Thermochimica Acta 655 (2017) 358–362

Contents lists available at ScienceDirect

Thermochimica Acta

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

Determination of sublimation enthalpies of substituted benzophenones, fluorenes and diphenyl ethers by solution calorimetry approach

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ARTICLE INFO

Keywords:
Benzophenone
Aromatic compounds
Enthalpy of solvation
Enthalpy of solution
Enthalpy of sublimation

ABSTRACT

An approach for the determination of solvation enthalpies of substituted aromatic compounds is developed. In this work the solvation enthalpy of a reference unit (benzophenone, fluorene and diphenyl ether) is calculated as the difference between solution enthalpy and sublimation enthalpy at 298 K. An additive approach for the determination of solvation enthalpies of substituted aromatic compounds was used. Solvation enthalpies of sixteen substituted benzophenones, fluorenes and diphenyl ethers were calculated by this approach. Thermochemical data of solution enthalpies of benzophenones, fluorenes and diphenyl ether were measured by a precision solution calorimeter at 298 K. Then sublimation enthalpies of the studied compounds were derived by a solution calorimetry (SC) approach at 298 K.

We have also found that in a number of cases instead of the solution enthalpy in benzene at 298 K the fusion enthalpy at the melting temperature can be used. A comparison between literature data and the calculated vaporization and sublimation enthalpies demonstrates a satisfactory performance of the proposed approach.

1. Introduction

Substituted benzophenones, fluorenes and diphenyl ethers are widely used in the pharmaceutical industry and perfumery. Consequently thermochemical properties of phase transitions are necessary to determine the solubility of these compounds. For example the solubility of fluorenes and benzophenones is an important property because many of its derivatives are pollutants [1,2].

However thermochemical data of these compounds are poorly studied in the literature. The enthalpies of the sublimation of some compounds haven't been derived yet. This is due to the difficulties in the determining of the sublimation enthalpy by conventional methods [3,4]. Only the sublimation enthalpies of unsubstituted benzophenone and fluorene were studied well. Eleven values of sublimation enthalpies of benzophenone and eight values for fluorenone are available in the literature. This is due to the fact that thermochemical properties of unsubstituted compounds are usually easier to study. It is related to the fact that unsubstituted compounds as a rule are more easily volatile and stable than substituted compounds. Thermochemical properties of benzophenone derivatives were studied in [5–7], fluorene derivatives in [8–12] and diphenyl ether derivatives in [13,14]. In some cases, values obtained by various authors are in disagreement (for example: 2,7-dibromofluorene [8–10]), in other cases only one value is available in the literature (for example: 4-chlorobenzophenone [6]).

In previous works [15–21] we have shown that enthalpies of sublimation at 298 K can be derived using a solution calorimetry (SC) approach. One of the most important advantage of using the SC approach is that vaporization/sublimation enthalpies are derived directly at the reference temperature (298 K) that's why the SC approach can be used for studies of thermally instable and explosive compounds. Another advantage of the SC approach appears from the well-known fact that conventional methods for measurements of phase transition enthalpies are highly sensitive to impurities. Moreover, solution calorimetry can be used for low volatile compounds [21]. In this case, only several experimental methods can be applied for these compounds [3].

According to the SC approach the vaporization and sublimation enthalpies can be calculated as the difference between the solution enthalpy of compound A_i in solvent S and solvation enthalpy in the same solvent at 298 K. The solution enthalpy can be experimentally measured by a solution calorimeter. In works [18,20,21] it was shown that solvation enthalpies can be estimated by a linear dependence of the solvation enthalpy of compound A_i and molar refraction. This approach is most universal for cyclohexane. The most multipurpose approach for the determination of solvation enthalpies of different compounds and various solvents was proposed in the works [15–17,19]. According to this approach, the solvation enthalpy is calculated as a sum of the solvation enthalpy of the reference unit and contributions due to the substitution of the hydrogen atoms in the reference unit by any other

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http://dx.doi.org/10.1016/j.tca.2017.08.003
Received 7 February 2017; Received in revised form 20 July 2017; Accepted 3 August 2017
Available online 04 August 2017