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A study of solvation of benzaldehyde and cinnamaldehyde in CO_2 by molecular dynamics simulation

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ABSTRACT

The solvation of benzaldehyde and cinnamaldehyde in CO_2 was simulated at 323 K at a density range from 0.135 to 0.807 g/cm^3. It was observed that the spatial distribution of CO_2 molecules around solutes closely follows the negative electrostatic potential in the solute molecules. The solvent density distribution maps and radial distribution maps at different densities provided the details of the local solvent density augmentation around each solute. In order to understand the difference of the local density augmentation, the interaction energies between CO_2 molecules and solutes were discussed.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is readily available (T_c = 31.1 °C and P_c = 7.4 MPa), inexpensive, nontoxic, nonflammable and its density and diffusion coefficient can be tuned by the slight change of the pressure and the temperature [1–3]. It has shown great potential as a replacement for conventional organic solvent. Therefore, $scCO_2$ has been attracting more and more studies in both practical applications [4–7] and fundamental studies [8–10]. For the later, the investigations have been focused on the local density augmentation around the attractive solute as well as the effect of the augmentation on solvatochromism [11–17], chemical reactions [18–23] and the solubility of organic molecules [24–26]. Eckert group [11] and Maroncelli group [12–14] have investigated the local environment surrounding the solute such as coumarin 153 in CO_2-expanded liquids by electronic absorption, emission spectra and molecular dynamics simulations. By combining the molecular simulation and experimental spectra, Maroncelli and co-workers have also explored the interplay between local density augmentation and solute–solvent interaction in $scCO_2$ [15,16]. On the other hand, Leitner et al. have studied the interaction between biomolecule and water by molecular dynamics simulation combining with THz, IR spectroscopic and X-ray scattering [27]. Wipff and co-workers [24] found that the enhancement of the CO_2-philicity upon fluorination does not stem from enhanced individual interaction with CO_2, but from the higher coordination number according to the molecular dynamics study on the solvation of benzene and its fluoride in $scCO_2$.

In this work, the solvation of benzaldehyde and cinnamaldehyde in $scCO_2$ has been investigated by using the molecular dynamics simulation. The two solutes are of interest because in high-pressure FTIR spectra, the vibration of carbonyl group (C=O) showed a red-shift in compressed CO_2 and with increasing CO_2 pressure it shifts much more for cinnamaldehyde compared with benzaldehyde [28]. In addition, the solubility of benzaldehyde in CO_2 at 323 K is approximately two orders of magnitude higher than that of cinnamaldehyde [28,29]. This may ascribe to the difference in the molecular structures between cinnamaldehyde and benzaldehyde, which may induce different solute–solvent and solute–solute interactions. In this work, the molecular interaction was investigated by molecular dynamics simulation of the local solvation structure, and the solvation structure of benzaldehyde and cinnamaldehyde in $scCO_2$ was compared by spatial distribution functions (SDFs) [30,31] and radial distribution functions (RDFs), which provides the difference of local density augmentation behavior around each solute. In addition, the interaction energy between solute and solvent has been calculated in order to explore the difference of the local density augmentation.

2. Computational details

All simulations were performed using the Gromacs 3.3.3 simulation package [32]. Our studied system is based on an equilibrated cubic, periodic simulation box containing 1500 CO_2 solvent molecules and 1 solute molecule. For the CO_2 solvent the 'EMP2'

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potential parameters were used, which was constructed to reproduce the coexistence curve of the real CO_2 fluid [33]. The molecular geometries and the CHelpG atomic charges for benzaldehyde and cinnamaldehyde were determined from ab initio quantum chemical calculations at MP2/6-31G(d) level. The solutes' Lennard–Jones parameters and bonded parameters were extracted from the OPLS-AA force field [34]. Cubic periodic conditions (PBCs) were used throughout, but the box length of the system was scaled to satisfy the specified fixed density for each set of conditions. Coulombic interactions were handled using the Ewald summation method. A summary of the charges and Lennard–Jones parameters are provided in Supplementary material.

The simulations reported here were performed in the NVT ensemble at a temperature of 323.15 K using a Nose–Hoover thermostat with a 0.5 ps relaxation time constant. The equations of motion were integrated using a leapfrog scheme with a 2 fs time step. All bond lengths were kept constant using the SHAKE algorithm [35]. The simulation data were obtained in production run of 2 ns that were started after an equilibration period of 500 ps.

3. Results and discussion

3.1. Analysis of solvation structure

Molecular dynamics simulations provide a direct comparison of solvation structure between benzaldehyde and cinnamaldehyde by using SDFs and RDFs at different CO_2 densities, e.g., 0.135 g/cm^3 ($0.3\rho_c$), 0.448 g/cm^3 (ρ_c) and 0.807 g/cm^3 ($1.8\rho_c$), respectively. The RDFs give the probability of finding the center of a particle at a given distance from the center of another particle. Consequently, the peaks in RDFs are associated with solvation shells, which are of interest as local probes of the environment around a given particle. The SDFs are determined so as to get solvent distribution map around benzaldehyde and cinnamaldehyde, which provide more details than RDFs.

The SDFs of the carbon atoms in CO_2 molecules around benzaldehyde and cinnamaldehyde indicate that the carbon atoms of CO_2 molecules are aggregated around carbonyl group, above and below aromatic ring (Fig. 1a). The carbon atom with positive charge in CO_2 molecule can attract negative charge. Thus, the electrostatic potential maps of benzaldehyde and cinnamaldehyde are given, which can provide the electronic distribution of the molecule (Fig. 1b). By comparing SDFs with the electrostatic potential maps, it can be found that one important feature of SDFs is that the carbon atoms are accumulated around carbonyl group, above and below the aromatic ring (Fig. 1a), corresponding to the negative parts in the electrostatic potential of the solute molecule (Fig. 1b). This revealed that the interaction between CO_2 molecule and the region of solute molecule with the negative electrostatic potential controls the distribution of CO_2 molecule around the solute molecule.

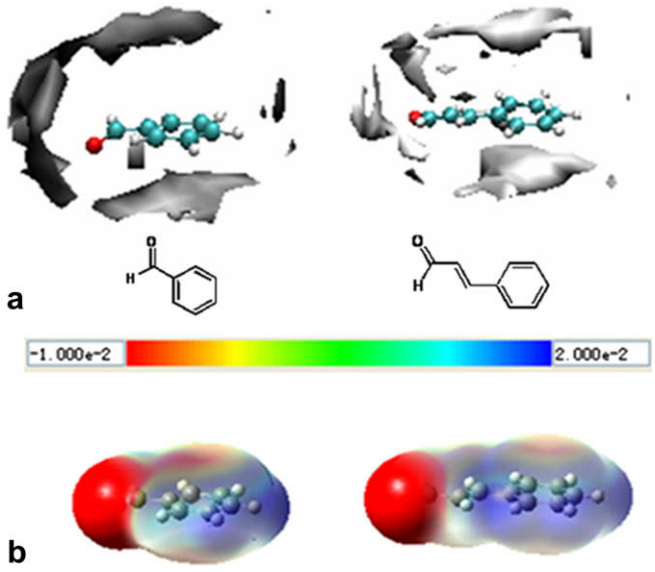

Fig. 1. (a) The spatial distribution functions of carbon of CO_2 around benzaldehyde and cinnamaldehyde at CO_2 density of 0.448 g/cm^3 at an isosurface value of 44.5 (Gray regions are the distributions of CO_2 molecule around solutes). (b) The electrostatic potential maps (B3LYP/6-311+G(d,p)) of benzaldehyde and cinnamaldehyde at an isosurface value of 0.0004.

The two-dimensional (2D) solvent density contour maps of benzaldehyde and cinnamaldehyde at the CO_2 densities of $0.3\rho_c$, ρ_c and $1.8\rho_c$ were investigated, which are shown in Figs. 2 and 3. The scale is relative to the corresponding bulk density. At the lowest density ($0.3\rho_c$), the solvent environment is similar to the high density gas and the number of the solvent molecule in the vicinity of the solute fluctuates significantly. At densities approaching ρ_c, there are more solvent molecules around the solute and the solvent–solute interactions become significant. While at the highest density ($1.8\rho_c$), environment of solute is like a liquid. In this case, it can be assumed that the solute surroundings are effectively homogeneous as they are in liquids, as suggested in the previous study [16]. From Fig. 3, it is found that the local density is enhanced around the carbonyl group (Fig. 2), both above and below the aromatic ring. However, the magnitude of local density enhancement decreases with the increase of density (Figs. 2 and 3). In other words, at low density ($0.3\rho_c$) the solvent distribution is highly non-uniform, while at high density ($1.8\rho_c$) the solvent distribution is more homogeneous around the solute. This is because at low density region the solute–solvent interaction has dominating effect, and control the local density enhancement around solutes. At high density region, however, the local density enhancement is governed not only by the solute–solvent interaction but also by the solvent–solvent interaction which increases with the increase of density [36]. For a slab cut through the molecular planes of both solutes (Fig. 2), the local density enhancement around the carbonyl group of cinnamaldehyde is slightly higher than that of benzaldehyde at each studied density. However, for a slab perpendicular to the molecular planes along one C2 symmetry axis of aromatic ring (Fig. 3), the local density enhancement above and below the aromatic ring of benzaldehyde is slightly higher than that of cinnamaldehyde. These features may be caused by the difference in the molecular interaction, in which the interaction between CO_2 and carbonyl group of cinnamaldehyde is stronger than that of benzaldehyde, and the interaction between CO_2 and aromatic ring of benzaldehyde is stronger than that of cinnamaldehyde.

In order to get further insights into the local density augmentation of carbonyl group and aromatic ring for benzaldehyde and cinnamaldehyde, the radial distribution functions between the O site of carbonyl group and the C site of CO_2, $g_{o-c}(r)$, and between the center of mass of aromatic ring and the C site of CO_2, $g_{com-c}(r)$, were also investigated at different densities, which are shown in Figs. 4 and 5, respectively. For $g_{o-c}(r)$ of benzaldehyde (Fig. 4a) and cinnamaldehyde (Fig. 4b), it should be noted that the location of first peak near 0.3 nm has no change but the peak height decreases with the increase of density. Moreover, the first peak of cinnamaldehyde is always higher than that of benzaldehyde for a given density. In other words, the local density around the carbonyl group of cinnamaldehyde is higher than that of benzaldehyde. This indicated that the interaction between CO_2 and carbonyl group of cinnamaldehyde is more attractive compared with that of benzaldehyde. Similar behavior is also obtained from SDFs (Fig. 2).

For the $g_{com-c}(r)$ of benzaldehyde (Fig. 5a) and cinnamaldehyde (Fig. 5b), the first peak near 0.56 nm decreases with the increase of