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Estimation of the Size of Alcohol Clusters through PFG NMR Diffusion Measurement

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1. Introduction

Simple alcohols form supramolecular clusters that are held together by hydrogen bonding between their hydroxyl groups. In order to determine their size we propose a novel combination of experimental and computational methodologies. The experimental methodology is based on PFG NMR. The theoretical approach consists of quantum chemical calculations that provide input for HydroNMR program [1] that is used for calculation of a diffusion coefficient.

2. Experiments and Methods

Ethanol was dissolved in deuterated n-hexane in concentration of 0.16 mol/dm^3. Self-diffusion coefficients were determined by means of double stimulated echo pulse sequence [2] in a broad temperature range 180 – 330 K (spectrometer Bruker Avance working at 500 MHz for ^{1}H). The possible structures of ethanol were computed on a DFT level of theory using using B3LYP combination of functionals and 6-31+G* basis set (Gaussian 98).

The obtained structures were used to calculate theoretical diffusion coefficient by HydroNMR program [1]. The hydrodynamic calculation consists of three major steps: (1) transformation molecular geometry to a primary model by replacement of all non-hydrogen atoms by a sphere of given radius, (2) transformation of the primary model into a shell model and (3) calculation of diffusion tensor within approximations of the Einstein-Stokes approach.

3. Results and Discussion

The comparison of the measured diffusion coefficients with the values calculated for the theoretical structures is presented in Figure 1. The increase of hydrodynamic radius of alcohol upon decreasing the temperature is attributed to the formation of supramolecular clusters. The average cluster size ranges from 1 to roughly 6 ethanol molecules. It is interesting to note that the decrease of the hydrodynamic radius stops above 310 K for our rather low ethanol concentration. The experimentally determined diffusion coefficient

is in agreement with the theoretically calculated counter-part. This observation provides an independent justification of the presented methodology.

HydroNMR was devised for calculation of diffusion coefficients of biological macromolecules. Its application to small molecules requires modification of the size of atomic spheres used for creation of the primary hydrodynamic model. This goal was achieved through comparison of the calculated and experimental diffusion coefficients of tetramethyl silane dissolved in n-hexane. It was found that optimal atomic sphere radius is 0.08 nm instead of 0.32 nm as recommended for proteins [1].

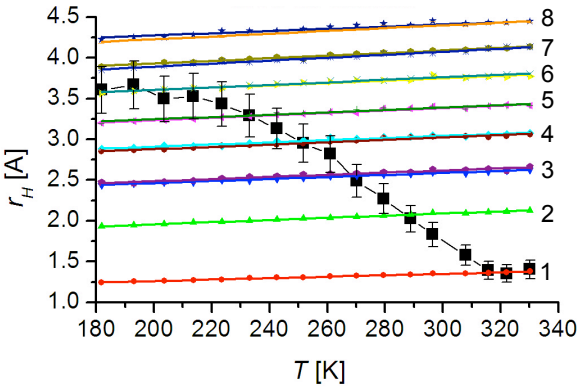

Fig. 1: Temperature dependence of the hydrodynamic radii r_H of ethanol clusters determined experimentally (black data points with error bars). Horizontal lines are the calculated hydrodynamic radii of ethanol clusters of various sizes, as indicated by the numbers on the right-hand side.

3. Conclusion

We have determined an average size of alcohol clusters present in solution of alcohol in hexane in a broad range of temperatures. The novel methodology consists of PFG NMR measurement accompanied by quantum chemical and hydrodynamic calculations. The HydroNMR program with the settings properly modified can be applied also to small molecules.

References

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Acknowledgement The financial support by the Czech Science Foundation (P204/11/1206), by Charles University (GAUK 81410) and by the Ministry of Education of CR (research plan MSM 0021620835) is gratefully acknowledged.