



# Thermodynamic functions of hydrogen bonding of amines in methanol derived from solution calorimetry data and headspace analysis

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## ABSTRACT

Reactivity and equilibrium properties of organic molecules in self-associated liquids greatly depend on the hydrogen bonding with solvent. This work contains comprehensive thermodynamic analysis of hydrogen bonding of aliphatic and aromatic amines in self-associated solvent methanol. Enthalpies of solution at infinite dilution and limiting activity coefficients for the studied systems were measured experimentally. Enthalpies and Gibbs energies of hydrogen bonding of amines with neat methanol were determined. These values were found to be decreased compared with hydrogen bond energy in equimolar complexes "methanol–amine" determined in inert solvent or base media. A linear dependence between enthalpies and Gibbs energies of hydrogen bonding of amines with neat methanol was observed. It was firstly revealed that the entropy of specific interactions of amines with neat methanol can be about zero or positive. Disruption of solvent–solvent hydrogen bonds can be regarded as the most important step during dissolution of amine in methanol. It was found that the cooperative effect influences on the Gibbs energies of hydrogen bonding of amines in methanol, but in a lesser extent than in aqueous solutions. The new results show that the hydrogen bonding process in the self-associated solvents differs significantly from equimolar complexation in aprotic media.

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## 1. Introduction

The non-covalent interactions in condensed phase influence greatly on various physical, chemical and biological processes [1]. Among all non-covalent interactions, hydrogen bonding takes a special place [2]. H-bonds play a huge role in substrate–enzyme binding [3], and determine the specificity of DNA molecule [4]. They regulate the structure and reactivity of supramolecular assemblies [5] and control an association of molecules in condensed phase [6]. One of the most widely-spread examples of self-associated liquids by hydrogen bonds is methanol. This solvent is used in oil and chemical industry. Methanol is the most similar molecule to water. It presents a mixture of the complexes of varied structure (linear and cyclic) [7,8] and stoichiometry (dimer, trimer, . . . , polymer) [9,10]. Solute molecules can be completely H-bonded in methanol environment and their reactivity is largely determined by the thermodynamic parameters of hydrogen bonding. This makes

the estimation of hydrogen bonding thermodynamic functions of solutes with neat methanol a crucial problem.

Hydrogen bonding in equimolar complexes of methanol with organic substances is broadly investigated using various experimental methods. Solution calorimetry [11–16], FTIR-spectroscopy [16–18] and NMR-spectroscopy [16,19] measurements were applied to obtain extensive data on thermodynamic functions of equimolar complexation  $\text{CH}_3\text{OH} \cdot \cdot \text{B}$  (B – proton acceptor) in inert or aprotic media [11,16,19–21]. Also empirical equations, such as logansen [22], Badger–Bauer [23], Raevsky [24], Abraham [25] and other relations [26,27] were created for estimating enthalpies and equilibrium constants in binary hydrogen bonded complexes. The complexation of solute molecules with neat methanol is on the other hand much less investigated. The application of spectral methods is hardened by the overlapping of O–H bands related to various hetero- and self-associated species in methanol environment. Empirical equations also cannot be used in this case because they only deal with parameters for equimolecular complexes.

Problems in examination of hydrogen bonding between solute molecules and methanol are related to special properties of self-associated liquids, which are stipulated by the existing hydrogen bonded species of varied composition in their media. Thermodynamic function of hydrogen bonding process of solutes in

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