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Solution calorimetry as a complementary tool for the determination of enthalpies of vaporization and sublimation of low volatile compounds at 298.15 K

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ABSTRACT

In this work a new solution-based calorimetry approach for determination of the sublimation and vaporization enthalpies of low volatile compounds was proposed. The approach is based on the measurement of solution enthalpy of a molecule of interest in benzene and as well as the measurement of molar refraction index for this molecule. Enthalpies of solution at infinite dilution in benzene for a set of 18 aromatic and polyaromatic hydrocarbons were measured at 298.15 K. Experimental data on vaporization/sublimation enthalpies for this set were collected from the literature. For validation of the literature data additional sublimation experiments were performed for phenanthrene, 1-phenylnaphthalene, 1,2-diphenylbenzene, 1,2,3,4-tetraphenylnaphthalene, hexaphenylbenzene, and rubrene using transpiration, quartz crystal microbalance, and thermogravimetry. Vaporization/sublimation enthalpies derived from the solution calorimetry approach were in good agreement (within experimental uncertainties) with those measured by conventional methods. The solution-based calorimetry approach gives a reliable and quick appraisal of vaporization/sublimation enthalpies. This approach constitutes a complementary additional thermochemical option for vaporization/sublimation enthalpies data evaluation as well as for rapid data gathering for low volatile and/or thermally unstable organic compounds.

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Introduction

Energetics of vaporization and sublimation processes impairs industrial phase separation operations. It governs solubility in pharmaceuticals or volatilization of chemicals from soil. Enthalpies of vaporization/sublimation are also required to obtain energetics of molecules and chemical reactions in the gas state, and in this context the knowledge of vaporization/sublimation enthalpies is indispensable (in combination with classic combustion calorimetry) for validation of the modern high-level quantum chemical calculations [1]. During the last two centuries, a large number of direct (calorimetric) and indirect (from vapor pressure temperature dependences) experimental methods have been developed to obtain vaporization/sublimation enthalpies [2]. Yet, most of the available methods are only sufficiently developed for measurements of highly volatile and volatile compounds. As a rule, the available vaporization enthalpies of these compounds are consistent. The discrepancies sometimes observed among the data are typically due to possible impurities in the sample under study. In contrast, only few experimental methods are well established for the low volatile compounds: the mass effusion Knudsen method (ME), the quartz crystal microbalance (QCM), the transpiration method, and thermogravimetric analysis (TGA) [2]. The latter methods are less affected by possible impurities because of the careful preconditioning of the sample in the measuring unit prior to beginning of the experiment. However, it should be noticed, that the quality of results from these four methods is crucially dependent on operator competency and experience. Conventionally, for the sake of comparison, the measured vaporization/sublimation enthalpies are reported in original works or compilations at the reference temperature 298.15 K. The highly

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volatile and volatile compounds are easily measured by calorimetric methods directly at 298.15 K. Measurements of low volatile compounds require increasing of temperature of about 100–200 K above the T = 298.15 K. The Kirchhoff's equation is used for the temperature adjustment of vaporization/sublimation enthalpies from T_{av} (average temperature of the experimental range) to T = 298.15 K. Heat capacity differences required for the Kirchhoff's equation are usually derived from empirical correlations. One of the most frequently used procedures was suggested by Chickos et al. [3]. This method was parameterized using the data set of the gaseous heat capacities restricted to small volatile molecules because experimental heat capacities for large molecules are absent. Due to this fact using of the Kirchhoff's equation for adjustment from T_{av} to the reference temperature T = 298.15 K may be possibly uncertain, especially when the vaporization experiment was performed at T_{av} lying by 100–200 K above 298.15 K [4].

Summing up, results from conventional experimental methods for measurement of vaporization/sublimation enthalpies are sensitive to possible impurities, operator experience, and ambiguity of the temperature adjustment to 298.15 K. Each of these factors could affect, in different extents, the reliability of the vaporization/sublimation enthalpies reported in the literature. Thus, a careful evaluation of the experimental data with the recommendation of the reliable enthalpies including their uncertainties is a highly valuable work [5,6]. In this respect, any additional independent method to assess vaporization/sublimation enthalpies could be very helpful to resolve contradictions in the data available in the literature. For example, the available sublimation enthalpies of 9,9′-bianthracene 128.4 kJ mol^{-1} [7] and 148.1 kJ mol^{-1} [8] are different by nearly 20 kJ mol^{-1}. Both values were measured with well established methods in thermochemical research labs with sufficient experiences. However, it is hardly possible to determine the preferred value without an additional study. Also, very often only a single value can be found in the literature, e.g. the sublimation enthalpy 178.2 kJ mol^{-1} of 5,6,11,12-tetraphenylnaphthacene (rubrene) was measured by using the ME method [7]. Thus, another method is required to prove validity of this value.

Some time ago we have revealed [9,10], that the solution calorimetry measurements at 298.15 K could provide an additional method to assess vaporization/sublimation enthalpies especially for large compounds. The solution calorimetry approach utilizes an empirical correlation of the solvation enthalpy of a molecule of interest with its molar refraction. For example, the sublimation enthalpy of biphenyl available in the literature was measured using five different methods with values spreading from 81 to 84 kJ mol^{-1}, with an average value of (82.1 ± 2.1) kJ mol^{-1} recommended in Ref. [5]. The value of (82.8 ± 1.5) kJ mol^{-1} derived from the enthalpy of solution of biphenyl in cyclohexane in our preliminary study [10] is in fair agreement with the recommendation. Thus, the solution calorimetry seems to be a promising tool for evaluation of vaporization/sublimation enthalpy data. The main goal of this work was to establish a reliable approach based on the results from solution calorimetry. There are at least three crucial advantages in the utilization of solution calorimetry. First, this method is already well established in physical chemistry classes. Second, inexpensive commercial devices are used. Third, experiments are performed directly at the reference temperature (298.15 K) favorably overcoming the temperature adjustment limitations inherent in vapor pressure measurements.

In this work we have been challenged to develop and apply the solution calorimetry approach to derive vaporization/sublimation enthalpies for a number of aromatic and polyaromatic hydrocarbons, where the experimental data according to recent compilation [5] seem to be in disarray. For validation of the results from solution calorimetry we additionally used the well established transpiration, QCM, and TGA methods.

2. Experimental part

2.1. Materials

All aromatic hydrocarbons studied in this work were of commercial origin with mass fraction purities >0.97. They were further purified by repeated crystallization or by fractional sublimation in vacuum. Purities of aromatic hydrocarbons were analyzed by using the Konik 5000 gas chromatograph (GC) equipped with a flame ionization detector (FID). Some samples were analyzed using simultaneous TGA and differential scanning calorimetry (DSC) (Thermoanalyzer Netzsch STA 449C Jupiter) coupled with evolved gas analysis by mass spectrometry (quadrupole mass-spectrometer QMS 403C Aeolos).

The calorimetric solvent, benzene, was carefully purified from traces of thiophene by shaking with the concentrated H_2SO_4. Then it was washed with the dilute aq. NaOH and water and then distilled over CaH_2. The mass fraction of benzene after purification was 0.999 according to GC analysis.

Water used for calibration of solution calorimetry, densimetry and refractometry techniques was distilled twice and deionized using the purification system Easy Pure II (Thermo Scientific). Its electrical resistivity was 18.2 MΩ cm.

2.2. Solution calorimetry

Enthalpies of solution of aromatic hydrocarbons in benzene were measured at T = 298.15 ± 0.01 K using the commercial TAM III solution calorimeter. In a typical experiment, 100 mL of benzene were placed in a glass calorimetric cell equipped with a gold stirrer, a Joule heater, and a thermistor. The detailed description of the standard solution procedure has been published elsewhere [11,12].

2.2.1. Liquid samples

Dissolution experiments with liquid samples were performed by using the titration procedure: 100 μL of solute were dropped into the thermostatted cell in small portions of 10–20 μL with help of an electronically operated microliter syringe equipped with a long gold cannula with the tip immersed in the measuring cell. The heat effect of each addition was calculated from a calorimetric curve. Experimental and data acquisition procedures were tested by measuring the solution enthalpy of propan-1-ol in water. The average value of the solution enthalpy of (−10.16 ± 0.03) kJ mol^{-1} determined across 5 experiments was in excellent agreement with the recommended value (−10.16 ± 0.02) kJ mol^{-1} [13].

2.2.2. Solid samples

Dissolution of solid samples was carried out using the ampoule technique. A cylindrical glass ampoule was filled with the sample (0.01–0.05 g), sealed, weighed (±0.01 mg), inserted in the sample holder, and immersed into the solvent. After thermal equilibration with the solvent the ampoule was broken and the temperature change in the cell was registered. Each solid sample was measured at least 4 times. Experimental and data acquisition procedures were tested by dissolution of KCl in water. The average value of the solution enthalpy of (17.41 ± 0.04) kJ mol^{-1} measured across 5 experiments was in excellent agreement with the recommended value (17.47 ± 0.07) kJ mol^{-1} [14].

All experimental enthalpies of solution for aromatic hydrocarbons in benzene measured in this work are listed in Table S1. Analysis of the measured values did not reveal any concentration dependence of solution enthalpies within the boundaries of their uncertainties. This fact proved the assumption that a solute (A_i) dissolves in sufficient amount of solvent (S) to give a solution of infinite dilution. Average values of solution enthalpies of aromatic hydrocarbons in benzene obtained from at least 4 measurements

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