Thermochimica Acta 646 (2016) 26–31

Contents lists available at ScienceDirect

Thermochimica Acta

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

Estimation of sublimation enthalpies of aromatic amides at 298.15 K from the values of fusion enthalpies

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ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form 24 October 2016
Accepted 29 October 2016
Available online 3 November 2016

Keywords:
Enthalpy of sublimation
Enthalpy of fusion
Enthalpy of solution
Aromatic amides

ABSTRACT

In this work a method for determination of sublimation enthalpies of amides substituted in aromatic ring from data on fusion enthalpies at the melting temperature was proposed. This method was checked by calculation of sublimation enthalpies of 12 substituted benzamides, containing $-CH_3$, $-OCH_3$, $-F$, $-OH$, $-NH_2$ and $-NO_2$ substituents, as well as *m*- and *p*-pyridinecarboxamides, which were compared to literature values. Sublimation enthalpies of 3-aminobenzamide, 3- and 4-nitrobenzamides at 298.15 K were determined by solution calorimetry approach and amounted to 123.9 and 124.5 kJ·mol^{-1}, respectively. This method showed good congruence with the results of direct experiment, as well as with solution calorimetry approach. In most of the cases, divergence does not exceed 2–3%.

1. Introduction

Aromatic amides are known to have useful biological activity [1,2]. Phase transitions thermodynamics of aromatic and heteroaromatic amides was studied in the works [3–14]. Sublimation enthalpies were determined with good reproducibility by Knudsen method [3,4,6,12,14], static method [3], transpiration [5,9,10]. In the last works solution calorimetry approach was also applied for determination of sublimation enthalpies of substituted benzamides [5] and *m*- and *p*-pyridinecarboxamides [9] and gave the results consistent with those obtained by conventional methods.

Solution calorimetry approach [15–18] is based on well-known relationship, according to which sublimation enthalpy may be calculated as a difference between solution and solvation enthalpies. Solution enthalpy is measured directly, solvation enthalpy may be calculated from a group-additivity scheme [18]. Solution calorimetry approach has a number of advantages over conventional methods: experiment is carried out under standard conditions so there is no need to adjustment of the results obtained at elevated temperatures to 298.15 K, as well as no problems with thermally unstable compounds arise. Furthermore, impurities influence on the results decreases. Non-additivity of solvation enthalpy arising in special cases may be considered with help of IR-spectroscopy [19]. At the same time, solution calorimetry has a number of drawbacks due to the complexity of attainment of infinite dilution in the case of compounds that are self-associated because of the occurrence of hydrogen bonding, as well as with an increase of measurement uncertainty in the case of high magnitudes of solution enthalpy (> 30 kJ mol^{-1}).

We proposed a new approach [20] based on interrelation between sublimation enthalpy at 298.15 K and fusion enthalpy at the melting temperature. This approach was successfully applied in the case of aromatic compounds that are not self-associated due to hydrogen bonding. Sublimation enthalpies of more than 100 compounds were calculated and compared to the literature data [20–22].

In the present work the relationship between sublimation enthalpy at 298.15 K and fusion enthalpy at the melting temperature is investigated on example of amides substituted in benzene ring, nicotinamide and isonicotinamide. It is well known that aromatic and heteroaromatic amides are capable of self-association, due to presence in the molecules of these compounds of both basic and acidic functions.

2. Experimental part

2.1. Materials

3-Aminobenzamide, 3- and 4-nitrobenzamides were of commercial origin with mass fraction purities better than 0.98. All samples for solution calorimetry were used without any purification (see Table S1).

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http://dx.doi.org/10.1016/j.tca.2016.10.015
0040-6031/