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

CrossMark

Ruslan N. Nagrimanov *, Aizat A. Samatov, Tansu M. Nasyrova, Boris N. Solomonov

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

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 naphthols 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 Iogansen'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

---

* Corresponding author.
E-mail address: Rnagrimanov@gmail.com (R.N. Nagrimanov).

sublimation under reduced pressure. Phenothiazine and 1,2,4-triazole were purified by recrystallization from ethanol. 1,2,3-Benzotriazole was recrystallized from benzene. All samples were dried in a vacuum oven at 65 °C after recrystallization. Other samples for solution calorimetry were used without purification (see Table 1). All solvents were purified before use according to [9]. The purity of the samples was analyzed using an Agilent 7820 A gas chromatograph (GC) equipped with a flame ionization detector. Water content in solvents was checked using Karl Fischer titration.

2.2. Solution calorimetry

Solution enthalpies of samples in tetrahydrofuran and 1,4-dioxane at infinite dilution were measured at $T = 298.15$ K in a concentration range from 0.4 to 57.0 mmol kg^{-1} using TAM III precision solution calorimeter. The infinite dilution was shown by independence of solution enthalpy due to increasing of concentration of solute in the solvent. Solid samples were dissolved by breaking a glass ampule in a glass cell containing pure solvents. For liquid samples an electronically operated micro liter syringe equipped with a long gold cannula was used. The details of the solution calorimetry experimental procedure have been fully described elsewhere [10,11].

Experimental solution enthalpies of NH-containing compounds in various solvents are listed in Table S1.

2.3. IR spectroscopy

Infrared spectrum was obtained using a Bruker Vector 22 FT-IR Spectrometer. All measurements were recorded at room temperature in the wavenumber range from 400 to 4000 cm^{-1}, with a resolution of 1 cm^{-1}. Each spectrum consisted of the sum of 128 scans. Blackman–Harris function was used as approximation. KBr cells were used with different spacers (1.0–3.2 mm) to achieve the best signal/noise ratio. Concentrations of base were 4 vol% in carbon tetrachloride solvent.

3. Results and discussion

3.1. Solvation enthalpy calculation

The approach for determination of vaporization and sublimation enthalpies based on the relationship between vaporization/sublimation enthalpy of compound A_i, solvation and solution enthalpies of solute

Table 1
Origin, purity, methods of purification and analysis of heterocyclic compounds and organic solvents (tetrahydrofuran and 1,4-dioxane).

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity[a]	Mass fraction of water[b]
Pyrrole (l)	Aldrich	0.98	None	–	0.0008
Pyridine (l)	Ecos-1	0.998	None	–	0.0006
Furan (l)	Aldrich	0.99	None	–	0.0004
Thiothene (l)	Aldrich	0.99	None	–	0.0005
1,4-Benzoquinone (cr)	Aldrich	0.98	None	–	–
Indole (cr)	Aldrich	0.99	Sublimation	0.999	–
Phenoxazine (cr)	Aldrich	0.97	None	–	–
Phenothiazine (cr)	Aldrich	0.98	Recrystallization	0.999	–
1,2,4-Triazole (cr)	Aldrich	0.98	Recrystallization	0.998	–
1,2,3-Benzotriazole (cr)	Aldrich	0.99	Recrystallization	0.997	–
Phthalimide (cr)	Aldrich	0.99	Sublimation	0.996	–
Tetrahydrofuran (l)	Ekos-1	0.99	Distillation	0.999	0.0004
1,4-Dioxane (l)	Ekos-1	0.99	Distillation	0.998	0.0004

[a] Determined by gas chromatography.
[b] Determined by Karl Fischer titration.

A_i in solvent S:

$$\Delta^{\mathrm{g}}_{\mathrm{cr(l)}}H^{A_i} = \Delta_{\mathrm{soln}}H^{A_i/S} - \Delta_{\mathrm{solv}}H^{A_i/S}, \tag{1}$$

where solution enthalpy of studied compound can be measured by solution calorimetry.

Solvation enthalpy can be regarded as the sum of the non-specific solvation enthalpy ($\Delta_{\mathrm{solv(nonsp)}}H^{A_i/S}$) and the enthalpy of solute-solvent specific interactions ($\Delta_{\mathrm{int(sp)}}H^{A_i/S}$):

$$\Delta_{\mathrm{solv}}H^{A_i/S} = \Delta_{\mathrm{solv(nonsp)}}H^{A_i/S} + \Delta_{\mathrm{int(sp)}}H^{A_i/S} \tag{2}$$

In the previous works [2,6] we chose the solvent to exclude the formation of specific interaction or make this contribution to the enthalpy of solvation insignificant. Thus the solvation enthalpy can be calculated using that additive scheme [2,6]. The solvation enthalpies values of heterocyclic compounds or carbonyl-containing aromatic compounds can be calculated by the following equation:

$$\Delta_{\mathrm{solv}}H^{A_i/S} = \Delta_{\mathrm{solv}}H^{\mathrm{ArH/S}} + \sum \Delta_{\mathrm{solv}}H^{X_i \to \mathrm{CH/S}} \tag{3}$$

$\Delta_{\mathrm{solv}}H^{\mathrm{ArH/S}}$ is a solvation enthalpy of parent aromatic compound in a solvent S, $\Delta_{\mathrm{solv}}H^{X_i \to \mathrm{CH/S}}$ is a contribution to the solvation enthalpy related with CH-group replaced by group X which represents a heteroatom (—S—, —O—, —N=, >NH, >NCH$_3$) or carbonyl (>C=O). Details of the determination of these contributions in benzene were spelled out in ref. [6]. According to procedure offered in [6] the contributions to the solvation enthalpy related to replacement CH group in aromatic ring by heteroatom or heteroatomic functional group in tetrahydrofuran and 1,4-dioxane were calculated and presented in Table 2 (for details on the calculations look Supporting material).

The correct measurement of the solution enthalpies of NH–containing compounds in the solvent which cannot form specific interaction is difficult, because the solubility of most solutes is very poor. The solubility increases in the presence of the solute-solvent hydrogen bonds. However in this case the non-additivity contribution ($\Delta\Delta H$) must be added to the enthalpy of solvation of NH – containing compounds calculated using Eq. (3):

$$\Delta_{\mathrm{solv}}H^{A_i/S} = \Delta_{\mathrm{solv}}H^{\mathrm{ArH/S}} + \sum \Delta_{\mathrm{solv}}H^{X_i \to \mathrm{CH/S}} + \Delta\Delta H \tag{4}$$

In the work [7] was shown that this non-additivity contribution can be estimated using the Iogansen's equation and IR spectroscopy method:

$$-\Delta_{\mathrm{HB}}H^{A\cdots S} = \sqrt{1.92 \cdot (\Delta_{\mathrm{HB}}\nu^{A_i/S} - 40)} \tag{5}$$

This equation is more correct if frequency shifts is within to 100–850 cm^{-1} [8].

However the Iogansen's equation was introduced for substituted phenols and the plausibility of using this equation for NH–containing compounds should be verified. Generally hydrogen bond enthalpy (H-bond) can be determined from IR-spectrum using approaches based on the temperature dependence of spectral absorption of XH group in

Table 2
Contributions into solvation enthalpy related to the exchange of CH-group of hydrocarbon with corresponding substituent atom or group in tetrahydrofuran (THF) and 1,4-dioxane (1,4-DO).

X	$-\Delta_{\mathrm{solv}}H^{X \to \mathrm{CH/THF}}$/kJ·mol^{-1}	$-\Delta_{\mathrm{solv}}H^{X \to \mathrm{CH/1,4\text{-}DO}}$/kJ·mol^{-1}
>NH	22.8	21.6
>C=O	7.6	8.3
—S—	7.0	7.0
—O—	0.8	1.2
—N=	4.8	5.3