

UNIVERSITY OF PÉCS

Doctoral School of Chemistry

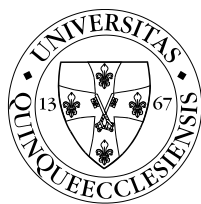
Structure and stability of clusters of primary alcohols in the liquid phase – their interaction with aromatic molecules

PhD Thesis

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1. Introduction

Hydrogen bonded liquids are still under intense investigation, since their own structure has considerable effect on the solvation shell of the solute molecules dissolved in those solvents. This property has significant consequences both on the conformation of the solvated compounds and conversely, the presence of the solute modifies the structure of these liquids stabilized by hydrogen bonds.

These aforementioned points include the necessity of the investigation both the structure of the bulk phase and the interaction between the solute and the solvent molecules. Theoretical and experimental possibilities are available for the studies. The theoretical investigations include the molecular dynamics simulations and Monte-Carlo simulations using classical force-fields, the *ab initio* molecular dynamics (AIMD) studies, and also the possible application of the Quantum Cluster Equilibrium (QCE) model which is based on statistical thermodynamics and quantum chemical calculations. For experimental investigations of the liquid structure, X-Ray diffraction or neutron-diffraction methods and spectrophotometric measurements (e.g. infrared and Raman spectroscopy) are useable.

In the present work, the investigation of the structure of the bulk phase of primary alcohols (e.g. methanol, ethanol, propan-1-ol, butan-1-ol) and the study of the interaction between the aromatic segments and the cluster of alcohols (i.e. of methanol) have been carried out, using the QCE model and quantum chemical calculations

2. Objectives

Until recent days the picture about the structure of hydrogen bonded solvents (both neat and mixed liquids) is not consistent, which is true for example water and various relatively simple primary alcohols. The determining interaction patterns between hydrogen bonded liquids and aromatic segments (e.g. systems of benzene – methanol, or anthracene – binary mixture of primary alcohols) are still in a question. The structure of the liquid structure also depends on the temperature.

The aims of the present work are to give a description about the liquid structure of primary alcohols from the methanol to the butan-1-ol using the QCE model, and in case of benzene – methanol clusters try to obtain a picture regarding the liquid phase using quantum chemical (*ab initio* and DFT) calculations performed in vacuum.

3. Methods

The structure of the clusters and the geometries of the molecules, furthermore the interaction energies between the molecules constituting the clusters were investigated by quantum chemical (*ab initio* and DFT) methods. The B3LYP functional and the second order Møller-Plesset perturbation theory (MP2) were used, and in case of the benzene – methanol clusters the M06-2X functional should be mentioned together with the MP2 method. The 6-31+G(d,p) basis set was used for the geometry optimizations, while the interaction energies were calculated using the 6-311++G(2d,2p) and (d,p) basis sets, the basis set superposition error (BSSE) was corrected by the counterpoise correction (CP) and also with complete basis set (CBS) extrapolation schemes. The Gaussian 03 and Gaussian 09, the Gamess-US 2009 R3, the ORCA 2.8 and the NWChem 6.0 programs were used. In case of the benzene – methanol clusters, preliminary calculations were performed using the DFTB method with the DFTB+ program. In the present studies, the QCE model was implemented in a FORTRAN 77 computer programming language code, then its application has been done for homologous series of primary alcohols, upto the butan-1-ol. The few carried out molecular dynamics simulations were done with the DFTB+ program, while the initial structures of the simulations were prepared with the PACKMOL program.

4. Results

In this work, I have investigated the liquid structure of primary alcohols (methanol, ethanol, propan-1-ol and butan-1-ol) by applying the QCE model. The aforementioned quantum chemical calculations (at 0K temperature and in vacuum) have been done to determine cluster structures which were used in the QCE model to describe the structure of the liquid. Then, the interactions between the methanol molecules or clusters with the benzene molecule have been studied. The results are summarized in the followings:

1. In case of methanol, the model showed the preference of the five and six membered ring topology clusters. Based on this finding the following statements could be done. The applied second order Møller-Plesset perturbation theory (MP2), when compared to the B3LYP density functional, gives similar cluster geometries and intracuster interaction energies. The B3LYP functional have been applied previously for liquid methanol within the QCE model. All of these results suggest that the B3LYP geometries and interaction energies are acceptable in case of the methanol. Differently said, the dispersion interaction and the weak C-H...O interactions, which are implied

in the MP2 method but not or only in small amount by the B3LYP DFT theory, do not significantly modify the cluster distributions resulted by the QCE method for the liquid methanol.

2. The MP2 theoretical level and the QCE model resulted only in small amount of chain (i.e. not ring) and lasso structures. The lasso structures are those where a chain is connecting to the ring. The MP2 method takes the weak interactions within the clusters into account, so that the results obtained here could be associated with the implementation of the QCE model. Differently said, the interactions between the clusters treated within the QCE model by empirical parameters fitted to experimental data, where the intercluster interactions are weaker than the intracluster interactions, lead to the consequence that the structure of the liquid seems to be more structured than in real.
3. In case of the higher members of the homologous series (ethanol, propan-1-ol and butan-1-ol) the QCE model was applied with the B3LYP density functional. While in case of methanol, the liquid structure is mainly determined by the O-H...O hydrogen bonded ring topology network within the QCE model (where the B3LYP density functional gives appropriate description, corresponding to the above points), in case of the members of the homologous series possessing longer alkyl chains, the calculated thermodynamical functions (e.g. the constant pressure heat capacity, C_p) will be less accurate, especially in case of propan-1-ol and butan-1-ol. Corresponding to these, in case of the butan-1-ol, the B3LYP density functional was applied augmented with dispersion (van der Waals) correction, while the role of the conformation of the alkyl chains was studied particularly.
4. In case of the butan-1-ol, the dispersion corrected B3LYP functional (B3LYP-D) has given significantly better agreement between the experimental and the theoretically calculated C_p values than without the vdW correction.
5. By applying the model for the butan-1-ol, the QCE/B3LYP-D results show the preference of such a clusters where the number of alcohol molecules are less, so that formation of four- and five membered ring clusters is the most probable. In contrary, without correction, seven membered clusters are found to be preferred in case of butan-1-ol, ethanol and propan-1-ol; this is especially pronounced in case of the ethanol.

6. In case of the benzene – methanol clusters, two different structure types were found to be significant. In one case, the methanol molecules are forming three-, four-, five-, or six membered rings and then make the connection to the benzene molecule via weak $\text{H}_2\text{C-H}\dots\pi$ and (benzene) $\text{C-H}\dots\text{O}$ bonds. In the other case, the methanol molecules are forming a chain, and the free O-H group connect to benzene via $\text{O-H}\dots\pi$ interaction, while the other end of the chain have a connection to the benzene via (benzene) $\text{C-H}\dots\text{O}$ bond. Thus the methanol chain closing into a ring through the benzene molecule.
7. It is important in practice that the benzene form a 2:3 mole ratio minimal boiling point azeotrope with methanol. In low temperature gas-phase IR/R2PI spectroscopic experiments, Pribble and coworkers found clusters with the $(\text{C}_6\text{H}_6)_2(\text{MeOH})_3$ composition, thus in this work I have determined the structures and interaction energies of these clusters using *ab initio* quantum chemical methods. These computational results can contribute to the studies regarding the understanding of microsolvation of benzene.

5. List of publications

I. Publications in refereed journals related to these thesis

1. **G. Matisz**, A-M. Kelterer, W.M.F. Fabian, S. Kunsági-Máté:
Coordination of Methanol Clusters to Benzene: A Computational Study
Journal of Physical Chemistry A, 115 (2011) 10556-10564. **IF: 2,732** (2010)
2. **G. Matisz**, A-M. Kelterer, W.M.F. Fabian, S. Kunsági-Máté:
Application of the Quantum Cluster Equilibrium (QCE) Model for the Liquid Phase of
Primary Alcohols Using B3LYP and B3LYP-D DFT Methods
Journal of Physical Chemistry B, 115 (2011) 3936-3941. **IF: 3,603** (2010)
3. **G. Matisz**, W.M.F. Fabian, A-M. Kelterer, S. Kunsági-Máté:
Weinhold's QCE model – A modified parameter fit. Model study of liquid methanol based on
MP2 cluster geometries
Journal of Molecular Structure –THEOCHEM, 956 (2010) 103-109. **IF: 1.288** (2010)

II. Publications in non-refereed journals, conference abstracts, lectures and posters related to these thesis

1. **G. Matisz**, S. Kunsági-Máté:
Molecular clusters in liquid methanol
Molecular Modeling in Chemistry and Biochemistry (MOLMOD 2009), Cluj-Napoca,
Romania, April 2-4, 2009.
2. **G. Matisz**, S. Kunsági-Máté:
Thermodynamic properties of liquid methanol calculated by the quantum cluster equilibrium
theory
The 8th Central European Symposium on Theoretical Chemistry, Dobogókő, Hungary,
September 25-28, 2009.
3. **G. Matisz**, W. M. F. Fabian, S. Kunsági-Máté:
Hydrogen bonded clusters around aromatic π -systems
The 9th Central European Symposium on Theoretical Chemistry, Novy Smokovec, Slovakia,
September 12-15, 2010.
4. **G. Matisz**, W. M. F. Fabian, S. Kunsági-Máté:
Liquid structure of the primary alcohols (methanol, ethanol, 1-propanol, 1-butanol) within the
QCE theory
The 9th Central European Symposium on Theoretical Chemistry, Novy Smokovec, Slovakia,
September 12-15, 2010.
5. **G. Matisz**, W. M. F. Fabian, S. Kunsági-Máté:
Methanol clusters around the aromatic ring of benzene
Molecular Modeling in Chemistry and Biochemistry (MOLMOD 2010), Cluj-Napoca,
Romania, May 25, 2010.

6. **G. Matisz**, W. M. F. Fabian, S. Kunsági-Máté:
Primer alkoholok szerkezete folyadékfázisban, benzol mikroszolvatációja metanolban
XXXIII. Kémiai Előadói Napok (Chemistry Lectures), Szeged, Hungary, October 24-27, 2010.
7. **G. Matisz**, A-M. Kelterer, W. M. F. Fabian, S. Kunsági-Máté:
A Quantum Cluster Equilibrium (QCE) modell alkalmazása primer alkoholok
folyadékszerkezetének modellezésére
MKE 1. Nemzeti Konferencia, Sopron, Hungary, May 22-25, 2011.
8. **G. Matisz**, A-M. Kelterer, W. M. F. Fabian, S. Kunsági-Máté:
The Structure of Benzene – Methanol Clusters
MKE 1. Nemzeti Konferencia, Sopron, Hungary, May 22-25, 2011.
9. **G. Matisz**, Á Eördög, S. Kunsági-Máté:
Rayleigh Scattering Study of Hydrogen-bonded Liquids – Connection with the Liquid
Structure
Advanced Spectroscopies on Biomedical and Nanostructured Systems - BioNanoSpec 2011.,
Cluj-Napoca, Romania, September 4-7, 2011.

III. Other publications in refereed journals

1. G. Tasi, B. Nagy, **G. Matisz**, T. S. Tasi:
Similarity analysis of the conformational potential energy surface of n-pentane
Journal of Molecular Structure -THEOCHEM 963 (2011) 378-383. IF: **1.288** (2010)
2. B. Peles-Lemli, **G. Matisz**, A-M. Kelterer, W. M. F. Fabian, S. Kunsági-Máté:
Noncovalent Interaction between Aniline and Carbon Nanotubes: Effect of Nanotube
Diameter and the Hydrogen-Bonded Solvent Methanol on the Adsorption Energy and the
Photophysics
Journal of Physical Chemistry C, 114 (2010) 5898-5905. IF: **4.520** (2010)
3. G. Tasi, R. Izsák, **G. Matisz**, A. G. Császár, M. Kállay, B. Ruscic, J. F. Stanton:
The Origin of Systematic Error in the Standard Enthalpies of Formation of Alkanes
Computed via Atomization Schemes
ChemPhysChem, 7 (2006) 1664-1667. IF: **3.449** (2006)

IV. Other publications in non-refereed journals, conference abstracts, lectures and posters

1. G. Tasi, **G. Matisz**, B. Nagy, I. Hannus, I. Kiricsi:
Exploring the Full Conformational Potential Energy Surface of n-Pentane
An International Conference in Honor of Professor Peter Pulay, Budapest, Hungary, May 29
– June 3, 2007.
2. B. Peles-Lemli, A-M. Kelterer, **G. Matisz**, S. Kunsági-Máté and W. M. F. Fabian:
 π - π Interactions between Single-walled Carbon Nanotubes and Aniline: a Photophysical
Study
The 8th Central European Symposium on Theoretical Chemistry, Dobogókő, Hungary,
September 25-28, 2009.