

Thermodynamic properties of liquid methanol calculated by the quantum cluster equilibrium theory

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The chemical reactions perform in condensed phase are highly affected by the individual structure of the solvents used. This is because the solvation shell of the interacted species has to be at least partially destroyed prior molecular association and the structure and stability of the solvation shell [e.g.1] depends on the interaction between the solvent molecules. The latest effect is known to be pronounced in case of the hydrogen-bonded liquids. As a first step the structure of the solvent itself has to be examined with special emphasis on the formation of molecular clusters in liquid phase. From a theoretical point of view primary alcohols were found to be a fruitful testing ground to understand the formation and composition of clusters in hydrogen-bonded protic liquids. Most theoretical and experimental works support the presence of cyclic structures and state that preferably six or eight molecules form clusters in the case of methanol and water. We have started to investigate the structure of pure liquid methanol with the quantum cluster equilibrium (QCE) theory [2]. With the QCE model we can get the cluster distribution in liquid phase, i.e. the probability of their presence in the liquid. The PM6 semiempirical quantum chemical model [3] was used to get the low energy cluster structures via conformational analysis. Both the result of the QCE analysis and the comparison of the results derived by the PM6 method with the results available at *ab initio* and DFT levels [4,5] showed clearly that PM6 provides poor structures especially for cyclic ring structures. This is probably due to the overestimated C-H...O hydrogen bonds in the PM6 method. However, despite this failure, we have described a full model to calculate the structure of the liquid methanol. This method based on the cluster partition functions obtained from the quantum chemical calculations and on the experimental density of the liquid. Because of the poor geometries obtained with PM6, we have started to repeat the Monte Carlo conformational analysis with the SCC-DFTB+ density functional method augmented with dispersion correction [6] for cluster structures in the pure liquid methanol. This density functional method hopefully gives good structures for weak-interacting complexes presented in the protic liquids [7].

References:

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