Short communication

Crystallization of ionic salts for calibration of differential scanning calorimeters

Calla McCulley, Sergey Vyazovkin*

Department of Chemistry, University of Alabama at Birmingham, 901 S. 14th Street, Birmingham, AL 35294, USA

ABSTRACT

This study explores the possibility of using inorganic salts for temperature calibration of Differential Scanning Calorimeters (DSC) on cooling. The crystallization and melting of sodium nitrate, potassium nitrate, and rubidium nitrate has been studied at several cooling and heating rates. It has been found that these salts crystallize at almost the same temperature, at which they melt, meaning that they do not practically supercool. The DSC data have indicated that the median value of the supercooling is around 0.4–0.8 °C. The study suggests that the process of crystallization of these and possibly other inorganic salts can be considered for developing new standards to calibrate DSC on cooling.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

DSC is the most widely used thermal analysis technique for measuring the heats and temperatures of physical and chemical processes. DSC provides accurate values of temperature through calibration with melting point standard substances that typically are metals such as indium and zinc. It is not possible to measure the true temperature and heat values directly by DSC, and so calibration standards have to be used to calculate the true values [1]. Requirements for the standards have been laid out by Cammenga et al. [2]. The problem with the typical standards such as metals is that they do not allow for calibration in cooling mode. This is because of the phenomenon of supercooling which causes the substances to crystallize at significantly lower temperatures than that of melting.

The best known processes that do not practically supercool are certain phase transitions in liquid crystals that prompted Menczel and Leslie [3] to propose employing liquid crystals for calibration on cooling. The disadvantages of these materials are that they are organic substances which are prone to oxidation and also quite expensive. Nevertheless, organic substances are commonly used for temperature and enthalpy calibration of DSC [4–6]. The initiatory work by Menczel and Leslie [3] has been followed by comprehensive studies by Martins and Cruz-Pinto [7], Sarge et al.

[8], and Neuenfeld and Schick [9]. Although the studied liquid crystalline substances have been found suitable for calibration purposes, the respective temperature range they cover is not very wide, roughly 65–165 °C [3,7–9].

According to Sarge et al. [8], substances for calibration on cooling must be available with sufficient purity; must not react with crucible material, light, or the ambient atmosphere; should be of long-term stability; should be non-hygroscopic; should be of low volatility; should be physiologically safe; must have a clearly-defined transition temperature from a thermodynamics point of view; must not undergo measurable supercooling; and must have a high rate of transition. Inorganic salts, such as sodium nitrate, potassium nitrate, and rubidium nitrate appear to align well with these criteria which made them compounds of interest in the present study. In addition, melting and crystallization of the nitrate salts is of practical interest because of their use as phase change materials for latent heat storage.

In this note, we demonstrate that inorganic salts, such as the alkali nitrates, can be used as a complement to the current liquid crystal standards. Generally, the melting temperature of inorganic salts is markedly larger than that of liquid crystals. Also the respective range of melting temperatures is significantly wider. For instance, for the alkali nitrates the melting temperature ranges from 253 °C (lithium nitrate) to 409 °C (cesium nitrate) [10]. The range can be potentially expanded by using, for example, chlorides that melt at even higher temperatures. The prediction that nitrates and other inorganic salts will not supercool much below the melting temperatures follows from the experimentally observed

extremely fast rates of crystallization. This appears to be a common property of many inorganic salts that have relatively small and simple anions. The prediction will be verified using the DSC data on the crystallization and melting of each inorganic salt. The purpose of this work is not to propose the salts studied as standards. Such a proposal would require and extensive joint effort of the community. Rather, we intend to provide a proof of the concept that adequate standards for temperature calibration on cooling can be found among ionic salts.

2. Experimental

Sodium nitrate was obtained from Fisher Scientific (99.5 wt.% pure), potassium nitrate was obtained from Alfa Aesar (99.0 wt.% pure), and rubidium nitrate was prepared by reacting 5.00 mg of rubidium carbonate from Acros Organics (99.0 wt.% pure) with a 10 mL of 1:1 nitric acid (from Fisher Scientific) and water mixture. All salts were purified by recrystallization in methanol (99.8 wt.% pure). The above purity values based on assay provided by the suppliers. The purity of synthesized rubidium nitrate is unknown. However, it was found to be unsatisfactory as discussed further.

All calorimetric measurements were carried out using a heat flux DSC (Mettler-Toledo 823e). The heat and temperature calibration were performed by using indium and zinc standards supplied by Mettler-Toledo in the form of 'disk' shaped pellets. The calibration uncertainty was defined by the uncertainties in the measurements of the calibration standards. For indium, the melting temperature and enthalpy respectively are $156.6 \pm 0.3\,^\circ C$ and $28.5 \pm 0.6\,J\,g^{-1}$. For zinc they respectively are $419.6 \pm 0.7\,^\circ C$ and $107.5 \pm 3.2\,J\,g^{-1}$. The measurements were made using roughly 10 mg of each alkali nitrate in open 40 μL aluminum crucibles. The purge gas for these experiments was nitrogen at a flow rate of 80 mL/min. Care was taken to ensure good thermal contact between the sample and crucible. Before use the alkali nitrates were crushed with mortar and pestle to produce fine powder.

The onset temperature measurements were recorded at the three different heating/cooling rates (2, 5, and $10\,^\circ C\,min^{-1}$), and a new sample was used at each rate; thirty minute isothermal holds also occurred between each heating and cooling steps. The measurements were made at ambient pressure in triplicate with a new sample for each rate unless otherwise indicated.

3. Results and discussion

Several runs on heating and cooling at scan rates from 2 to $10\,^\circ C\,min^{-1}$, were performed on three samples of each alkali nitrate. The typical DSC curves for melting and crystallization of sodium nitrate at the $5\,^\circ C\,min^{-1}$ are given in Fig. 1. Similar DSC data are shown for the crystallization and melting of potassium nitrate and rubidium nitrate in Figs. 2 and 3 respectively. The temperatures of melting (T_m) and crystallization (T_c) as well as the respective values of the enthalpy changes (ΔH_m and ΔH_c) derived from the DSC data are summarized in Table 1. The values of T_m and T_c were determined as the extrapolated onset temperature, which is the intersection point of the tangent lines passing respectively through the baseline and the front edge of the DSC peak.

For sodium nitrate, the mean values of T_m and ΔH_m found in this work respectively are $306.0 \pm 0.2\,^\circ C$ and $183 \pm 1\,J\,g^{-1}$. The literature reports several T_m values for this compound. In particular, an extensive study of Jiriri et al. [11] collects 16 literature values whose mean value is $308 \pm 4\,^\circ C$. Eight of these values fall within the range 306–307 °C. The value determined experimentally by Jiriri et al. [11] is 306 °C. The value recommended by the ICTAC working group "Thermochemistry" is 307 °C [12]. The same value has been recommended by Janz et al. [13]. Both recommended values have
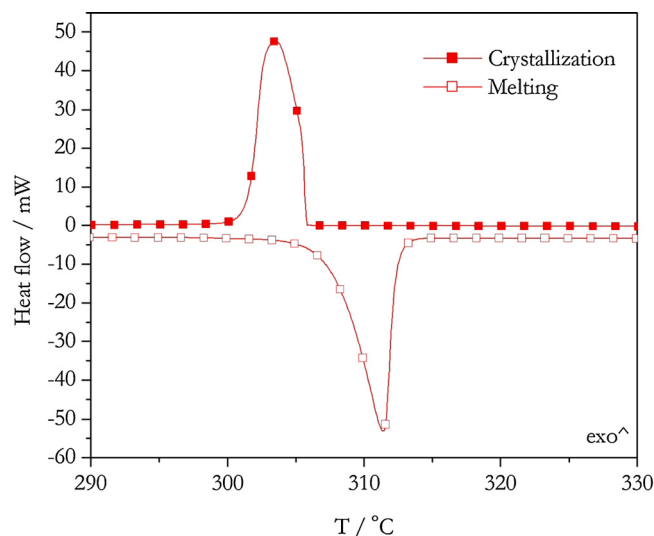

Fig. 1. Typical DSC curves of the crystallization and melting of sodium nitrate on heating and cooling at $5\,^\circ C\,min^{-1}$. Here and in all other figures temperature is the reference temperature.
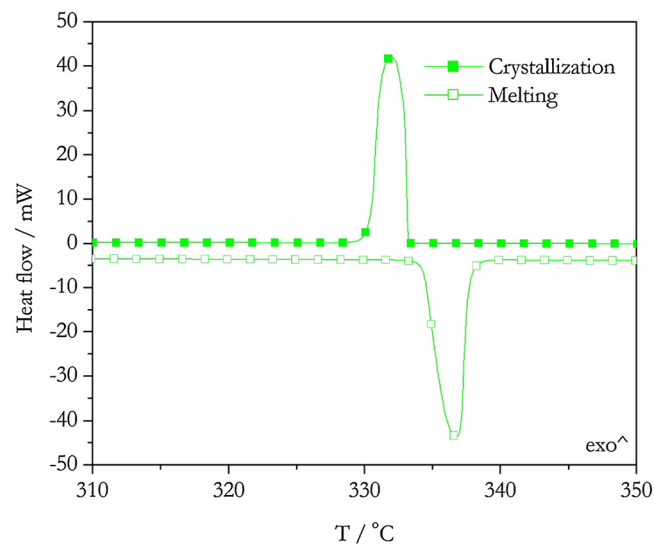

Fig. 2. Typical DSC curves of the crystallization and melting of potassium nitrate on heating and cooling at $5\,^\circ C\,min^{-1}$.

been reported without uncertainty. Considering that they have been reported with three significant digits, one can assume that the uncertainty is in the third digit, i.e., it is at least $\pm 1\,^\circ C$. In other words, our value appears consistent with most of the literature. A markedly larger $T_m = 310\,^\circ C$ has been reported by Carling [14] who before performing the measurements dried the compound for 48 h at 152 °C in vacuum. It is conceivable, albeit not tested, that the presence of water may somewhat depress the melting temperature of the compound. There are multiple literature values of ΔH_m as well. Jiriri et al. have collected seventeen values that vary from 14.6 to 15.8 kJ mol^{-1} that correspond to 172–186 J g^{-1}. It is also consistent with the recommended [12] value, $178 \pm 5\,J\,g^{-1}$. Either way, our value is in agreement with the literature.

For potassium nitrate, the mean values of T_m and ΔH_m found in this work respectively are $333.8 \pm 0.2\,^\circ C$ and $103 \pm 3\,J\,g^{-1}$. Jiriri et al. [11] have reported twelve literature values of T_m that range from 333 to 346 °C. Our T_m value is right at the lower limit of this range just as the value found by Jiriri et al. [11]. They also have collected twelve literature values of ΔH_m that cover the range