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Molecular dynamics simulation studies of some new aspects of structural and dynamical properties of *n*-butyl formate at varying temperature

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Using classical molecular dynamics simulation, liquid density and isobaric expansion coefficient of *n*-butyl formate were studied in the temperature range 298.15 to 623.15 K. Fluctuations in ensemble volume and energy were used to determine the isothermal compressibility and heat capacities, hence the internal pressure. In addition, self-diffusion coefficient and viscosity were determined from dynamic properties of the ensemble. The low viscosity of the ester, which is of considerable interest as a solvent in extraction processes, was substantiated by results of the simulation. The structural properties were studied by atom–atom pair correlation function, and the results are discussed. From the structural analysis, it was found that the formate head group could form a specific hydrogen bonding extended only at short range.

1. Introduction

Oxygenated compounds are widely used in paints as solvents and degreasing agents. Esters are an important class of these oxygenated compounds that are used as food flavorings and solvents of perfume as well. They also exist in some fruits like strawberries [1] and thus are constantly emitted to the atmosphere naturally. In addition, they are produced in the tropospheric degradation of some volatile organic compounds [2]; for example, the atmospheric degradation of the two fuel additives, methyl *tert*-butyl ether and ethyl *tert*-butyl ether, yields mainly *tert*-butyl formate [3–7]. Esters are often used as industrial solvents. In particular, formic acid and its derivatives are used for decalcification, reduction in dyeing for wool fast colors, dehairing and plumping hides, tanning, electroplating, as an additive in regenerating old rubber, as lacquers, and as an intermediate for the production of a wide variety of products in the chemicals and pharmaceutical industries [7b]. With these wide functions, properties, and applications for formates, their structural, dynamical, and equilibrium thermodynamic properties are of prime interest for industrial applications. Thus, such properties are vital to be undertaken experimentally or theoretically. In spite of such wide applications, thermophysical properties of these compounds have not been paid much attention by experimental methods. Information on their densities, surface tensions, viscosities, and vapor pressures is very limited, and in most cases, they have been reported only at standard temperature and pressure. The reason for this scarcity of the data might be laid in the difficult experimental condition.

Having available an accurate force field to determine the interactions between the molecules, classical molecular dynamics (MD) simulation of liquid is an alternative to experimental measurement providing accurate properties of the liquid and offers an accessible, powerful, cost-effective substitute for experiment. Computational methods provide a succession of configurations of a liquid at some specified temperature and density or pressure from which one can find the average local structure as well as equilibrium thermodynamic and transport properties. In classical MD, the interactions between molecules are modeled by empirical force fields. There is much experience in developing force fields for molecular liquids and solutions, which need to be a satisfactory compromise between accuracy and efficiency. Development of force fields that are sufficiently accurate and describe physics of the processes involved is an important part of simulation research. For molecular liquids, two-body site-site interactions give a qualitative picture of liquid structure and dynamics on a molecular scale.

The structural analysis shows that C–O and C=O functional groups are the building blocks of humic acid and esters. Since MD simulation of complex compounds is hardly feasible due to their not fully resolved structures, an alternative way to proceed is considering simpler organics of these compounds. These can serve as model functional groups of different complex organics to be compared with that of the small ones. To our knowledge, no extensive simulation on *n*-butyl formate was reported to date and exclusively presented

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here for the first time, although Yang et al. [8] and Tung and et al. [9] have performed some MD simulations on *n*-butyl acetate and studied its dynamical and transport properties.

To this goal, the present study reports results of extensive sets of MD simulations on *n*-butyl formate, with the objection of determining thermodynamic properties, site–site relative structures, and transport properties as well as comparison with experiment and mutual relationships with their structure. Such comparisons help benchmark the quality of force field. In addition to macroscopic transport properties, such as self-diffusivities and viscosities, the simulations enable interrogation of dynamical behavior of the liquid, thereby shedding light on the molecular-level phenomena that give rise to these observable properties. For the optimal force field, results by AMBER and DREIDING force fields are compared. We investigate the validity and accuracy of the potential function applied to the liquid phase of *n*-butyl formate by computing various physical properties as functions of temperature. Liquid density and its variation with temperature are important properties. In addition to the density and thermal expansion coefficient, isothermal compressibility coefficient, isobaric and isochoric heat capacities, internal pressure, bulk modulus, and solubility parameter are the thermodynamic properties computed from simulation. Furthermore, we consider the structural properties in search of particular intermolecular interaction and transport properties of the liquid system to account for the characteristic experimental data as a function of temperature in quest of practical application of the liquid.

2. Simulation details

Density functional theory (DFT) as implemented in GAUSSIAN 03 program [10] was used to find the structural parameters for the ground state of *n*-butyl formate. The DFT method is known to handle geometries and vibrational frequencies of different systems specially hydrogen bond systems appropriately [11–13]. B3LYP functional coupled with 6-311++G(d,p) basis set was employed in all calculations. No restrictions on symmetries were imposed on the initial structure. A vibrational analysis was performed to ensure the absence of negative vibrational frequencies and verify the existence of a true minimum [14,15]. The optimized structure of *n*-butyl formate is shown in Fig. 1. Bond lengths, bond angles, and dihedral angles, computed at B3LYP/6-311++G(d,p) level of theory, are listed in Table 1.S of the supplementary material. Moreover, the atomic charges calculated by natural bond orbital (NBO) analysis at the same level of theory are presented in Table 2.S of the supplementary material. The force field chosen was applied to implement the MD simulations; the standard form of molecular mechanics force field [16] used is

$$\begin{aligned} V_{tot} = {} & \sum\nolimits_{bonds} k_b (r-r_0)^2 + \sum\nolimits_{angles} k_\theta (\theta-\theta_0)^2 \\ & + \sum\nolimits_{dihedrals} k_\chi [1+\cos(n\chi-\delta)] + \sum\nolimits_{improper} k_\psi (\psi-\psi_0)^2 \\ & + \sum_{i=1}^{N-1} \sum_{j\rangle i}^{N} \left[\varepsilon_{ij} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right) + \frac{q_i q_j}{r_{ij}} \right] \end{aligned} \qquad (1)$$

where V_{tot} is the total interaction potential energy of the system. Harmonic potentials govern bond length, bond angle, and improper angle motion about nominal values, r_0, θ_0, and ψ_0 and dihedral angles are modeled using a standard cosine series. We used our results of geometry optimization by *ab initio* computation, as listed in Table 1.S, for r_0, θ_0, ψ_0, and δ in Eq. (1). The Lennard-Jones (12–6) parameters for unlike atoms, ε_{ij} and $r_{\mathrm{min},ij}$, are obtained using the Lorentz-Berthelot combining rule (arithmetic mean for the $r_{\mathrm{min},ij}$ and geometric mean for ε_{ij}). Columbic interactions are modeled using fixed partial charges on each atom center obtained by NBO analysis. NBO atomic charges are very often used in simulation as Kohagen et al. have recently used in simulation of ionic liquid [17]. Regarding the level of accuracy for the calculations, all intramolecular parameters r_0, θ_0, ψ_0, and δ besides the atomic charges were taken directly from the *ab initio* calculation, Tables 1.S and 2.S, and the Lennard-Jones (12–6) intermolecular parameters from reference [18].

Lowering atomic charges is expected to relax the liquid system and to increase the accuracy of some properties resulted by simulation. Therefore, to test this idea, the initial atomic charges (Table 2.S) extracted from the SCF total electron density by NBO population were scaled by a factor of 0.8*e*. A key aspect of any force field is how the electrostatic interactions are represented. Usually, partial point charges centered on atomic nuclei are used to approximate the electron population or electrostatic potential obtained from electronic structure calculations [19]. Typically, these charge sets are all calculated from the isolated molecules in vacuum. Regardless of the environment surrounding, fluctuations are not allowed; therefore, by the introduction of polarization this simplification can be improved. An alternative to the use of polarizable force fields is the use of scaled charge. This suggests that fixed charge models might be more accurate if non-integer net charges were used. Working specifically with reduced electrostatics started around 1994 when Müller-Plathe and van Gunsteren observed for salt-polymer mixtures that this affects the mobility [20]. After that, Youngs and Hardacre [21] found a scaling factor of 0.7*e* for [C$_n$mim]Cl gave the best results

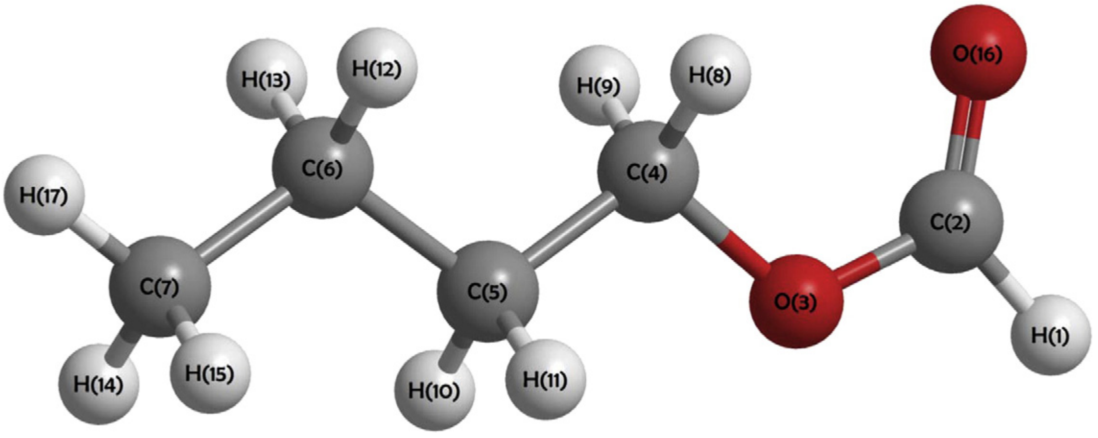

Fig. 1. The optimized structure and labels for *n*-butyl formate (oxygen, red; carbon, dark gray; and hydrogen, light gray).