) from the measured value. Figure 1 shows the reference values (red diamonds) as well as the measured values (blue squares) for the average heat capacity of the seven sapphire runs. The measured values are slightly off (b_R =0.005 J/g.K) at low temperatures, but the accuracy increases above 360 °C (b_R =0.001 J/g.K). The average error for the temperature range from 300 to 380 °C was (b_R =0.004 J/g.K).

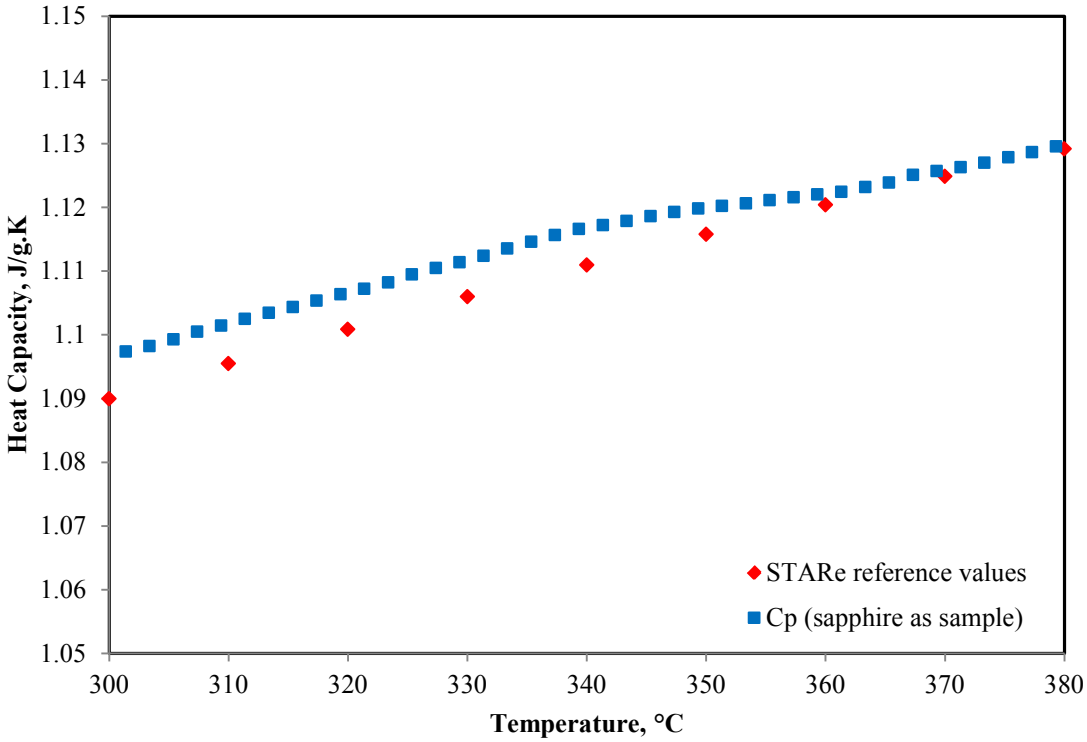


Fig. 1: Heat capacities of a single-crystal sapphire disk used as the reference and the sample to determine the systematic uncertainty of the differential scanning calorimeter DSC1 Stare System from Mettler-Toledo.

To determine the heat capacity of the synthetic oil Therminol VP-1 (eutectic of biphenyl/diphenyl ether), the same temperature method used to determine the systematic uncertainty was employed. As this oil has a boiling point of 257 °C and a maximum operating temperature of 400 °C at elevated pressure [3], high-pressure crucibles with a capacity of 30 µL were employed to keep the sample in the liquid state. A sample of Therminol VP-1 was provided by its manufacturer, Solutia, Inc. High-pressure crucibles maintained the sample in the liquid state at constant volume because the containing vessel is rigid and very strong. The test occurred at the saturation pressure of the sample where the DSC measured the constant volume specific heat. Constant pressure specific heat is virtually equivalent to constant volume specific heat for incompressible liquids.

Handling of the sample has a significant impact on the random uncertainty. It was determined that Therminol VP-1 is difficult to handle, and a high variability of the data was produced. It was found that the placement of the oil inside the crucible was a difficult task because of the small amount of mass required. Because the maximum temperature in which Therminol VP-1 is stable is 400 °C, the highest temperature for the heat capacity measurement was 390 °C. In DSC measurements, there is a thermal lag in the heat flow at the beginning and the end of the heating cycle. This artifact of approximately 20 °C makes the recordable heat flow values at these temperatures useless. For this reason the heat capacity values reported for Therminol VP-1 are from 300 to 370 °C.

To decrease the variability of the results, each of the 25 samples tested was run consecutively during three heating cycles without removing them from the measuring cell. The average heat capacity for 25 samples is shown in Fig. 2 as a function of temperature. Using equations 2 – 5 with the data of Therminol heat capacities

and the Student's t for 24 degrees of freedom as 2.064, the total uncertainty at 95% confidence (U_{95}) was ± 0.074 J/g.K (3.09 %). The heat capacity of Therminol VP-1 between 300 and 370 °C was measured to be equal to 0.0025T+0.8672 ± 0.074 J/g.K with T (temperature) in Kelvin.

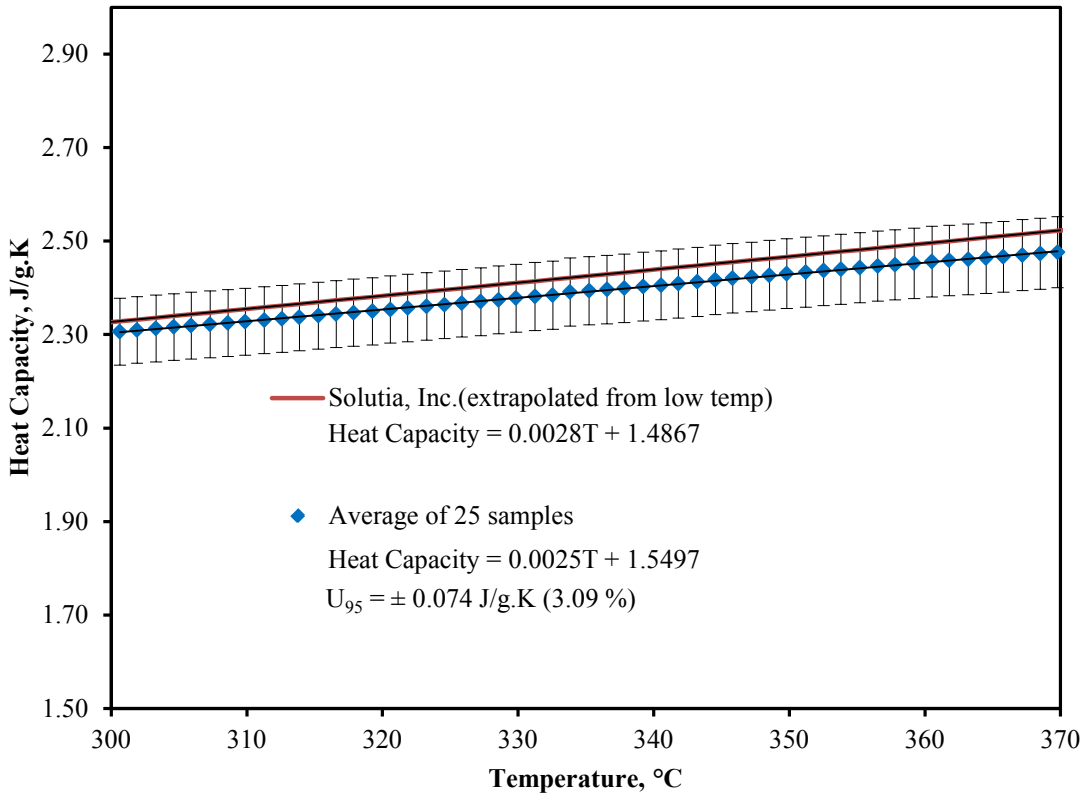


Fig. 2: Heat capacity of 25 samples of biphenyl/diphenyl ether eutectic (Therminol VP-1). Uncertainty at 95% confidence (U_{95}) is provided. Solid line represents the extrapolated values from low temperatures reported by its manufacturer, Solutia, Inc.

4. Conclusions

The heat capacity of Therminol VP-1 (eutectic of biphenyl/diphenyl ether) from 300 to 370 °C was measured in a differential scanning calorimeter (DSC) following the standard ASTM E-1269-05. Three heating cycles were used per run per sample to decrease the scatter in the results. Isothermals of 10 minutes were employed before and after the dynamic section in which a heating rate of 20 K/min was employed. The uncertainty of the heat capacity of Therminol VP-1 was calculated. Both systematic and random uncertainties were determined. The heat capacity for 25 samples was found to be 0.0025T+0.8672 with T (temperature) in Kelvin. The total uncertainty of ± 0.074 (3.09 %) J/g.K was obtained. Volatile samples such as Therminol VP-1 must be carefully handled to minimize the uncertainty associated with the scatter of the results and thus obtain accurate thermal properties measurements using a DSC.

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