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Thermochemistry of phase transitions of aromatic amines: Estimation of the sublimation enthalpy at 298.15 K through the fusion enthalpy

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ABSTRACT

In the present work two methods of determination of sublimation enthalpies at 298.15 K based on solution enthalpies at 298.15 K and fusion enthalpies at the melting temperatures were applied for aromatic amines. The sublimation enthalpies of 17 substituted anilines and 1- and 2-naphthylamines at 298.15 K were calculated using their fusion enthalpies at the melting temperatures found in the literature, the solvation enthalpies in benzene and vaporization enthalpy of aniline. Additionally, the sublimation enthalpies of 9 substituted anilines and 1- and 2-naphthylamines were determined from their solution and solvation enthalpies. In this work we measured the solution enthalpies of aniline, its five derivatives and 2-naphthylamine in benzene while the solution enthalpies of other five aromatic amines were taken from the literature. The solvation enthalpies were calculated by means of the group-additivity scheme. The sublimation enthalpies values obtained as such were compared to the reference data. This method showed the good congruence with both direct experiment and solution calorimetry approach. In most cases the divergence does not exceed 2–3%. The consistency between independently determined sublimation enthalpies values validates the reliability of the relationship between the sublimation enthalpy at 298.15 K and fusion enthalpy at the melting temperature.

1. Introduction

Aromatic amines have been extensively used in the chemical industry for well over 150 years. They are applied for the production of polymers, azo dyes, rubber processing materials, herbicides, medicines, etc. The thermochemical data on the phase transitions of amines, in particular evaporation, solution and fusion enthalpies, are necessary for predict on of the solid-gas, solid-liquid and liquid-gas equilibria. The sublimation enthalpies of substituted anilines and naphthylamines were extensively studied in the works [1–27]. Various experimental techniques were employed in these studies, such as mass effusion Knudsen method [4,9–11,16–18,21], torsion-effusion technique [9,12,13,16,25], transpiration [1,3,14,24,27,28], thermogravimetric analysis [8], Calvet vacuum sublimation technique [5–7,10,19,20,22,23,26], static method [18], and gas chromatography [15].

A number of problems arise when the sublimation enthalpies are obtained with experimental measurements [29,30]. These problems include an inappropriate experimental setup, impurity of the samples, measurements of different polymorphic states. Thereby, indirect methods for determination of the sublimation enthalpy are useful for validation of experimental data.

Several empirical schemes have been recently applied for determination of the sublimation enthalpies of substituted anilines [30,31]. These schemes are based on a group-additivity of the sublimation enthalpy.

A solution calorimetry approach was also employed for determination of the sublimation enthalpies at 298.15 K of a number of aromatic amines [32] and showed good consistency with the conventional methods.

According to the solution calorimetry approach [32–35], the sublimation enthalpy at 298.15 K is determined as a difference between the solution enthalpy at 298.15 K measured experimentally and solvation enthalpy calculated from a group-additivity scheme [32]. The solution calorimetry approach has several advantages over the conventional methods, which can be crucial in the work with low volatile and unstable compounds. First, the experiment is carried out at the ambient temperature and does not lead to the thermal destruction of the compounds of interest. Note that it is also not necessary to adjust the results to 298.15 K. Second, the experiment has lower demand to the purity of the sample.

Recently we have developed a new approach which allows one to determine the sublimation enthalpy at 298.15 K by means of

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the technique combining the fusion enthalpy at the melting temperature and the group-additivity scheme applied to the solvation enthalpy for the aromatic compounds which do not form hydrogen bonds [36–38]. Further, we showed that this approach can be modified for determination of the sublimation enthalpies of the aromatic compounds which are capable of self-association in the condensed phase due to the hydrogen bonding. These substances, in particular, include benzoic acid derivatives and heteroaromatic carboxylic acids [39], substituted phenols [40], substituted benzamides and 3- and 4-pyridinecarboxamides [41]. This method is especially valuable when the measurement of the solution enthalpy is complicated.

In the present work we test both of the above mentioned indirect approaches for determination of the sublimation enthalpy of the substituted anilines and naphthylamines at 298.15 K from the solution enthalpy at 298.15 K and from the fusion enthalpy at the melting temperature.

2. Experimental part

2.1. Materials

Aniline, 4-toluidine, 4-chloroaniline, 1,3-diaminobenzene, 4-aminoacetophenone, 2-naphthylamine and 4-nitroaniline were of commercial origin with mass fraction purities better than 0.97. Aniline was distilled under reduced pressure over KOH. 4-Toluidine, 4-chloroaniline, 1,3-diaminobenzene and 2-naphthylamine were sublimed under vacuum (1 Torr). 4-Nitroaniline was recrystallized from ethanol. 4-Aminoacetophenone was used without further purification (see Table S1).

Benzene was purified before use according to [42]. Purity of the samples was analyzed using an Agilent 7890 B gas chromatograph (GC) equipped with a flame ionization detector. Water content was checked using Karl Fischer titration (see Table S1).

2.2. Solution calorimetry

The solution enthalpies of 4-toluidine, 4-chloroaniline, 1,3-diaminobenzene, 4-aminoacetophenone, 2-naphthylamine in benzene were measured at T = 298.15 K in the concentration range from 2.9 to 12.1 mmol kg^{-1} using a TAM III precision solution calorimeter. The calorimeter was tested by measuring the solution enthalpies of potassium chloride and propan-1-ol in water. The details on the solution calorimetry experimental procedure have been fully described elsewhere [32].

Substituted anilines and 2-naphthylamine were dissolved by breaking a glass ampule filled with 0.01–0.1 g of the studied sample in a glass cell containing 90 ml of pure solvent. Aniline was injected in 15 μL portions using an electronically operated syringe equipped with a long gold cannula immersed in the solvent. For each solute-solvent system, the solution enthalpies were measured at least 4 times.

Detailed data on the measurements of the solution enthalpies of aromatic amines in benzene are listed in Table S2.

3. Methodology

In the present work we used the following basic principles and definitions. The molar enthalpy of solution ($\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}$) is the enthalpy of transfer of 1 mol of a solute A_i to an infinitely diluted solution in a solvent S. The molar enthalpy of solvation ($\Delta_{\text{solv}}H^{\text{A}_\text{i}/\text{S}}$) is the enthalpy change observed when 1 mol of a solute A_i in a gaseous state at 0.1 MPa dissolves in a solvent to give a solution at infinite dilution. The molar enthalpy of vaporization/sublimation ($\Delta^{\text{g}}_{\text{cr}(l)}H^{\text{A}_\text{i}}$) is equal to the difference between the solution and solvation enthalpies at 298.15 K:

$$\Delta^{\text{g}}_{\text{cr}(l)}H^{\text{A}_\text{i}}(298.15\ \text{K}) = \Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}(298.15\ \text{K}) - \Delta_{\text{solv}}H^{\text{A}_\text{i}/\text{S}}(298.15\ \text{K}) \tag{1}$$

The group-additivity scheme can be used for calculation of the solvation enthalpy [32], while the solution and sublimation enthalpies are measured experimentally.

The enthalpies of solution of aromatic hydrocarbons and their derivatives in benzene were shown to be approximately equal to the sum of the fusion enthalpies at the melting temperature and the enthalpies of polymorphic phase transitions occurring between 298.15 K and the melting temperature (T_m) [36,37]:

$$\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{C}_6\text{H}_6}(\text{cr},298.15\ \text{K}) \approx \Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(T_\text{m}) + \sum \Delta_{\text{trns}}H^{\text{A}_\text{i}}(T_{\text{trns}}) \tag{2}$$

Combination of Eqs. (1) and (2) leads to the expression for the sublimation enthalpies of aromatic hydrocarbons and their derivatives at 298.15 K through the fusion enthalpies at the melting point and solvation enthalpies in benzene at 298.15 K:

$$\begin{aligned}\Delta^{\text{g}}_{\text{cr}}H^{\text{A}_\text{i}}(298.15\ \text{K}) = {} & \Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(T_\text{m}) + \sum \Delta_{\text{trns}}H^{\text{A}_\text{i}}(T_{\text{trns}}) \\ & - \Delta_{\text{solv}}H^{\text{A}_\text{i}/\text{C}_6\text{H}_6}(298.15\ \text{K})\end{aligned} \tag{3}$$

Eq. (3) was tested on more than 100 aromatic and heteroaromatic compounds which are not capable of self-association [36–38] and showed good reproducibility with the literature values. Also, the solution enthalpy of a solid compound A_i in a solvent S can be expressed as the sum of the fusion enthalpy ($\Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}$) of A_i at 298.15 K and the enthalpy of solution ($\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}$(l) of a virtual liquid A_i in the same solvent at 298.15 K:

$$\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}(\text{cr},298.15\ \text{K}) = \Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(298.15\ \text{K}) + \Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}(\text{l},298.15\ \text{K}) \tag{4}$$

For the solvent and solute with similar physical-chemical properties and structure, the $\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}$ (l, 298.15 K) value is negligibly small in comparison with $\Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}$ (298.15 K) and $\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}$ (cr, 298.15 K) (for example, the solution enthalpies of liquid 1-phenylnaphthalene and toluene in benzene are equal to 0.56 [33] and 0.50 kJ mol^{-1} [43], respectively). Consequently:

$$\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{S}}(\text{cr},298.15\ \text{K}) \approx \Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(298.15\ \text{K}) \tag{5}$$

Combination of Eqs. (2) and (5) gives the following equation:

$$\Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(298.15\ \text{K}) \approx \Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(T_\text{m}) + \sum \Delta_{\text{trns}}H^{\text{A}_\text{i}}(T_{\text{trns}}) \tag{6}$$

However, Eq. (3) is not applicable to the aromatic compounds prone to self-association due to the formation of intermolecular hydrogen bonds [39]. In this case, $\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{6H}_6}$ (l, 298.15 K) cannot be neglected because the breaking of intermolecular hydrogen bonds in the liquid state of A_i is not compensated by the solvation enthalpy in benzene (for example, $\Delta_{\text{soln}}H^{3-\text{MeOPhOHC}_6\text{H}_6}$ = 8.7 kJ mol^{-1} [37]). Therefore, $\Delta_{\text{soln}}H^{\text{A}_\text{i}/\text{C}_6\text{H}_6}$ (cr, 298.15 K) substantially exceeds $\Delta^{\text{l}}_{\text{cr}}H^{\text{A}_\text{i}}(T_\text{m}) + \sum \Delta_{\text{trns}}H^{\text{A}_\text{i}}(T_{\text{trns}})$. In the works [36–38] the modification that considers the non-zero dissolution enthalpy of such compounds in benzene was proposed. The sublimation enthalpies of total of 78 compounds were calculated (34 aromatic and heteroaromatic carboxylic acids, 26 substituted phenols and 14 aromatic amides) and compared to the literature data. In most cases divergence did not exceed 2–3%.

For the X_i substituted anilines $(\text{X}_\text{i})_n\text{PhNH}_2$ not self-associated due to the formation of intermolecular hydrogen bonds (Alk, Hal, COOMe, CHO, COCH_3, NO_2), the standard molar sublimation