

Cooperative Hydrogen Bonding in Solution

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Cooperative hydrogen bonding (HB) has become the basic object of investigation in chemistry and biology. It is one of the formation instruments of proteins, nuclear acids and different supra-molecular structures. The concept of cooperativity between hydrogen bonds implies that the primary hydrogen bond between a proton donor X-H and a proton acceptor B (X-H...B) becomes stronger, when a third partner A forms the complex with a lone electron pair of atom X (A...X-H...B).

In present work we have investigated cooperative HB formation in different systems by calorimetry and IR-spectroscopy methods.

A new method of self-association enthalpy determination was proposed. Self-association enthalpies of aliphatic alcohols were determined using this method. For all investigated alcohols except methanol the average self-association enthalpy fall in the range from -16.9 to -17.7 kJ mol⁻¹. A slightly smaller value of -15.1 kJ mol⁻¹ was observed for methanol. From the proton-acceptor ability of an aliphatic alcohol relative to a standard proton acceptor (diethyl ether) linear dimer formation enthalpies of aliphatic alcohols were determined (-8.6 0.7 kJ mol⁻¹). Difference between linear dimer formation enthalpy and self-association enthalpy is the result of cooperative effect contribution in clusters of aliphatic alcohols. Cooperativity factors for investigated H-bonding liquids were determined. Cooperativity factors increase with increasing of alkyl group in alcohol molecule. Obtained results are in good agreement with literature data. Solutions of different proton donors in self-associated solvents were also investigated. Enthalpy of cooperative HB of different proton donors with methanol as a solvent was determined using a proposed method. Cooperative interaction contribution to hydrogen bonding enthalpy of proton donors with methanol was discussed.

Solution enthalpies of proton acceptors in aliphatic alcohols and aliphatic alcohols in proton acceptors were measured by calorimetric method. Based on method [1] specific interaction enthalpies of proton acceptors with aliphatic alcohols were calculated. Specific interaction enthalpies of proton acceptors in aliphatic alcohols values are dramatically lower than specific interaction enthalpies of aliphatic alcohols in proton acceptors environment. The decrease of specific interaction enthalpies of proton acceptors in aliphatic alcohols is the result of competition for the most acidic H-atom in self-associated alcoholic solvent between the alcohol and proton acceptor molecules. The specific interaction enthalpies of proton acceptors in alcohols present the difference between cooperative HB formation enthalpy of proton acceptor with alcohol clusters and self-association enthalpy of alcohol. Average cooperative HB enthalpies of proton acceptors with associated species of the alcohol were calculated. Obtained values exceed the enthalpies of specific ROH...B interaction determined in proton acceptor environment by 20 – 30 % in average.

Hydrogen bonding in cooperative complex ROH...ROH...B was investigated using IR spectroscopy and calorimetry methods. A new equation for determining the cooperative HB enthalpy of proton acceptors with dimer ROH...ROH was proposed. Cooperative HB enthalpies of pyridine with dimers of aliphatic alcohols were determined. Comparison of these values with average cooperative HB enthalpy of pyridine with associated species of aliphatic alcohols shows that they coincide within 2 kJ/mol. It means that the cooperativity effect will reach a certain value after which all additional molecules extending the chain will be stabilized by a constant amount.

[1] B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, and N.M. Milesenko, *J. Phys. Org. Chem.* **18**, 49 (2005).