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Calculation of diffusion coefficient of long chain molecules using molecular dynamics

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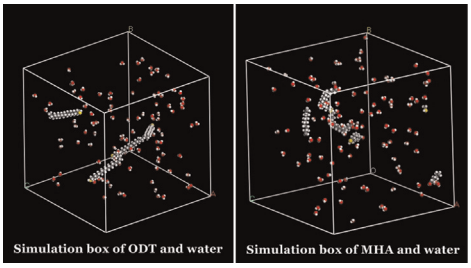
HIGHLIGHTS

- Molecular dynamics simulation coupled with Einstein relationship is employed to determine the diffusivity of two important long chain molecules MHA and ODT.
- Diffusivities are calculated at different temperatures in a humid environment containing few number of water molecules.
- Simulations are performed based on four different types of forcefield, one of which is general atomic parameter based (UFF) and the other one is ab initio data based (COMPASS). Another two forcefields are CVFF and PCFF which are also used for diffusivity calculation to show an overall comparison of the results.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular dynamics (MD) is a powerful tool for calculating several thermo-physical properties of wide range of materials. In this study, the diffusivities (D) of two widely used long chain molecules MHA and ODT are calculated at various temperatures using MD simulations coupled with Einstein relationship. Four different kinds of forcefields COMPASS, UFF, CVFF and PCFF are employed in the MD simulation and the results are compared. Diffusivity values are evaluated in a humid environment in presence of water molecules.

1. Introduction

The extraordinary advancement of computational tools in the last couple of decades has supported molecular dynamics (MD)

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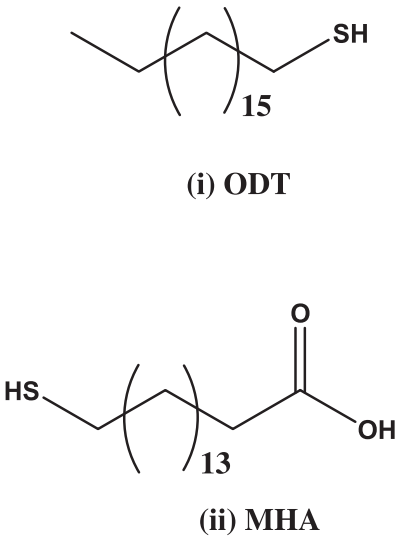

Fig. 1. Geometry optimized structure of (i) ODT and (ii) MHA.

simulation [1,2] to emerge as an important method for investigating fundamental aspects of several physico-chemical phenomena [3,4]. It also successfully predicts phase behavior, critical properties, conductivities, diffusivities etc [5,6] for a wide range of materials which are necessary for different industrial applications. Such in-silico experiments for calculating the thermo-physical properties of molecules help to design new materials with special characteristics without doing hardcore experiments. It reduces the time and cost associated to the experimental trials. Thus MD simulations are now a day's widely accepted by the research community all over the world.

Diffusivity is an important transport phenomena and prediction of diffusivity of newly developed molecules will be important for several technological applications. Molecular dynamics (MD) simulations have recently been successfully used as a tool to estimate the diffusion coefficients [6–8]. Although few reports are available in literature on successful MD calculation of small molecule diffusivity [8], only handful reports deals with long chain molecules. Camarada et. al. [9] have recently reported the calculation of diffusivity of some thiophene oligomers at different concentrations and temperatures. However, the effect of solvent molecules is not considered therein. In the present work we have selected two long chain molecules octadecanethiol (ODT) and merceptohexanoic acid (MHA) for MD study. These molecules are most widely used and commercially available ink molecules to be used in dip pen nanolithography (DPN) for self assembly based nanostructure formation [10–12]. These are also used in micro-contact based printing [13]. Both of these molecules show good self assembling behavior. During the process of DPN, ink molecules diffusivity has an important role. For modeling and simulation of ink molecule transport process [14,15], due to lack of experimental data, often diffusivity values are assumed in spite of being an important parameter. To address this issue, we attempted to calculate the diffusivity of MHA and ODT through MD simulations using some available generalized forcefields. Our objective is to show the calculation of diffusivity at several conditions without doing hard-core experiments. If some new molecules are designed in future for the same purpose, their approximate diffusivity values can be found out using the same route and those values can be fitted into the transport model. Accuracy of the MD results depends on the nature of interaction potentials or forcefields used during simulations. Hence, selection of appropriate forcefield is an important step for MD simulations.

In the present study, we attempted to calculate the diffusion coefficient of the long chain molecules (MHA and ODT) at different temperatures using four different generalized forcefields. The Einstein expression has been applied to calculate the diffusion coefficients after getting the mean square displacement profile from MD simulations.

2. Models and simulation details

In this study, prior to MD simulation the MHA and ODT molecules are constructed separately from atomic level and geometry optimization of their structures are performed separately using Smart algorithm which starts with steepest descent method followed by conjugate gradient method and ends with a Newton method. With these optimized structures (Fig. 1) cubic simulation boxes of $78.8 \times 78.8 \times 78.8$ Angstrom dimension containing four number of long chain molecules (MHA or ODT) and 100 water molecules are created. Periodic boundary condition is applied in all three x, y, z directions. Long chain molecules and water molecules are placed randomly inside the box and geometry optimization of the simulation box is done and optimized simulation boxes are shown in Fig. 2.

For equilibration of the system, MD simulations are performed using canonical ensemble where number of atoms (N), volume (V), and temperature (T) are kept fixed. Temperature is kept constant using Berendsen thermostat [16]. Then for the production run, we continue the dynamics again under NVT ensemble. The equations of motions have been integrated using Verlet velocity algorithm [17] with a time step of 1 fs and for the production stage we run the dynamics for 800–1000 ps (ps). For calculation of electrostatic interaction, an atom based approach [18] is considered for MHA

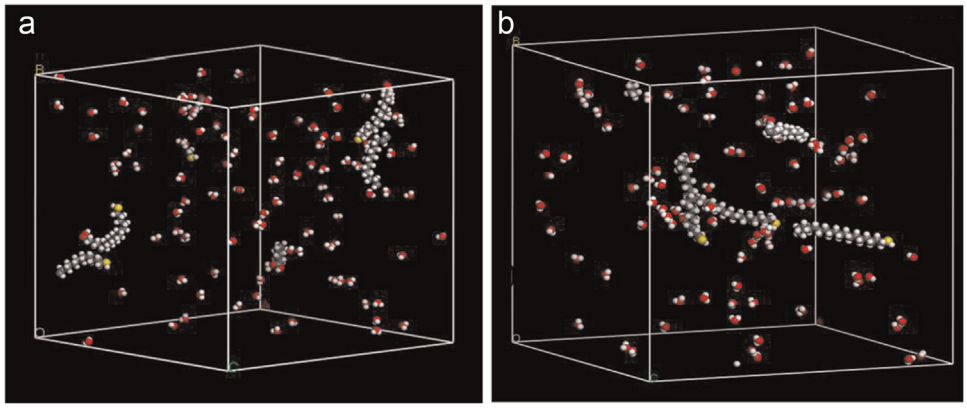

Fig. 2. Geometry optimized simulation box of (a) MHA and water molecules and (b) ODT and water molecules.