

Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Application of fast scanning calorimetry to the fusion thermochemistry of low-molecular-weight organic compounds: Fast-crystallizing *m*-terphenyl heat capacities in a deeply supercooled liquid state



Mikhail I. Yagofarov^{a,*}, Semen E. Lapuk^a, Timur A. Mukhametzyanov^a, Marat A. Ziganshin^a, Christoph Schick^{a,b}, Boris N. Solomonov^a

^a Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia

^b University of Rostock, Institute of Physics, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany

ARTICLE INFO

Keywords:

Heat capacity
Fast scanning calorimetry
Differential scanning calorimetry
Fusion enthalpy
Solution enthalpy
Supercooled liquid

ABSTRACT

Fusion enthalpy temperature dependence is related to the difference in heat capacity of the liquid and solid. Below the melting temperature, it is hard to measure the liquid heat capacity using conventional methods due to fast crystallization.

Based on an indirect solution calorimetry approach, we previously concluded that the temperature dependence of heat capacities below the melting temperature is the extrapolation of the linear function above it. In this study, we employed a fast scanning calorimetry technique to test the validity of this conclusion.

Three compounds were studied: two organic glass formers, benzophenone and *o*-terphenyl, for which the liquid and supercooled liquid heat capacities were known to be accurately described by a linear function of temperature, and *m*-terphenyl, which had never been studied in the supercooled liquid state. The results were in good agreement with the literature for liquid benzophenone and *o*-terphenyl heat capacities above and below the melting temperature. The heat capacity of the supercooled liquid and glassy *m*-terphenyl was obtained for the first time. The measured molar heat capacity of supercooled liquid *m*-terphenyl was the linear extrapolation of the temperature dependence of the heat capacity of the melt found in the literature.

The molar heat capacity of the solid, the enthalpy and fusion temperature of *m*-terphenyl were determined by conventional DSC. Kirchoff's integral, calculated from the measured molar heat capacities of solid and liquid *m*-terphenyl, was in accordance with the fusion and solution thermochemistry data.

1. Introduction

Fusion enthalpy is one of the key parameters of solid-liquid transitions. It governs solubility [1], the shape of phase diagrams [2], and heat transfer during solidification and melting [3]. Fusion enthalpies of individual compounds are only measured at the melting temperature. However, the temperature dependence of fusion enthalpy is of significant interest, for at least two reasons.

Firstly, the reasons why different compounds melt with particular heats of fusion are currently unknown. Among other things [4], it seems that one of the major obstacles is the fact that fusion enthalpies of different compounds are measured at different temperatures. Since the fusion enthalpy depends on temperature, correct interpretation of its magnitude is only possible after adjusting to a unified temperature, e.g., 298.15 K.

Secondly, determination of the temperature dependency of fusion enthalpies will improve the quality of solubility calculations. A well-known ideal solubility equation is currently used with various simplifications (neglecting the difference between the heat capacities of the liquid and solid [5], approximating it using the fusion entropy at the melting temperature [6], and other simplifications [7,8]) that may significantly affect the results [9].

Fast scanning calorimetry allows controlled heating and cooling at rates of up to 1 MK s^{-1} [10]. Scanning at such rates allows crystallization on supercooling and decomposition on melting to be avoided, and also allows direct measurement of the heat capacity of supercooled liquids. This technique was recently used for the determination of the heat capacities of a supercooled liquid and liquid silk [11], polyvinyl alcohol [12], and cytosine [13]. These data are a primary source of information that can be used to adjust the fusion enthalpy to

* Corresponding author.

E-mail address: MilYagofarov@kpfu.ru (M.I. Yagofarov).

<https://doi.org/10.1016/j.tca.2018.08.015>

Received 21 June 2018; Received in revised form 9 August 2018; Accepted 14 August 2018

Available online 17 August 2018

0040-6031/ © 2018 Elsevier B.V. All rights reserved.