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Investigation of freezing point for liquid samples with using differential scanning calorimetry

Aim of scope: Investigation of freezing point for two samples with 1°C accuracy:

1. Liquid sample with name defroster for windows (odmrażacz do szyb)
2. Liquid sample with name concentrate of windscreen washer (koncentrat płynu do spryskiwaczy)

1. Differential scanning calorimetry (DSC) - theoretical background

Differential Scanning Calorimetry (DSC) is a one of method using in thermal analyses. The mail goal of thermal analysis is investigation and characterization of sample during temperature changes. In the midst important and popular thermo analytical methods the crucial role is noticed for differential thermal analysis (DTA), differential scanning analysis (DSC), thermogravimetric analysis (TGA) and thermomechanical analysis (TMA).

DSC is a sophisticated technique where difference between energy of two heat flux (for sample and reference) is measurement. This difference is noticed during forced changes of temperature. This method is useful for investigation of phase transition or chemical reactions where heat is taken or emitted. For the sake of own versatility differential scanning calorimetry is the most popular thermo analytical method.

Rule of differential scanning calorimetry measurement

Both containers with sample and thermal inert reference are connected with independent heaters (heating of head with containers is linear in time). Both pans (with sample and reference) are kept in equilibrium temperature and difference (ΔT) between them is constant and equal to 0.

During the phase transition (freezing or melting point) this equilibrium between sample and reference is disturbed. The gradient of difference temperature is created.

Signal about this unbalance is sent to computer which check both heaters. The heater supplies for one of containers proper energy, which is necessary for compensation of this unbalance. In dynamic calorimeter we measure the heat flux $\frac{dH}{dT}$ between heaters for sample and reference in function of temperature or time. Fundamentally difference between DSC and TGA methods is noticed during the measurement. In DSC calorimeter we measure electric energy directly on heaters, whereas in TGA method we measure difference of temperature between sample and reference, only.

2. Setup measurement

Differential scanning calorimetry (DSC) measurements were performed on the DSC8000 calorimeter produced by Perkin-Elmer. For low temperature measurement this calorimeter was connected with LN2 low temperature attachment. As cooling medium, the liquid nitrogen was used. The aluminum pans were used. Before measurement the device was calibrated with using preferred by Perkin-Elmer company standards. For high temperature the indium and for low temperature range the cyclohexane were used as standard. The mentioned above standard were analytically pure. On the basis of standard measurement, the accuracy for samples measurement was determined as ± 1°C.

During heating and cooling cycles 20K/min scan rate was used. Mass of samples were determined as: 7.853 mg for windows defroster (odmrażacz do szyb) and 5.513 mg for windscreen washer concentrate (koncentrat płynu do spryskiwaczy) sample. Both samples were measurement in the range 20 - -150°C. For both samples the first measurement cycle was cooling. After this the heating measurement was performed. This measurement procedure was twice repeated.

3. Investigation results

3a. Sample with name defroster for windows (1) – called as O1 (Figure 1)

During fist cooling cycle the characteristic peak on curve was observed. This peak was connected with first order phase transition. On the basis of huge energetic effect and full symmetry of observed peak, the phase transition can be interpreted as freezing point of sample. **According to special computer program, which was dedicated for this DSC device the temperature of freezing point for sample O1 (defroster for windows) was determined as -76.18°C (as onset point).** The enthalpy of this freezing point is equal to 31.9239 J/g (Joule per gram). The maximum of peak (point where the transition process is the fastest was specified as equal to -77.40°C.

In heating cycle the unregular peak connected with melting process was observed. **On the basis of this peak the melting point of this sample was determined as equal to -65.96°C (onset).** The energetic effect f this process was equal to 35.0208 J/g (Joule per gram). The maximum of peak was noticed at -63.71°C.

In next cooling and heating cycles identical results were obtained.

3b. Sample with name concentrate windscreen washer (2) -called as K1 (Figure 2).

During the first cooling cycle the characteristic for fist order phase transition peak was observed. This peak was fully symmetric and huge energetic effect was observed. On the basis of this assumption this peak was recognized as freezing point of sample K1. **The temperature of freezing point was established as equal to -91.36°C (onset)**. Energetic effect of observed phase transition was described as equal to 13.9974 J/g (Joule per gram). The maximum of peak was calculated as -93.20°C (point where phase transition is the fastest).

In heating cycle of DSC measurement, the unregular peak derived from melting process of investigated sample was observed. **The temperature of melting point was determined as -83.13°C (onset)**. The enthalpy of this process was equal to 11.7813 J/g (Joule per gram). The maximum of peak was noticed at -73.15°C.

In next cooling and heating cycles identical results were obtained.

4. Attachments

Figure 1 – The DSC results for sample with name defroster for windows (1) – called as O1

Figure 2 – The DSC results for sample with name concentrate windscreen washer (2) -called as K1

5. Conclusions

According to performed measurement and DSC curves analysis the clear-cut freezing points for two liquid samples were established:

1. Sample with name defroster for windows – freezing point at **-76.18°C**.
2. Sample with name concentrate windscreen washer – freezing point at **-91.36**
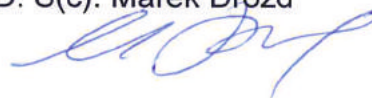

Author of measurement and analysis

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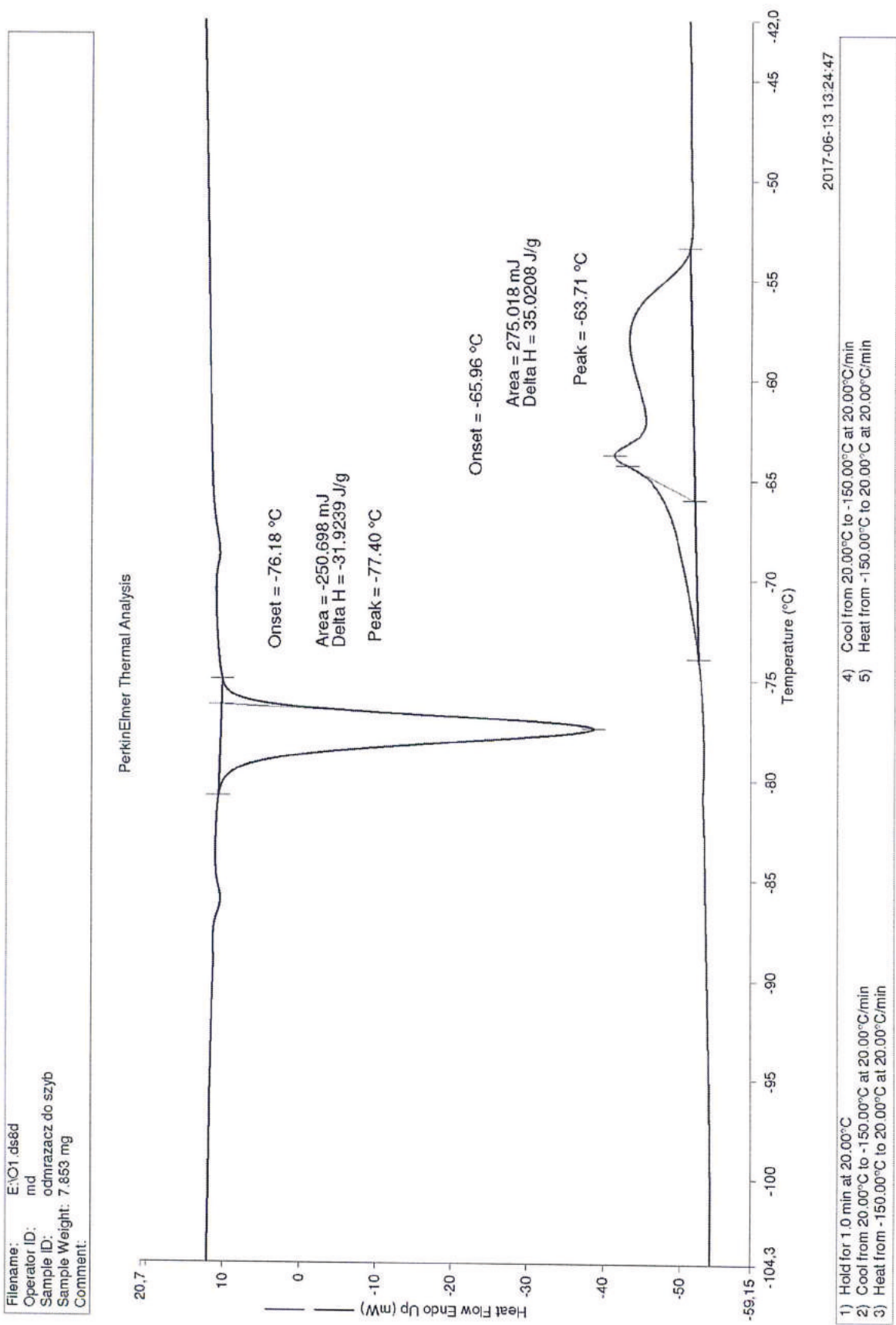Figure 1- DSC results for sample with name defroster for windows (O1).

Figure 2 – DSC results for sample with name concentrate windscreen washer (K1)