Improved Chiral Self-Sorting of Gamma-Valerolactone (GVL) Racemic Mixtures in the Presence of CNTs Studied by Means of Molecular Dynamics Simulations

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Abstract

Molecular dynamics (MD) simulations are becoming the tools of choice in material science to assess atomic-level information on the structure and dynamics of complex systems. This report presents a detailed description of the improved self-sorting of chiral molecules confined inside carbon nanotubes (CNTs) cavities of different diameters, using the racemic R/S-GVL - a chiral green solvent - as the model system. Analysis of 100 ns trajectory under NVT ensemble at T = 300 K, very distinguishable energetic and structural profiles were observed when chiral nanotubes were compared to the achiral counterparts.

Introduction

Chirality plays a fundamental role in chemistry and biological sciences, since it is quite common that just one isomer presents itself as a substance with the desired effects while the other isomer presents disadvantageous effects or, at best, no effects at all. As the synthesis of chiral compounds results in racemic mixtures, the development of high yield enantioselective synthesis and separation techniques are fundamental in many technological applications. Within this scenario, there are papers highlighting the role of chiral confinement due to cavity funcionalization on the stereochemical outcome of chemical reactions [1,2].
Although previous computational study comparing adsorption energies of both enantiomers of chiral hydrocarbons in different chiral CNT without functionalization found no significant differences[3], liquid phase simulations could provide more detailed information.

Results and Discussion

Although somehow idealized as compared to actual physical systems, short CNT segments may be conveniently used in computer models to investigate how these nanocavities may interact with complex liquids. Thus, 3 nm length CNTs were simulated: achiral (40,0) and chiral (30,15), both with 3 nm diameter. Radial distribution functions corresponding to the correlation between GVL asymmetric carbon and CNT structures are show in Fig. 1.

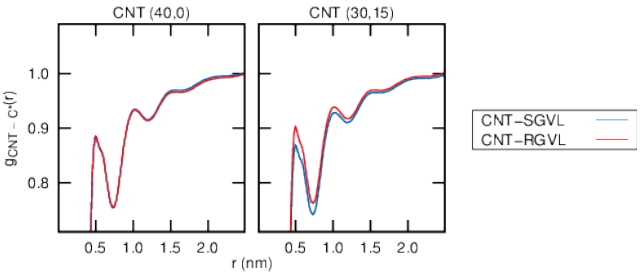

Figure 1. Radial distribution functions of GVL asymmetric carbons and CNT structure correlations.

For achiral CNT one could observe a fair agreement of both S-GVL and R-GVL correlations. On the other hand, chiral CNT presents a considerably difference on both first and second solvation shells, indicating a most favorable interaction of this CNT with R-GVL isomer. It is also noteworthy that the intermolecular potential energy between each GVL enantiomer and the CNTs presented an oscillatory behavior with large energy amplitude, which is consistent with the collective motion of self-sorted molecules.

Conclusions

Molecular dynamics simulations were carried out to predict interaction differences of gamma-valerolactone (GVL) optical isomers and both achiral and chiral carbon nanotubes (CNTs). RDFs for chiral (30,15) CNT presented noticeable differences when compared to its achiral (40,0) counterpart, which is in agreement with chiral recognition as a preferable interaction of R-GVL for the chiral nanotubes was noticed.

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