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Determination of Isobaric Enthalpy Differences of Heat Transfer Fluids

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Abstract. The heat capacity of eutectic diphenyl oxide (DPO) and biphenyl (BP) was investigated with Calvet-type differential scanning calorimetry. Significant impact of the sample mass per crucible was found. With 82 mg per 130 μ l lowest impact by heat of evaporation on the readings was achieved. With the linear data fit C (in $J/(g \cdot K)$) = $0.00268 \cdot T$ (in $^{\circ}C$) + 1.4917 in the range of 130 – 409 $^{\circ}C$ the calculated enthalpy difference between 300 $^{\circ}C$ and 400 $^{\circ}C$ is 0.6 – 3.7% smaller in comparison to the projections based on manufacturer's data sheets. The impact of pressure on the enthalpy difference was tested with a compression loop between 17 bar and 63 bar. It could be shown that additional mechanical pressure causes decreases of the enthalpy difference by -0.03% $J/(g \cdot bar)$.

INTRODUCTION

The mixture of 26.5 % biphenyl (BP) and 73.5 % diphenyl ether (diphenyl oxide, DPO) still is the heat transfer fluid (HTF) most commonly applied in parabolic trough systems. [1] The heat capacity of the fluid determines the mass flow that is required for collecting the heat from the solar field within the designated temperature limits and therefore impacts the plant design and economics of power generation.

Although precise heat capacity data are required scientific literature neither covers the relevant temperature range completely nor the impact of mechanical pressure, dissolved blanket gas or aging products. Gomez et al. presented a study on the heat capacity of Therminol[®] VP-1 with differential scanning calorimetry (DSC) according to ASTM E-1269-05 using steel crucibles with a capacity of 30 μ l and a DSC1 STARe system from Mettler-Toledo. The authors measured 25 samples each for three times and generated a linear fit from the results of these measurements. The heat capacity between 300 – 370 $^{\circ}C$ is reported with 3.09% uncertainty at 95% confidence. [2] Cabaleiro et al investigated the isobaric heat capacity of BP/DPO mixtures at 1 bar with DSC between 0 – 100 $^{\circ}C$. [3] In addition, the author published a study on the isobaric heat capacity of BP/DPO mixtures using a flow calorimeter at pressures up to 250 bar and 40 – 80 $^{\circ}C$. [4]

Data sheets of industrial products like DowthermTM A (Dow), Therminol[®] VP-1 (Eastman) and Diphyl[®] (Lanxess) include heat capacity without indicating their uncertainty. Lanxess proposes the smallest values and linear increase with rising temperature, Eastman and Dow present progressive trends from about 350 $^{\circ}C$ to 405 $^{\circ}C$ and 420 $^{\circ}C$ respectively (Fig. 1). [5-7]

The heat (Q) collected by the HTF during the passage through the solar field will be evaluated differently depending on the set of heat capacity data (C) taken into account. For comparison the manufacturer's data are fitted with a polynomial equation (1). The parameters (a_n) generated by such fits are presented in table 1.

$$C = a_6 T^6 + a_5 T^5 + a_4 T^4 + a_3 T^3 + a_2 T^2 + a_1 T + a_0 \quad (1)$$

By integration of (1) the heat stored in the HTF between two temperatures (T_1 and T_2) can be calculated according to (2).

$$Q = \frac{a_6}{7}(T_2^7 - T_1^7) + \frac{a_5}{6}(T_2^6 - T_1^6) + \frac{a_4}{5}(T_2^5 - T_1^5) + \frac{a_3}{4}(T_2^4 - T_1^4) + \frac{a_2}{3}(T_2^3 - T_1^3) + \frac{a_1}{2}(T_2^2 - T_1^2) + a_0(T_2 - T_1) \quad (2)$$

The designated temperature increase in solar fields typically is 100K. Taking the stability limit of BP/DPO into account a temperature difference of 300 – 400 °C is to be considered for parabolic trough plants. When the parameters calculated with Dow’s data are used the heat content of eutectic BP/DPO in this temperature range is rated 3.1% higher compared to the parameter set calculated with the data provided by Lanxess (table 2).

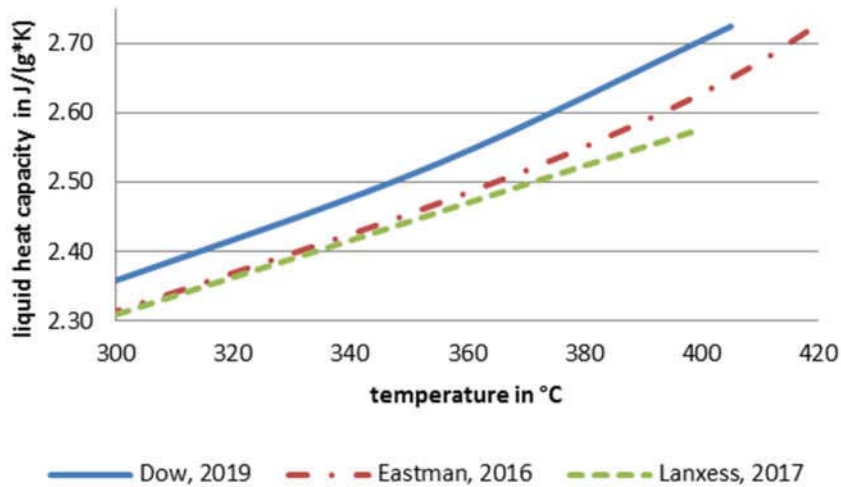


FIGURE 1. Heat capacity of eutectic BP/DPO according to manufacturer’s data sheets

TABLE 1. Coefficients of polynomial heat capacity fits with literature data for eutectic BP/DPO [5-7]

Data source	T _{min} (°C)	T _{max} (°C)	a ₆ (10 ⁻¹⁶)	a ₅ (10 ⁻¹³)	a ₄ (10 ⁻¹¹)	a ₃ (10 ⁻⁸)	a ₂ (10 ⁻⁶)	a ₁ (10 ⁻³)	a ₀
[7]	15	405			3.22	-1.99	3.68	2.61	1.5189
[6]	12	420	8.67	-9.49	40.5	-8.26	7.35	2.62	1.4914
[5]	20	400						2.68	1.5036
[2]*	300	370						2.5	1.5497

* Coefficients given in literature

TABLE 2. Enthalpy difference of eutectic BP/DPO between 300 – 400 °C based on coefficients of table 1 and equation (2)

Data source	ΔH (J/g)	ΔH (rel.)
[7]	251.8	103.1%
[6]	245.9	100.7%
[5]	244.3	100.0%
[2]	242.5	99.2%

In addition to the lack of high temperature data in the scientific literature and the ambiguity of manufacturer’s data there is also some uncertainty related to the difference of heat capacity at constant pressure, constant volume or at saturation pressure. The DSC experiment does obviously not directly deliver any of these properties in an ideal manner. This is as the pressure increases during the measurement according to the rising vapor pressure and the compression of blanket gas which is usually included in the crucibles. The volume is not constant as well although closed crucibles are used as the volume of the fluid increases during the measurement due to significantly decreasing liquid density at high temperature. The measurement would be at saturation pressure if the gas had been removed before sealing the crucible.

Given that a sample of HTF is filled into a crucible and sealed in a nitrogen atmosphere, the measurement will start at ambient conditions in temperature and pressure. During the heating up of the sample the fluid will expand and pressure will rise due to the compressed nitrogen blanket. Moreover, some sample will evaporate due to the steadily increasing vapor pressure. Hence, the signal will be sum of all effects occurring in the crucible.

According to the standard ASTM E-1269-05 measurements of heat capacity have to be performed with sample masses of 5 – 15 mg. As the size of crucible is not defined in this standard a severe lack of clarity arises concerning the condition of measurement. This is as larger gas space in a crucible will give rise to larger contributions of heat of evaporation to the apparent heat capacity finding.

The heat capacity of eutectic BP/DPO is important for economic considerations of CSP projects and for the qualification of components like collectors. In this study we aim at clarifying the heat capacity of eutectic BP/DPO under saturation pressure at temperatures at least up to 400 °C. Comparative enthalpy difference measurements between 300 - 400 °C at constant pressure conditions are performed to cover the typical operation conditions of parabolic trough systems.

EXPERIMENTAL METHODS, INSTRUMENTATION AND MATERIALS

Materials

A mixture of biphenyl (26.5%) and diphenyl ether (73.5%) was used without further purification. Purity of at least 99.5% was confirmed with gas chromatograph analysis with flame ionization detection (GC-FID). Gases (nitrogen, helium, hydrogen and oxygen) were applied with purity of 99.999%. Potassium nitrate (>99%), indium spheres (1 mm, 99.99%), rubidium nitrate (99.975%), tin shot (3 mm, 99.99%), potassium perchlorate (>99%), lead shot (3 mm, 99.99%), silver sulfate (99.999%) and cesium chloride (99.99%) were employed for calibrating the DSC. Sapphire (single crystalline) from Setaram was applied as reference material for heat capacity measurements.

Differential Scanning Calorimetry

A sensys evo instrument from Setaram was used. This heat flux DSC is calorically calibrated via Joule effect. The Calvet-type sensors detect the heat flow around the cylindrical sample and reference crucibles. Gold plated stainless steel crucibles (Tüv Süd, M130) with a volume of 130 μ l were used. Thermal calibration was performed for heating rates from 0.5 – 5 K/min with potassium nitrate, indium, rubidium nitrate, tin, potassium perchlorate, lead, silver sulfate and cesium chloride between 129 – 476 °C. Heat capacities were determined with the so-called step method to achieve maximum sensitivity. [8] After 20 min isothermal phase at 125 °C heating steps of 10 K at 2 K/min are followed by isothermal intervals of 20 min up to 425 °C with a carrier gas flow of 15 mL/min and auxiliary gas flow of 5 mL/min (both nitrogen). The correctness of the DSC calibration was confirmed by measurement of sapphire single crystals before the measurement of HTF samples. All crucibles were filled in an atmosphere of nitrogen.

Measurement of Isobaric Enthalpy Changes

For determining the enthalpy change of eutectic BP/DPO mixtures under constant pressure an experiment (compression loop) was constructed that allowed for heating up the pressurized HTF to a defined temperature at constant mass flow. The hot liquid was then passed through a heat exchanger and the thermal energy transferred to water was determined via its known heat capacity according to the IAPWS 95 formulation [9] by measuring the mass flow and temperature change. The set-up is shown in Fig. 2.

The so-called compression loop includes a pressurized vessel as fluid reservoir. The sample flows from the bottom of the vessel into a piston pump (Knauer, 80P) which allows for volume flow rates up to 250 ml/min at pressures up to 200 bar. The mass flow of the fluid is determined with a Coriolis sensor (Bronkhorst, Cori-Flow M14, 0.2 - 10 kg/h) before entering a heat exchanger that is supplied with hot air provided by a fan convection furnace (Carbolite, HT6/95). The hot HTF enters the inner tube of a concentric tube heat exchange while water is passed through the annular gap between its inner 1/8" and the outer 1/4" stainless steel tube. The pressure of the HTF is measured before and after the passage through the furnace and the heat exchanger using piezoresistive transmitters (before the furnace with Keller, 35XHTT, 0 - 100 bar, before and after the heat exchanger with Ashcroft, G2, 0 - 1000 PSI) and temperature is recorded with Pt 100 sensors (Greisinger, GMH3750) before and

after the heat exchanger. Pressure and temperature of the demineralized water is recorded with piezoresistive transmitters (Keller, 35XHTT, 0 - 100 bar) and Pt 100 sensors (Greisinger, GMH3750). Pressurized water is applied for cooling to prevent boiling and to allow for precise control of the HTF outlet temperature by cooling with pre-heated water. The latter is mainly obtained by heat exchange with the hot water outlet of the HTF heat exchanger. The mass flow of water is measured with a Coriolis sensor (Bronkhorst, Cori-Flow M14, 0.6 - 30 kg/h). The water pressure is maintained with a plunger pump (Speck, NP10/1-170REET). The pressures in the HTF and the water cycle are controlled by regulating valves. Additional measurements of temperature and pressure listed in Fig. 1 aim at avoiding critical conditions for the components in the cold parts of the system.

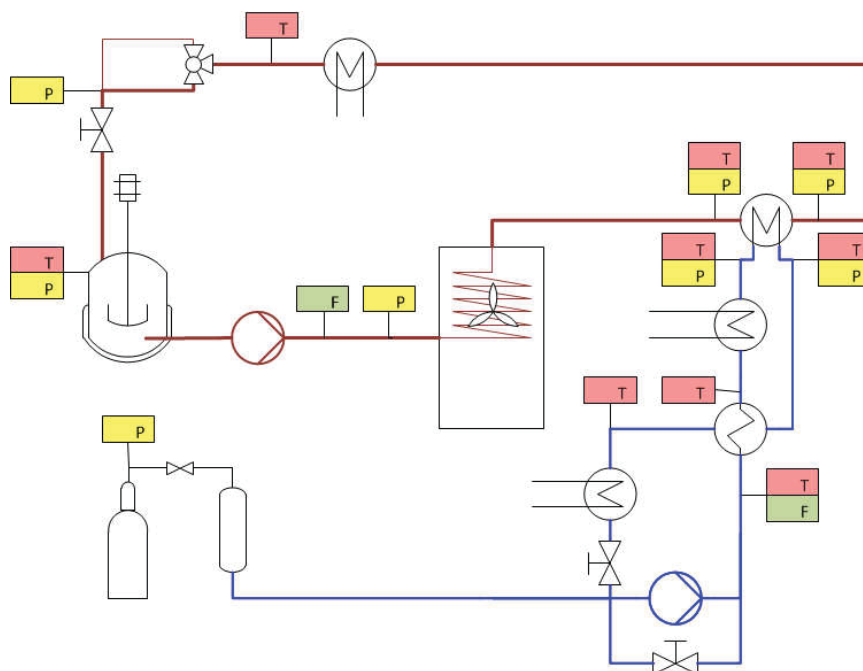


FIGURE 2. Compression loop for determining isobaric enthalpy changes of HTF

EXPERIMENTAL RESULTS AND DISCUSSION

Differential Scanning Calorimetry

The mass of eutectic BP/DPO per crucible was varied from 40 – 80 mg per 130 μl . 90 mg was also attempted but caused leakages most likely due to the thermal expansion at the maximum temperature. Each crucible was measured twice. Although 400 $^{\circ}\text{C}$ is considered as a stability limit of the fluid the readings of the second measurement are neither significantly larger nor smaller than those of the first run. The data presented in Fig. 3 and in table 3 have a relative uncertainty of 1.1% according to the average standard deviation of nine sapphire measurements compared to reference data. [10] A rigorous evaluation of uncertainty according to GUM is not yet available. [11] In Fig. 3 an uncertainty of 2% is assumed.

The heat capacities do not differ significantly among all samples at low temperatures. With the lower masses apparently stronger increase of heat capacity is found above 300 $^{\circ}\text{C}$ compared to crucibles with higher masses. Taking an uncertainty of 2% into account the deviation between the samples with 60 - 80 mg HTF is not significant within the measured range.

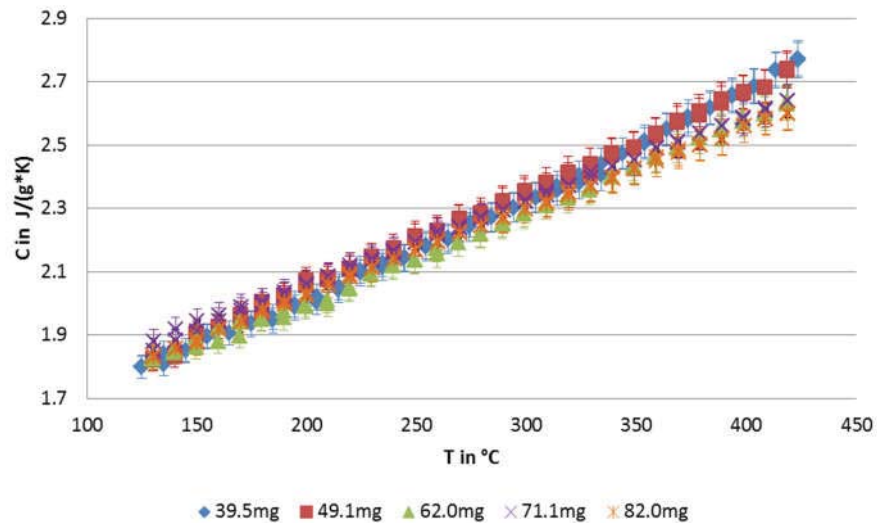


FIGURE 3. Experimental heat capacity of eutectic BP/DPO according to DSC for 40 – 80 mg per 130 μ l crucible

TABLE 3. Experimental heat capacity in J/(g*K) of eutectic BP/DPO at different temperatures in $^{\circ}$ C according to DSC (average of two measurements per crucible)

HTF mass per crucible in mg									
39.5		49.1		62.0		71.1		82.0	
T	C	T	C	T	C	T	C	T	C
125	1.80	130	1.82	130	1.83	130	1.87	130	1.83
135	1.83	140	1.84	140	1.85	140	1.90	140	1.86
145	1.85	150	1.90	150	1.88	150	1.93	150	1.88
155	1.90	160	1.93	160	1.90	160	1.95	160	1.92
165	1.91	170	1.96	169	1.92	170	1.98	170	1.94
175	1.94	180	1.99	179	1.95	180	2.00	180	1.98
185	1.95	189	2.02	189	1.97	190	2.03	190	2.00
195	1.99	199	2.07	199	1.99	200	2.06	200	2.03
204	2.01	209	2.08	209	2.01	210	2.09	210	2.06
214	2.05	219	2.11	219	2.05	220	2.11	220	2.09
224	2.10	229	2.14	229	2.10	230	2.14	230	2.11
234	2.12	239	2.17	239	2.12	240	2.16	240	2.14
244	2.14	249	2.21	249	2.14	250	2.19	250	2.17
254	2.18	259	2.23	259	2.17	260	2.22	260	2.19
264	2.20	269	2.27	269	2.19	269	2.24	270	2.22
274	2.25	279	2.28	279	2.22	279	2.27	279	2.25
284	2.27	289	2.32	289	2.25	289	2.29	289	2.27
294	2.30	299	2.35	299	2.28	299	2.32	299	2.30
304	2.33	309	2.37	309	2.31	309	2.35	309	2.32
314	2.36	319	2.41	319	2.34	319	2.37	319	2.35
324	2.39	329	2.42	329	2.36	329	2.41	329	2.37
334	2.42	339	2.47	339	2.40	339	2.43	339	2.40
344	2.47	349	2.49	349	2.43	349	2.45	349	2.42
354	2.51	359	2.53	358	2.46	359	2.49	359	2.46
364	2.55	369	2.58	368	2.49	369	2.51	369	2.48
374	2.59	378	2.60	378	2.52	379	2.54	379	2.50
384	2.62	388	2.64	388	2.55	389	2.56	389	2.52
393	2.66	398	2.67	398	2.58	399	2.59	399	2.56
403	2.69	408	2.68	408	2.60	409	2.61	409	2.58

According to the polynomials fitted to the complete range of experimental data the calculated enthalpy difference of the HTF between 300 - 400 °C decreases proportionally with the amount of sample per crucible (table 4 and Fig. 4).

TABLE 4. Polynomial fit coefficients for the experimental data of table 3 and resulting enthalpy differences between 300-400 °C

HTF mass (mg)	a_1 (10^{-3})	a_0	ΔH (J/g)
39.5	3.24	1.3660	250.0
49.1	3.09	1.4298	251.1
62.0	2.85	1.4366	243.4
71.1	2.67	1.5250	245.8
82.0	2.68	1.4917	242.8

Contributions of the heat of evaporation to the heat flow signal cause apparently larger heat capacities. Accordingly, the cause for the higher findings at low sample mass per crucible is increased evaporation of the fluid as more gas space is available. Thus, measurements at large filling levels are to be preferred before any numerical correction of the measurement is considered.

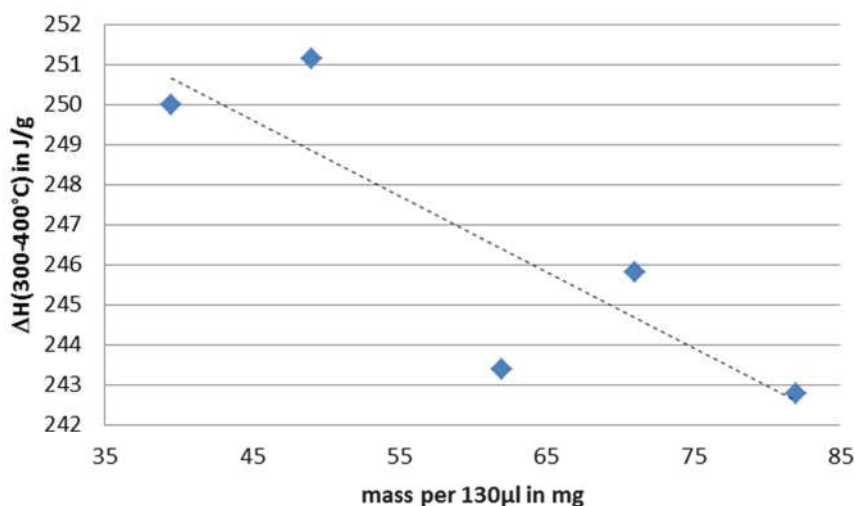


FIGURE 4. Calculated enthalpy differences between 300 - 400 °C according to the fit functions obtained for different sample masses per crucible

Evacuating the crucibles before closing would be beneficial in order to avoid any effects of the nitrogen which is used as inert gas. The latter will be compressed and partly dissolved during the measurement. As long as no extremely high pressures result from such compression of nitrogen no significant distortion of the heat capacity data is to be expected.

Taking this into account the most reliable data set from this study will be the one for 82 mg per crucible. The enthalpy difference of the eutectic BP/DPO mixture between 300 - 400 °C resulting from the polynomial fit matches with the polynomial published by Gomez et al [2] and also with the data according to Lanxess [5].

The experimental findings at vapor-liquid equilibrium in this study confirm that linear polynomials are valid for describing the heat capacity within 130 – 409 °C thus covering the relevant range of operation of parabolic trough plants.

Measurement of Isobaric Enthalpy Changes

The eutectic mixture of BP/DPO was degassed and subsequently flushed with nitrogen before starting the measurements in order to avoid any aging by dissolved oxygen. Thermal losses in the heat exchanger were minimized with vacuum insulation. Radiative heat losses of the heat exchanger were corrected via comparative measurement of the enthalpy of eutectic BP/DPO at small pressure (16 bar) taking the polynomial determined via DSC for 82 mg HTF per crucible into account. Mass flows of 131 –150 g/min were applied giving rise to pressure drops in the heat exchanger in the range of 0.9 – 1.3 bar at inlet pressures of 16 – 63 bar.

The enthalpy difference of eutectic BP/DPO between 300 - 400 °C was measured at pressures between 16 – 63 bar (Fig. 5).

The enthalpy difference between 300 – 400 °C can be fitted with the polynomial (3).

$$\Delta H_{300}^{400} = -0.0728 \frac{J}{\text{bar} \cdot \text{g}} \times p (\text{in bar}) + 244.4 \frac{J}{g} \quad (3)$$

As expected the effect of increased mechanical pressure on the enthalpy difference is rather small. Decreasing enthalpy difference in the range of -0.03% per bar result from (3).

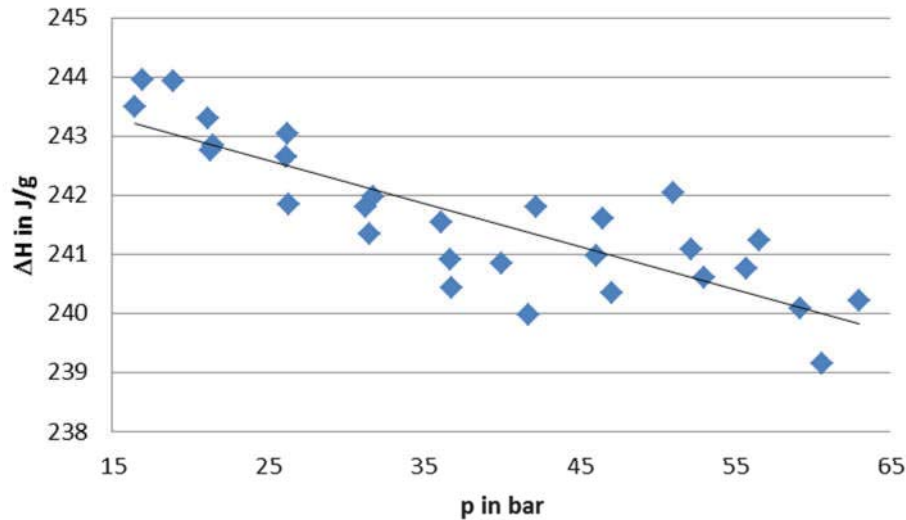


FIGURE 5. Experimental enthalpy difference of eutectic BP/DPO between 300 - 400 °C in terms of pressure

The initial series of measurements was performed with dissolved nitrogen of 1 bar at ambient temperature. No significant change was observed when the nitrogen pressure was increased to 10 bar i. e. the amount of dissolved nitrogen was ten times larger.

CONCLUSION

The heat capacity of eutectic BP/DPO can be determined with Calvet-type DSC instruments within the temperature range relevant for the operation of CSP plants. Low scanning rates like 2 K/min can be used thus ensuring measurements at well-defined sample temperature. The measurements allow studying the effect of sample mass on the results. When larger sample mass is applied apparently lower heat capacity is found due to lower distortion of the heat flow caused by cross detection of heat of evaporation. DSC measurement results are neither isobaric nor isochoric heat capacity but a measurement at saturation pressure. In this study it could be shown that linear polynomials describe the heat capacity of eutectic BP/DPO correctly between 130 – 409 °C.

Heat capacity data with increasing trends at higher temperature like presented in the data sheets of some manufacturers cannot be confirmed by these measurements. The fit parameters received with the maximum sample

mass according to table 4 lead to 0.6 – 3.7% lower enthalpy differences between 300 °C and 400 °C compared to manufacturer's data.

The measurement of the isobaric enthalpy difference of eutectic BP/DPO with a compression loop demonstrates small dependence on enhanced mechanical pressure. A reduction by -0.03 %/bar was found between 300 – 400 °C between 16 - 63 bar.

ACKNOWLEDGMENTS

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