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Enthalpies of fusion and enthalpies of solvation of aromatic hydrocarbons derivatives: Estimation of sublimation enthalpies at 298.15 K

Boris N. Solomonov*, Ruslan N. Nagrimanov, Mikhail A. Varfolomeev, Aleksey V. Buzyurov, Timur A. Mukhametzyanov

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

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ABSTRACT

Enthalpy of sublimation of solid compound can be found using the values of solution enthalpy and solvation enthalpy in any solvent. In this work enthalpies of solution at infinite dilution of a number of aromatic hydrocarbons derivatives in benzene were measured at 298.15 K. Comparison between experimental and literature solution enthalpies in benzene at 298.15 K and fusion enthalpies at melting temperature of aromatic hydrocarbon derivatives showed, that these values are approximately equal. Thereby, fusion enthalpies at melting temperature can be used instead of their solution enthalpies in benzene at 298.15 K for calculation of sublimation enthalpies at 298.15 K. Solvation enthalpies in benzene at 298.15 K required for this procedure were calculated using group additivity scheme. The sublimation enthalpies of 80 aromatic hydrocarbons derivatives at 298.15 K were evaluated as a difference between fusion enthalpies at melting temperature and solvation enthalpies in benzene at 298.15 K. Obtained in this work values of sublimation enthalpy at 298.15 K for studied compounds were in a good agreement with available literature data.

1. Introduction

We developed a new approach for determination of vaporization/sublimation enthalpy [1–6]. This approach is based on a well-known relationship between vaporization/sublimation enthalpy of studied compound at 298.15 K and its solution and solvation enthalpies at 298.15 K in the same solvent. Solution enthalpy at 298.15 K is measured experimentally, while solvation enthalpy at 298.15 K is calculated using a number of simple empirical approaches. These approaches include determination of values of solvation enthalpy of solute Ai in solvent S from linear relationship between solvation enthalpy and molar refraction [1,3,4,6] or using group-additivity schemes [2,5]. The latter present solvation enthalpy as a sum of contributions of unsubstituted compound and substituents. Group-additivity scheme was successfully implemented for determination of solvation enthalpies of 78 polycyclic and polysubstituted aromatic hydrocarbons and pyridine derivatives in different solvents.

In work [5] a simple method for calculation of solvation enthalpy at 298.15 K of the polyaromatic hydrocarbons in various solvents was proposed. According to this method, the enthalpy of solvation of any polyaromatic hydrocarbon can be calculated based on the value of solvation enthalpy of benzene in a solvent of interest, the quantity of carbon and hydrogen atoms in studied molecule. Furthermore, in work [5] we demonstrated that solution enthalpies of polyaromatic hydrocarbons in benzene at 298.15 K are approximately equal to their fusion enthalpies at melting temperature. Sublimation enthalpies at 298.15 K of a number of polyaromatic hydrocarbons were successfully calculated using fusion enthalpies at melting temperature instead of solution enthalpies in benzene at 298.15 K.

In present work we continue the testing of our method which is based on usage of fusion enthalpy at melting temperature instead of solution enthalpy in benzene at 298.15 K for determination of sublimation enthalpy at 298.15 K. Various derivatives of aromatic hydrocarbons, which contain nitro-, alkyl-, halogen-, cyano-, alkylcarboxy- and other substituents were taken as objects of our study.

* Corresponding author. Tel.: +7 8432495530.
E-mail address: boris.solomonov@kpfu.ru (B.N. Solomonov).

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2. Experimental part

2.1. Materials

All aromatic hydrocarbons derivatives were of the commercial origin with the mass fractions better than 0.96. Detailed information about samples is presented in Table S1. Before experiment 9-nitroanthracene was purified by vacuum sublimation. Benzene was purified by shaking with the concentrated H_2SO_4, NaOH and water and distilled over the CaH_2. Purity of samples was analyzed using Agilent 7890 B gas chromatograph (GC) equipped with the flame ionization detector.

2.2. Solution calorimetry

Solution enthalpies of aromatic hydrocarbons derivatives in benzene were measured using TAM III precision solution calorimeter. The procedure of measurements was described in detail previously [4]. Calorimeter was tested by determination of the solution enthalpy of potassium chloride in water at $T = 298.15$ K. The average value of the solution enthalpy of potassium chloride (17.41 ± 0.04 kJ mol^{-1}) in pure water is in good agreement with the recommended value (17.47 ± 0.07 kJ mol^{-1}) [7]. Masses of samples were determined using an analytical balance (Sartorius MSA225s-1ce-di) with a precision of 0.01 mg. Dissolution experiments were carried out for molalities of the solutes in the range from 1.35 to 10.55 mmol kg^{-1}. Enthalpy of solution for each solute–solvent system has constant value in studied range of concentrations. This fact confirms that obtained experimental data correspond to infinite dilution conditions. Each measurement of solution enthalpy was repeated at least 4 times (see Table S2).

3. Methodology

The following principles and definitions form the basis of our method. The solution enthalpy ($\Delta_{soln}H^{A_i/S}$) is the enthalpy of transfer of solute A_i from its standard state (solid or liquid) into an infinitely diluted solution in solvent S at 298.15 K and 0.1 MPa. The solvation enthalpy ($\Delta_{solv}H^{A_i/S}$) is the enthalpy of isothermal transfer of solute A_i from gaseous phase into an infinitely diluted solution in solvent S at 298.15 K and 0.1 MPa. Solvation and solution enthalpies are related with sublimation enthalpy ($\Delta^g_{cr}H^{A_i}_m$) at 298.15 K according to the following equation:

$$\Delta^g_{cr}H^{A_i}_m(298.15) = \Delta_{soln}H^{A_i/S}(298.15) - \Delta_{solv}H^{A_i/S}(298.15) \quad (1)$$

In Eq. (1) values of $\Delta_{soln}H^{A_i/S}$ and $\Delta^g_{cr}H^{A_i}_m$ are determined experimentally, while $\Delta_{solv}H^{A_i/S}$ can only be calculated. In present work we employed an additive scheme for calculations of $\Delta_{solv}H^{A_i/S}$ values which was described in detail in [2]. According to work [2], solvation enthalpy of aromatic compound ArX_n can be represented as a sum (Eq. (2)):

$$\Delta_{solv}H^{ArX_n/S} = \Delta_{solv}H^{ArH/S} + n \cdot \Delta_{solv}H^{X\to H/S} \quad (2)$$

where $\Delta_{solv}H^{ArH/S}$ is the solvation enthalpy of aromatic hydrocarbon in solvent S; $\Delta_{solv}H^{X\to H/S}$ is the solvation enthalpy related to the substitution of hydrogen atom in aromatic compound (e.g. benzene) by substituent X; n is the number of substituent X. The group contribution of any substituent X is calculated as follows (Eq. (3)):

$$\Delta_{solv}H^{X\to H/S} = \Delta_{solv}H^{C_6H_5X/S} - \Delta_{solv}H^{C_6H_6/S} \quad (3)$$

where $\Delta_{solv}H^{C_6H_5/S}$ is the solvation enthalpy of monosubstituted benzene in solvent S; $\Delta_{solv}H^{C_6H_6/S}$ is the solvation enthalpy of benzene in solvent S.

In present work benzene was used as a solvent S. Solvation enthalpies of aromatic hydrocarbons (naphthalene, diphenyl, anthracene and etc.), $\Delta_{solv}H^{ArH/S}$, were calculated from experimental values of solution and vaporization/sublimation enthalpies taken from works [2,5]. Step-by-step procedure of calculation of $\Delta_{solv}H^{ArX_n/S}$ value of aromatic hydrocarbons derivatives is described in Supplementary material.

Enthalpy of solution of solids at 298.15 K contains contribution from the enthalpy of fusion (a transition from the crystalline solid into liquid phase) as well as enthalpy of solution of liquid in solvent. The quantitative relation between fusion and solution enthalpy of solute A_i can be demonstrated as follows: in addition to Eq. (1) sublimation enthalpy can be represented as a sum of fusion enthalpy ($\Delta^l_{cr}H^{A_i}_m$) and vaporization enthalpy ($\Delta^g_l H^{A_i}_m$) at 298.15 K (Eq. (4)):

$$\Delta^g_{cr}H^{A_i}_m(298.15) = \Delta^l_{cr}H^{A_i}_m(298.15) + \Delta^g_l H^{A_i}_m(298.15) \quad (4)$$

Combination of Eqs. (1) and (4) gives the following equation:

$$\Delta_{soln}H^{A_i/S}(298.15) - \Delta_{solv}H^{A_i/S}(298.15) = \Delta^l_{cr}H^{A_i}_m(298.15) + \Delta^g_l H^{A_i}_m(298.15) \quad (5)$$

For solutes in liquid state vaporization enthalpy is calculated according to the following equation:

$$\Delta^g_l H^{A_i}_m(298.15) = \Delta_{soln}H^{A_i/S}(298.15) - \Delta_{solv}H^{A_i/S}(298.15) \quad (6)$$

If solute A_i is similar by structure and physical–chemical properties to the solvent S (≪like dissolves like≫), then $\Delta_{soln}H^{A_i/S}$ will be close to zero, e.g. liquid *n*-hexadecane in heptane (0.46 kJ mol^{-1} [8]) or 1-chloronaphthalene in benzene (0.13 kJ mol^{-1} [8]). We assume that the contribution to the solution enthalpy of aromatic compounds in benzene from nonspecific solute–solvent (endo) and solvent–solute (exo) interactions approaches zero [9]. In this case solvation enthalpy of solute A_i in solvent S would be approximately equal to the negative vaporization enthalpy:

$$\Delta_{solv}H^{A_i/S}(298.15) \approx -\Delta^g_l H^{A_i}_m(298.15) \quad (7)$$

Taking into account Eqs. (5)–(7) we can get the following equation:

$$\Delta_{soln}H^{A_i/S}(298.15) \approx \Delta^l_{cr}H^{A_i}_m(298.15) \quad (8)$$

In present work we compared measured in this work and literature solution enthalpies of aromatic hydrocarbons derivatives in benzene at 298.15 K with literature data on fusion enthalpies at melting temperature. The results are presented in Table 1. For each studied aromatic compound we have found a lot of literature sources of fusion enthalpies. All these data were collected in Table S3. Based on these values we have calculated average fusion enthalpies, which were used for comparison in Table 1.

Solution enthalpy values in benzene at 298.15 K are close to the corresponding fusion enthalpies at melting temperature practically for all compounds presented in Table 1. The average deviation is less than 1.5 kJ mol^{-1}. It should be noted that compounds containing substituents capable of forming solute–solute hydrogen bonds (—OH, —NH_2, —NH—, etc.) were not taken into account, since Eq. (7) does not work for them. Solution enthalpies of these compounds in liquid state in benzene deviate significantly from zero, e.g. *m*-cresol (10.8 kJ mol^{-1} [10]), aniline (5.2 kJ mol^{-1} [11]) and pyrrole (3.25 kJ mol^{-1} [12]).

Eq. (9) can be obtained on the basis of experimental data presented in Table 1.

$$\Delta_{soln}H^{A_i/S}(298.15) \approx \Delta^l_{cr}H^{A_i}_m(T) \quad (9)$$

It is unconventional result, because melting temperature of studied aromatic hydrocarbons derivatives varies in the range 286.3–505.0 K.