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Non-additivity in the solvation enthalpies of NH-containing compounds and estimation of their sublimation enthalpies at 298 K



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ABSTRACT

In the present work, we have developed an additivity scheme for the calculation of solvation enthalpies of NH-containing compounds capable of hydrogen bond formation with solvent. The solvation enthalpies of these compounds were calculated using an additivity scheme and taking into account the contribution due to hydrogen bond formation between solute and solvent. This contribution was calculated using several different equations which connected the enthalpies of hydrogen bonds with frequency shifts of N—H stretching vibrations. The efficiency of the scheme for calculating the enthalpies of solvation was tested on the heterocyclic NH-containing compounds in tetrahydrofuran and 1,4-dioxane. The vaporization and sublimation enthalpies of heterocyclic NH-containing compounds at 298.15 K were estimated using experimentally measured solution enthalpies and estimated values of solvation enthalpies. The vaporization and sublimation enthalpies obtained in the present work are in good agreement with available literature data.

The solution enthalpies of nineteen heterocyclic compounds were measured experimentally in the present work. © 2017 Elsevier B.V. All rights reserved.

1. Introduction

Heterocyclic amines are important chemical compounds with a wide range of using, from medicines to corrosion inhibitors. Most of them are used for the synthesis of alkaloids and pharmacophores [1]. Enthalpy of sublimation/vaporization is an important thermodynamic function of pure compound and it can be used to determine intermolecular interaction of a compound with solvents.

Traditional methods for determination of vaporization and sublimation enthalpies are based on the investigation of the process of transition from the condensed state to the gaseous phase. In addition, indirect methods may be used to determine the phase transition enthalpy based on the relationship between vaporization or sublimation, solvation and solution enthalpies [2–6]. According to these methods solvation enthalpy can be calculated in several different ways [2,3,6] or determined using a gas chromatography [4,5]. At the same time, solution enthalpy can be measured experimentally using calorimetry or also predicted from vaporization enthalpies of reference compounds [5].

In the previous study [7] we have developed an additive scheme for calculation of the solvation enthalpy of aromatic compounds containing a hydroxyl group. The solvation enthalpies of phenols and naphtholes in proton acceptor solvents cannot be calculated by the simple additive scheme, because solvation enthalpy includes terms of nonspecific and specific interactions. Enthalpies of specific interactions depend on

electronic and steric effects of the substitutions. At the same time enthalpy of nonspecific solvation can be calculated using the additive scheme [2,6] or some parameter related to the specific volume in particular molar refraction [3]. Therefore, prediction of solvation enthalpy for system with only nonspecific interactions is a simple task. Problems with non-additivity appear when enthalpy of specific interaction plays a significant part in the solvation enthalpy value. In this case, the solvation enthalpy could not be calculated as a sum of the group contributions because enthalpy of specific interaction depends on the properties of substitutes. It means that if acceptor or donor substitutions near to group, which is capable of forming hydrogen bond, enthalpy of intermolecular interaction between solute and solvent increases or decreases, respectively. The objective of research [7] was to find the contribution of specific interactions of substituted phenols with solvent to the solvation enthalpy. This contribution was estimated using the logansen's equation [8].

In the present study, we develop the approach for determination of solvation enthalpies of NH-containing heterocyclic compounds. Different methods of calculation of the contribution to the solvation enthalpy related to hydrogen bonds formation are tested and discussed.

2. Experimental part

2.1. Materials

All samples were of commercial origin with the mass fraction purities better than 0.95. Phthalimide and indole were purified by

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