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Energetic and structural profile of liquid phase dimers of the green-solvent Gamma-valerolactone (GVL)

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INTRODUCTION

In the past years, the use of Gamma-valerolactone (also known as GVL) as solvent in chemical processes has presenting an increasing interest due to its chemical and environmental friendly properties. In this work an optimized force field was parameterized to reproduce available experimental data for the liquid phase. Chirality effects were also investigated. The simulations were performed using Metropolis Monte Carlo (MMC) methodology.

METHODS

The liquid phase of both R and S GVL pure isomers and its racemic mixture were studied. From an equilibrated simulation box containing 500 molecules and using periodic boundary conditions, the most stable R-R, S-S and R-S dimers were searched at distances corresponding to the first and second solvation shell. To ensure a representative sampling the following protocol was used: *i)* a 10k configurations trajectory was generated; *ii)* the most stable dimers were searched in the following 2k configurations. The procedure was repeated 800 times therefore generating 800 different dimers pairs. The running averages of interaction energies and angles between dipoles vectors were calculated. Calculations were performed with MMC method in the NVT *ensemble* with T = 300 K using DIADORIM software.[1] For comparison purposes, interaction energies were also calculated with the HF-3c method[2] implemented in ORCA 3.0.1 software[3] for the dimers geometries obtained in the MMC search.

RESULTS AND DISCUSSION

The run average energies of R-R, S-S and R-S dimers are show in Fig. 1. One observes that R-R and S-S energies are statistically the same but the R-S dimers are energetically 10% more stable.

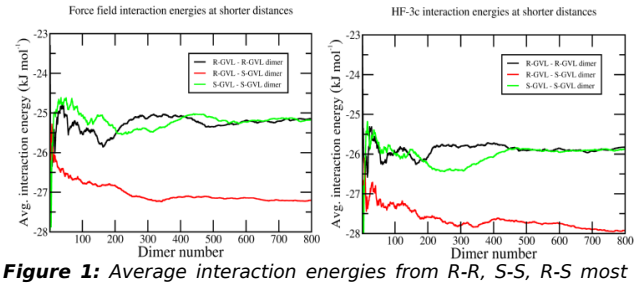

Figure 1: *Average interaction energies from R-R, S-S, R-S most stable dimers extracted from MC simulations. Values were calculated using the GVL optimized force field (left) and the quantum chemistry method HF-3c (right).*

Furthermore, analysis of the run average angle between dipole vectors are 147.5 degree for R-R and S-S and 153.3 degree for R-S species, showing a predominance of anti-parallel orientation leading to an almost apolar dimer. Contrasting with the high dipole moment of the monomer (4.3 D) the apolar dimers have great implications on dielectric properties of GVL liquid.

CONCLUSIONS

Chirality effects on GVL liquid structure were investigated via MC simulations. R-S GVL dimers are slightly more stable and the value of angle between dipole vectors shows a tendency to antiparallel orientations. The interaction energies calculated with force field and HF-3c methods differs about 0.7 kJ/mol, indicating a fair agreement.

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[1] L. C. G. Freitas, J. Braz. Chem. Soc., 20, 1541, (2009);
[2] R. Sure, S. Grimme, J. Comput. Chem., 34, 1672, (2013);
[3] F. Neese, Comput. Mol. Sci., 2, 75, (2012).