



Thermodynamic of dissolution and hydrogen bond of the pyrrole, *N*-methylpyrrole with proton acceptors



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ABSTRACT

Enthalpies of dissolution of pyrrole, *N*-methylpyrrole in proton acceptor solvents and proton acceptors in the medium of pyrrole, *N*-methylpyrrole were measured. The enthalpies of hydrogen bond of pyrrole, *N*-methylpyrrole with proton acceptors were calculated from experimental data of solution enthalpy of amines with organic compounds. The hydrogen bond enthalpies of proton acceptors with *N*-methylpyrrole are equal to zero unlike with pyrrole. The hydrogen bond enthalpies of proton acceptors (B) in pyrrole are significantly lower than the enthalpies of hydrogen bonding of systems of pyrrole-base in the complexes 1:1 due to reorganization effects of pyrrole as solvent. The cooperative effects in multi-particle complexes of pyrrole with bases are negligible.

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1. Introduction

Pyrrole and its derivatives are important molecules because they are widespread in the flora and fauna. Pyrrole and its derivatives are structural fragments of synthetic peptides which stability is realized through the formation of hydrogen bonds (HB) [1]. These compounds are involved in molecular recognition [2–4], determine the properties of polymers [5–7], are used as catalysts [8] and antibiotics [9] since they are responsible for the selectivity and affinity [10], are part of polyamides which anticancer properties are realized by means of hydrogen bonding with DNA system [11,12]. Pyrrole is capable to exhibit the properties of acidic and basic properties due to having a N–H group and π – electron system correspondingly. Hydrogen bonding between these active centers determine a self-association of pyrrole molecules [13–17] and a formation the complexes with another organic molecules [18–24]. Estimation of energy parameters and strength of hydrogen bonds of pyrrole and its derivatives assist in understanding the nature and mechanism of different processes and solution effects in supramolecular systems.

Hydrogen bonds of pyrrole and its derivatives in the complexes with organic molecules were studied by different structure meth-

ods: IR-spectroscopy [13–16,23–26], UV- spectroscopy [23,26], NMR-spectroscopy [27,28], Raman spectroscopy [16,29]. Energy parameters of hydrogen bond of pyrrole with organic molecules were determined by computational chemistry [13,14,22,25,26]. Hydrogen bonds of pyrrole with organic molecules were studied by structural methods in inert solvent, matrix of inert gas or proton acceptor solvents [13–16,23,25]. It should be noted, that only in several works [30–35] hydrogen bonds of pyrrole with organic molecules are investigated by thermodynamic solvation method. Enthalpies of specific interaction of pyrrole in proton donors and proton acceptors obtained by «pure-base» method [30] are close to enthalpies of specific interaction in the complexes pyrrole with proton acceptors [36]. However, an influence of proton acceptors structure on a strength of hydrogen bonds in complexes of pyrrole-base is not enough studied [30]. The question remains what happens when one dissolve proton acceptor in environment of associated amine such as pyrrole. Influence of reorganization effect of pyrrole and of cooperative effects in multi-particle complexes of pyrrole with bases on enthalpies of specific interaction in the environment of pyrrole was not investigated.

In the present work solution enthalpies of pyrrole, *N*-methylpyrrole in proton acceptor solvents and proton acceptors in the medium of pyrrole, *N*-methylpyrrole were measured. The enthalpies of specific interaction of pyrrole, *N*-methylpyrrole with bases were calculated using the solution enthalpies of amines in proton acceptors and vice versa. Relationship between enthalpies

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Table 1
Characteristics of the chemicals studied in this work.

Chemical Name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method	Mass fraction of water ^a
Acetonitrile (l)	Sigma Aldrich	0.99	Distillation	0.998	GC	0.0006
Acetone (l)	Sigma Aldrich	0.99	Distillation	0.997	GC	0.0008
Di- <i>n</i> -butyl ether (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0004
1,4-Dioxane (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0008
Diethyl ether (l)	Ekos	0.98	Distillation	0.997	GC	0.0006
Dimethylformamide (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0006
Ethyl acetate (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0004
<i>n</i> -Hexane (l)	Sigma Aldrich	>0.985	Distillation	0.995	GC	0.0004
<i>n</i> -Heptane (l)	Sigma Aldrich	0.99	Distillation	0.995	GC	0.0005
Methyl acetate (l)	Sigma Aldrich	0.99	Distillation	0.996	GC	0.0006
<i>N</i> -Methylimidazole (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0006
<i>N</i> -Methylpyrrole (l)	Sigma Aldrich	0.99	Distillation	0.997	GC	0.0006
<i>n</i> -Octane (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0005
Pentan-2-one (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0006
Propionitrile (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0005
Pyridine (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0006
Pyrrole (l)	Sigma Aldrich	>0.99	Distillation	0.997	GC	0.0006
Tetrahydrofuran (l)	Sigma Aldrich	0.98	Distillation	0.997	GC	0.0004
Triethylamine (l)	Sigma Aldrich	0.98	Distillation	0.996	GC	0.0006

^a Determined by Karl Fischer titration.

of hydrogen bond of pyrrole with proton acceptors and structures of the interacting molecules was determined. Knowledge of enthalpies of solution or enthalpies of solvation of pyrrole in organic solvent could be useful tool for prediction of solubility at any desired temperature.

2. Experimental

Pyrrole was purchased from company Aldrich, >0.99 (mass fraction purity min.) and additionally purified by vacuum distillation over calcium hydride, was selected the average fraction. *N*-methylpyrrole was purchased from company Aldrich, 0.99 (mass fraction purity min.) and additionally dried with calcium sulfate, then fractionally distillation from potassium hydroxide immediately before use. All organic solvents were purchased from Aldrich Fluka min. purity 0.98. They were dried and purified before usage by standard methods [37]. The content of organic impurities was controlled by chromatographic analysis by means of Agilent 7890 B. The content of water was determined by titration using Karl Fischer method. Detailed information about studied samples, their purity and water content are presented in Table 1.

Calorimetric experiments were carried out immediately after cleaning substance. The solution enthalpies of pyrrole, *N*-methylpyrrole in proton acceptors and solute compounds in the medium of amines were measured at 298.15 ± 0.01 K and 0.1 MPa on the two solution calorimeters. The first calorimeter is semi-adiabatic solution calorimeter constructed in Kazan Federal University. The apparatus was tested by the dissolution of potassium chloride in water. The average value obtained is 17.41 ± 0.04 kJ mol⁻¹, T = 298.15 K, m = 0.02783 mol kg⁻¹, that corresponds to the standard value of 17.47 ± 0.07 kJ·mol⁻¹ [38]. A detailed description of the apparatus is presented in previous studies [39,40]. Since the volume of the solvent in the calorimetric cell was 110 ml and the weight of the solute was 0.02–0.06 g with an uncertainty of 0.0001 g. The second calorimeter is isothermal solution calorimeter TAM III (TA Instruments). This device is intended for research of a long term dissolution process during a few days at 298.15 ± 0.01 K and 0.1 MPa. The calorimetric cell is a glass vessel equipped with a gold stirrer, a Joule heater, and a thermistor. In each experiment it was charged with 100 ml of a solvent. Titration technique was used for measurements of solution enthalpies of liquid solutes. According to standard procedure small portions of liquid solute (10–20 μl) were added to the solvent using an elec-

tronically operated microliter syringe equipped with a long gold cannula with the tip immersed in the measuring cell. Obtained calorimetric curve was used for determination of heat effect of each addition. The calorimetric measurement validity was verified by determination of enthalpies of 1-propanol dissolution in water; the measured value –10.08 ± 0.01 kJ mol⁻¹ at 298.15 K and m = 0.0238 mol kg⁻¹ corresponds with the reference value for the tested system –10.10 ± 0.02 kJ mol⁻¹ [41]. The detailed procedure of dissolution experiments was described previously [42,43]. All the values correspond to the limiting dilution, which was confirmed by conducted additional experiments in the calorimetric wide range of concentrations of the solute, Table S1.

3. Methodology

The behavior of molecules in different chemical and biological processes is greatly affected by the solvent. Such an influence is commonly described in terms of intermolecular interactions which may be of non-specific and specific type of solute molecules in the solvent. Hydrogen bonds of solute in solvent play key role in intermolecular interaction and also determine nature and mechanism of different processes and effects in solution. In our opinion the most appropriate method for assessing the energy of the hydrogen bond is approach based on thermodynamics of solvation, because this method allows to assess directly the energy formation of hydrogen bonds X-H...Y between molecules. The solvation enthalpy is defined as heat effect of transition of molecules from ideal gas state in the liquid phase to form a solution of certain composition, excluding those changes that are accompanied by breaking of chemical bonds, which includes the entire amount of energy and structural changes occurring in the transition at 298.15 K. The solvation enthalpies of compound A in solvent S ($\Delta_{\text{solv}}H^{\text{A/S}}$) is calculated as the difference between the experimentally measured dissolution enthalpy of A in S ($\Delta_{\text{soln}}H^{\text{A/S}}$) and vaporization (sublimation) enthalpy of A ($\Delta_{\text{vap(sub)}}H^{\text{A}}$), Eq. (1).

$$\Delta_{\text{solv}}H^{\text{A/S}} = \Delta_{\text{soln}}H^{\text{A/S}} - \Delta_{\text{vap(sub)}}H^{\text{A}} \quad (1)$$

The solvation enthalpy reflects the strength of intermolecular interactions between of solute and solvents. Contrariwise the solvation enthalpy can be represented as the sum of non-specific

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