



Enthalpy of cooperative hydrogen bonding in complexes of tertiary amines with aliphatic alcohols: Calorimetric study

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ABSTRACT

The work is devoted to the investigation of thermodynamics of specific interaction of the tertiary aliphatic and aromatic amines with associated solvents as which aliphatic alcohols were taken. Solution enthalpies of aliphatic alcohols in amines (tri-*n*-propylamine, 2-methylpyridine, 3-methylpyridine, *N*-methylimidazole) as well as amines in alcohols were measured at infinite dilution. The enthalpies of specific interaction (H-bonding) in systems studied were determined based on experimental data. The enthalpies of specific interaction of amines in aliphatic alcohols significantly lower than the enthalpies of hydrogen bonding in complexes amine–alcohol of 1:1 composition determined in base media due to the reorganization of aliphatic alcohols as solvents. The determination of solvent reorganization contribution makes possible to define the hydrogen bonding enthalpies of amines with clusters of alcohols. Obtained enthalpies of hydrogen bonding in multi-particle complexes are sensitive to the influence of cooperative effect. It was shown, that hydrogen bond cooperativity factors in multi-particle complexes of alcohols with amines are approximately equal for all alcohols when pyridines and *N*-methylimidazole as solutes are used. At the same time, H-bonding cooperativity factors in complexes of trialkylamines with associative species of alcohols decrease with increasing of alkyl radical length in alcohol and amine molecules.

This work shows that the thermodynamic functions of specific interaction of solutes with associated solvents cannot be described using the H-bond parameters for the complexes of 1:1 composition.

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1. Introduction

A great part of research literature on hydrogen bonding concerns the self-associated liquids. Such liquids can be considered as a mixture containing complexes with various structure (linear, branched, cyclic) and composition (monomer, dimer, tetramer, etc.), which are in equilibrium with each other. Formation of hydrogen bonds in these liquids significantly affects their physical and chemical properties [1,2]. The simplest self-associated solvents are aliphatic alcohols. This type of solvents is widely used in organic synthesis and industry. It should be noted, that various processes, which occur in aliphatic alcohols, greatly depend on the hydrogen bonding with the solvent. Therefore, quantification of the thermodynamic parameters of formation of hydrogen bonds in them has a great practical interest.

Studies of hydrogen bond formation in aliphatic alcohols have been carried out with different experimental methods, for example, vapor pressure [3,4] and calorimetric measurements [5–8],

infrared (FTIR) spectroscopy [9–14] and nuclear magnetic resonance (NMR) [15–19] techniques. The authors attempted to solve two major tasks in these studies. The first one was to determine the structure of associative species of alcohol and to describe thermodynamic parameters of their formation. Usually obtained experimental data were interpreted with a variety of statistical and empirical models postulating the specified association way in aliphatic alcohols [20].

Second, more complicated task, concerning non-covalent interactions in solutions of aliphatic alcohols, is the determination of hydrogen bond energy of solute molecule with associated solvent. Hydrogen bonding with solvent may significantly influence on the properties and reactivity of solutes. One should take into account two important peculiarities of associated liquids for analysis of hydrogen bonding in alcohols solution. The first one is the phenomenon of cooperativity. The concept of cooperativity implies that the hydrogen bonding energy in multi-particle complex is not equal to the sum of energies of pair-wise interactions [21]. The cause of the cooperative effect as follows from [22,23] is a change in the basicity and acidity of alcohols associative species in comparison with free molecules. Luck *et al.* [24] revealed by FTIR-spectroscopy, that in ternary complex $(ROH)_2 \cdot \cdot B$ (*B* – proton acceptor) both hydrogen bonds are strengthened and the value of

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