



A study of solvation of benzaldehyde and cinnamaldehyde in CO₂ by molecular dynamics simulation

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ABSTRACT

The solvation of benzaldehyde and cinnamaldehyde in CO₂ was simulated at 323 K at a density range from 0.135 to 0.807 g/cm³. It was observed that the spatial distribution of CO₂ 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 CO₂ molecules and solutes were discussed.

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1. Introduction

Supercritical carbon dioxide (scCO₂) is readily available ($T_c = 31.1^\circ\text{C}$ and $P_c = 7.4\text{ MPa}$), 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, scCO₂ 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 CO₂-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 scCO₂ [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 CO₂-philicity upon fluorination does not stem from enhanced indi-

vidual interaction with CO₂, but from the higher coordination number according to the molecular dynamics study on the solvation of benzene and its fluoride in scCO₂.

In this work, the solvation of benzaldehyde and cinnamaldehyde in scCO₂ 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 CO₂ and with increasing CO₂ pressure it shifts much more for cinnamaldehyde compared with benzaldehyde [28]. In addition, the solubility of benzaldehyde in CO₂ 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 scCO₂ 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 CO₂ solvent molecules and 1 solute molecule. For the CO₂ solvent the ‘EMP2’

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potential parameters were used, which was constructed to reproduce the coexistence curve of the real CO₂ 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 CO₂ densities, e.g., 0.135 g/cm³ (0.3ρ_c), 0.448 g/cm³ (ρ_c) and 0.807 g/cm³ (1.8ρ_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 CO₂ molecules around benzaldehyde and cinnamaldehyde indicate that the carbon atoms of CO₂ molecules are aggregated around carbonyl group, above and below aromatic ring (Fig. 1a). The carbon atom with positive charge in

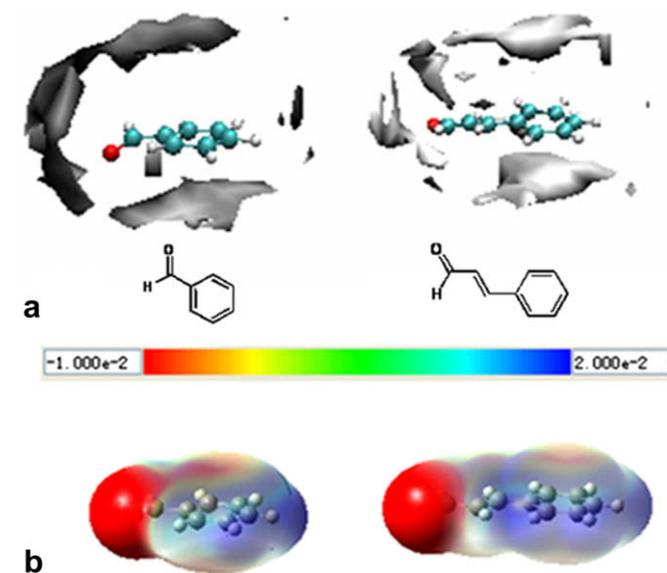


Fig. 1. (a) The spatial distribution functions of carbon of CO₂ around benzaldehyde and cinnamaldehyde at CO₂ density of 0.448 g/cm³ at an isosurface value of 44.5 (Gray regions are the distributions of CO₂ molecule around solutes). (b) The electrostatic potential maps (B3LYP/6-311+G(d,p)) of benzaldehyde and cinnamaldehyde at an isosurface value of 0.0004.

CO₂ 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 CO₂ molecule and the region of solute molecule with the negative electrostatic potential controls the distribution of CO₂ molecule around the solute molecule.

The two-dimensional (2D) solvent density contour maps of benzaldehyde and cinnamaldehyde at the CO₂ densities of 0.3ρ_c, ρ_c and 1.8ρ_c were investigated, which are shown in Figs. 2 and 3. The scale is relative to the corresponding bulk density. At the lowest density (0.3ρ_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 (1.8ρ_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 (0.3ρ_c) the solvent distribution is highly non-uniform, while at high density (1.8ρ_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 CO₂ and carbonyl group of cinnamaldehyde is stronger than that of benzaldehyde, and the interaction between CO₂ 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 CO₂, $g_{o-c}(r)$, and between the center of mass of aromatic ring and the C site of CO₂, $g_{com-c}(r)$, 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 CO₂ 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

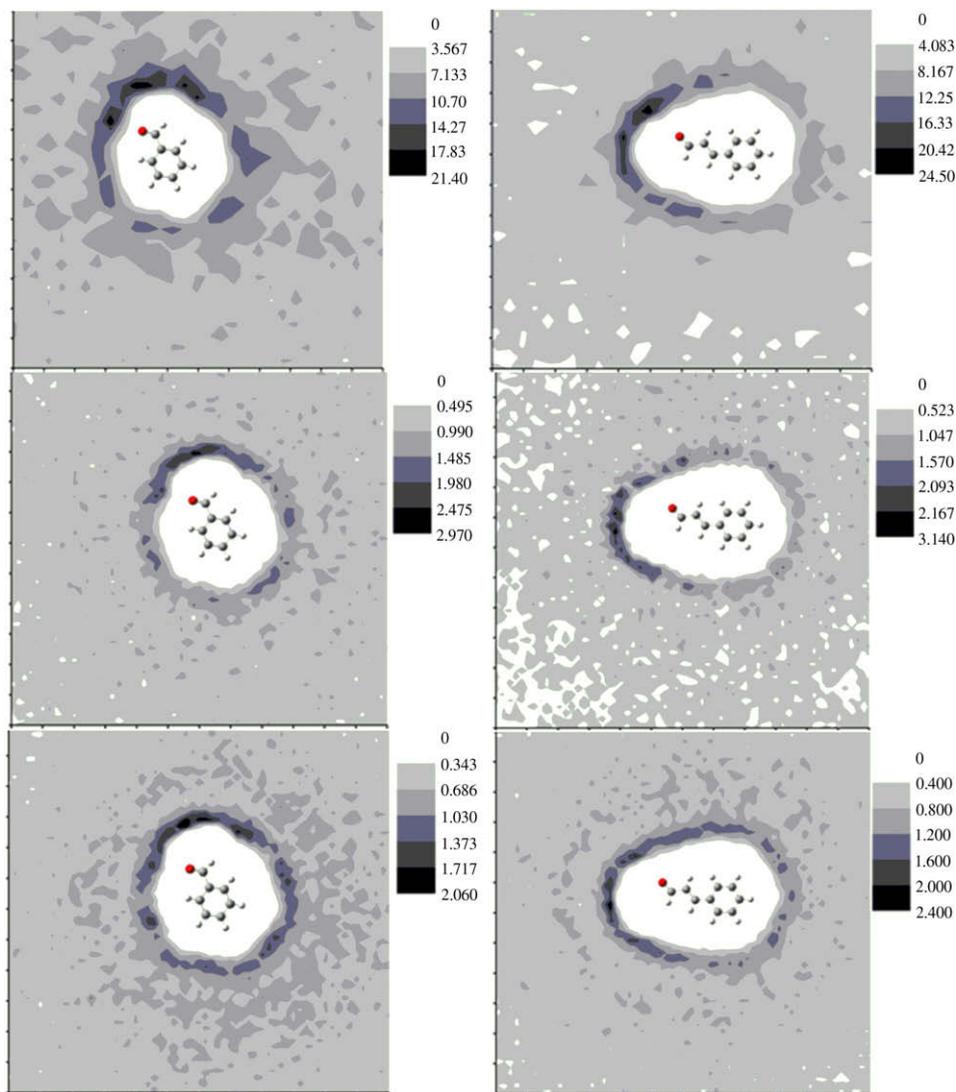


Fig. 2. The solvent density maps from a slab cut through the molecular planes for benzaldehyde-CO₂ and cinnamaldehyde-CO₂ system at CO₂ bulk densities of $0.3\rho_c$, ρ_c and $1.8\rho_c$ (from top to bottom).

density, and it is always slightly higher for benzaldehyde compared with cinnamaldehyde. In addition, the local density of above and below the aromatic ring of benzaldehyde is slightly higher than that of cinnamaldehyde. This means that the interaction between CO₂ and aromatic ring of benzaldehyde is more attractive compared with that of cinnamaldehyde. Similar behavior is also seen on solvent density distribution maps (Fig. 3).

In order to show how the local density is calculated, the following formula is introduced [14–16], in which the effective local density $\Delta\rho_{\text{eff}}$ is used to measure the local density augmentation from the coordinate number N :

$$\Delta\rho_{\text{eff}}^{(N)} = \rho_{\text{eff}}^{(N)} - \rho \equiv \frac{N(\rho)}{N(\rho_{\text{ref}})}\rho_{\text{ref}} - \rho$$

where $\rho_{\text{ref}} = 2\rho_c$. Fig. 6 shows the local density augmentation in the region of carbonyl group (Fig. 6a) and aromatic ring (Fig. 6b) for benzaldehyde and cinnamaldehyde. It is seen that the local density augmentation has a maximum at a density about $0.7\text{--}0.8\rho_c$, similar category as in the previous studies [14,17]. We used the maximum value, $\Delta\rho_{\text{max}}$, to measure the extent of augmentation. In Fig. 6a, $\Delta\rho_{\text{max}}$ is 0.252 and 0.300 (at $\rho = 0.7\rho_c$) for benzaldehyde and cinnamaldehyde, respectively. This indicates that for carbonyl

group, the cinnamaldehyde is more attractive solute than benzaldehyde. In Fig. 6b, $\Delta\rho_{\text{max}}$ is 0.172 and 0.160 (at $\rho = 0.8\rho_c$) for benzaldehyde and cinnamaldehyde, respectively, indicating that for aromatic ring, the benzaldehyde is more attractive solute than cinnamaldehyde. These conclusions are consistent with the results from SDFs and RDFs.

3.2. Analysis of energetic properties

In order to explore the effect of the interaction energies on local density enhancement, the interaction energies (ΔE_{whole} , ΔE_{CHO} , ΔE_{6C}) were calculated as shown in Tables 1 and 2. ΔE_{whole} is the interaction energy between CO₂ molecule in whole system and the whole solute molecule. ΔE_{CHO} is the local interaction energy between CO₂ in regions around carbonyl group and three atoms (CHO) of aldehyde group of solute. ΔE_{6C} is the local interaction energy between CO₂ above and below aromatic ring and six carbon atoms (6C) of aromatic ring of solute. CO₂ in the region around carbonyl group is defined as a sphere volume: the center of sphere volume is the oxygen atom of carbonyl group. The radius of sphere volume is $r_{\text{o-c,min}}$, which corresponds to the first minimum of $g_{\text{o-c}}(r)$. On the other hand, the region above

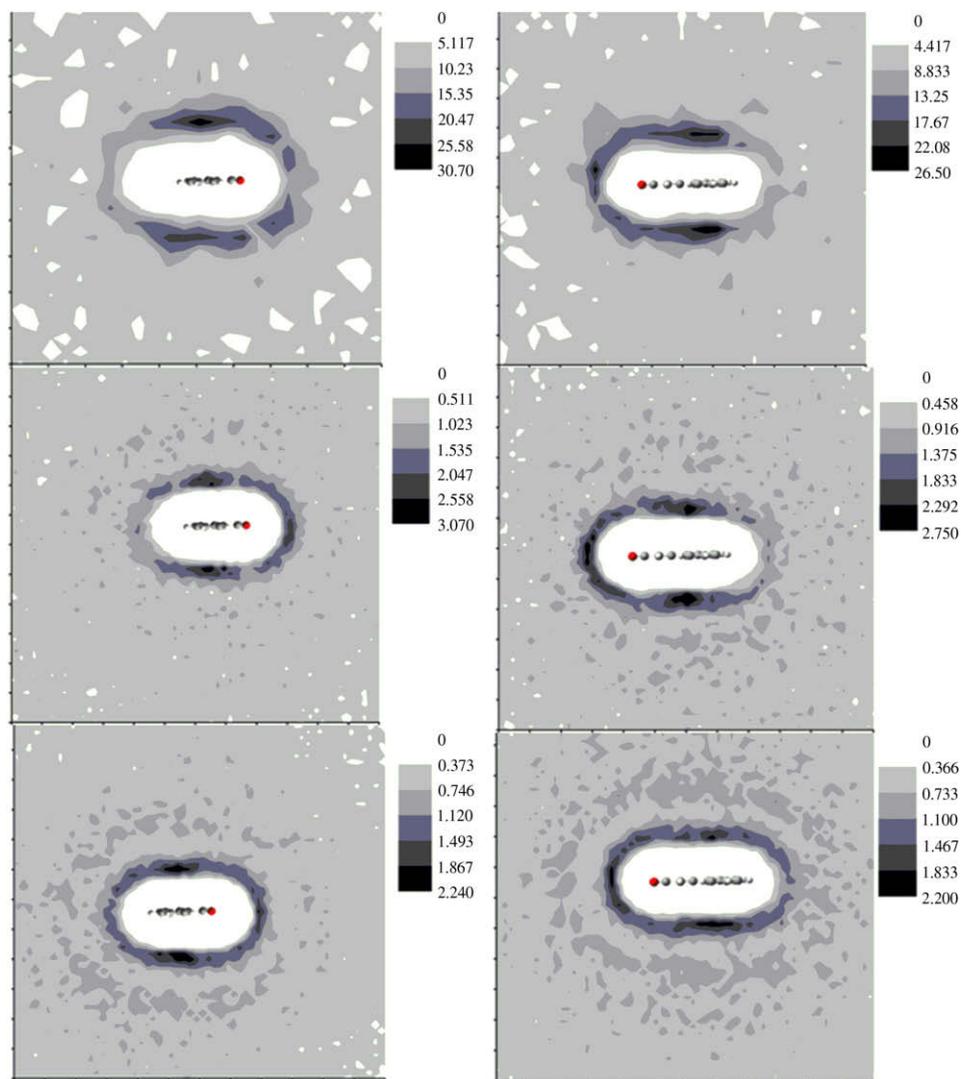


Fig. 3. The solvent density maps from a slab perpendicular to the molecular planes along one C2 symmetry axis of aromatic ring for benzaldehyde-CO₂ and cinnamaldehyde-CO₂ system at CO₂ bulk densities of $0.3\rho_c$, ρ_c and $1.8\rho_c$ (from top to bottom).

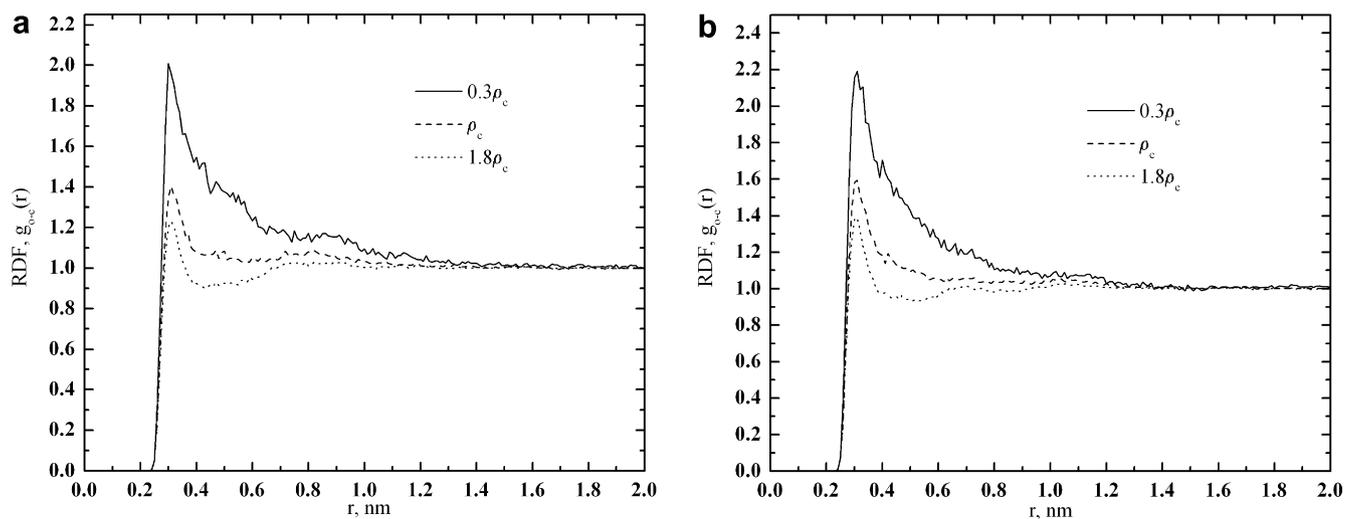


Fig. 4. The radial distribution functions between the O site of carbonyl group and the C site of CO₂, $g_{O-C}(r)$, for benzaldehyde (a) and cinnamaldehyde (b) at CO₂ bulk densities of $0.3\rho_c$, ρ_c and $1.8\rho_c$.

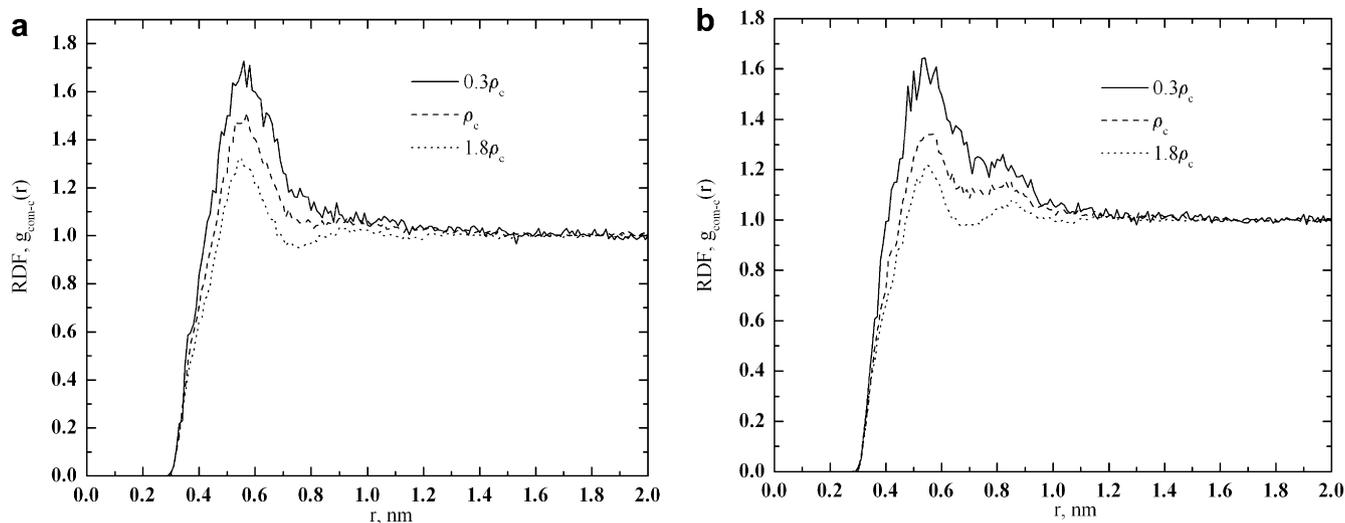


Fig. 5. The radial distribution functions between the O site of carbonyl group and the C site of CO₂, $g_{O-C}(r)$, for benzaldehyde (a) and cinnamaldehyde (b) at CO₂ bulk densities of $0.3\rho_c$, ρ_c and $1.8\rho_c$.

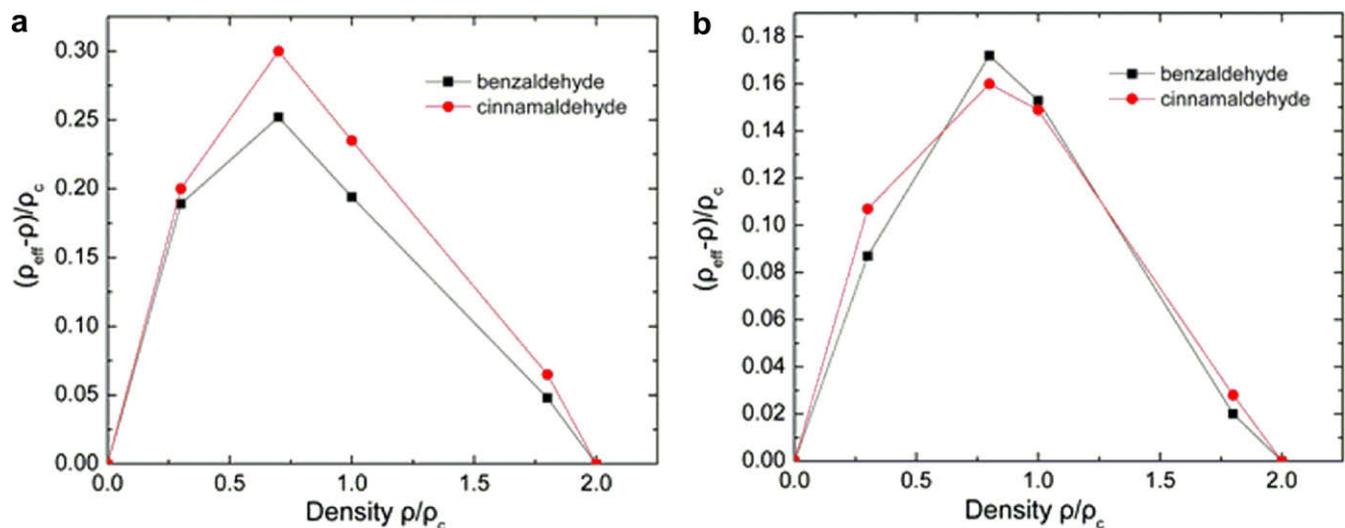


Fig. 6. Effective local density of benzaldehyde and cinnamaldehyde in CO₂ is determined. The top panel (a) is for the local density augmentation around carbonyl group and the bottom panel (b) for the local density augmentation around aromatic ring.

Table 1

The interaction energies between benzaldehyde and cinnamaldehyde with CO₂ molecule in whole system at different densities.

Density	Benzaldehyde $\Delta E_{\text{whole},1}$ (kJ/mol)	Cinnamaldehyde $\Delta E_{\text{whole},2}$ (kJ/mol)
$0.3\rho_c$	-11.66	-15.06
ρ_c	-32.96	-41.1
$1.8\rho_c$	-51.73	-64.23

and below aromatic ring is a cylinder volume along the C6 symmetry axis of aromatic ring but except for the plane of aromatic ring: the center of cylindrical volume is the center of aromatic ring. The radius of cylindrical volume r is set to 1.390 Å, which is the radius of aromatic ring. The half-height of cylindrical volume is $r_{O-\text{com},\text{min}}$, where the first minimum of $g_{O-\text{com}}(r)$ is observed.

The interaction energies (ΔE_{whole}) between both solute molecules and CO₂ in whole system are shown in Table 1. It is found that for both solute molecules, the interaction energies increase

with the increase of CO₂ density. At a given density, the interaction energy of cinnamaldehyde ($\Delta E_{\text{whole},2}$) is larger than that of benzaldehyde ($\Delta E_{\text{whole},1}$), suggesting that the cinnamaldehyde has higher affinity to CO₂ than benzaldehyde, in agreement to our previous results that cinnamaldehyde was more reactive in sCO₂ compared with benzaldehyde [29]. This might also explain that the experimental FTIR spectra for carbonyl group of cinnamaldehyde shift much more compared with benzaldehyde [28]. However, experimental study showed that the solubility of benzaldehyde in CO₂ is higher than that of cinnamaldehyde [28,29], contradicting with our calculations. This apparent contradiction is ascribed to the fact that stronger solute–solute interactions play an important role in the solubility [25], while in our calculation, only one solute is considered, thus the calculated data was disparity to the experimental data. The local interaction energies, ΔE_{CHO} and ΔE_{BC} , are calculated only at high density ($1.8\rho_c$). This is because at $1.8\rho_c$, $g_{O-C}(r)$ for benzaldehyde and cinnamaldehyde has a good peak shape with $r_{O-C,\text{min}}$ at 0.43 nm and 0.53 nm (Fig. 4), respectively. Similarly, $g_{O-\text{com}}(r)$ for benzaldehyde and cinnamaldehyde also has a good

Table 2The local interaction energy between benzaldehyde and cinnamaldehyde with CO₂ at a density of 1.8ρ_c.^a

	ΔE_{CHO}	$\Delta E_{\text{CHO,elec}}$	$\Delta E_{\text{CHO,vdW}}$	$\Delta E_{6\text{C}}$	$\Delta E_{6\text{C,elec}}$	$\Delta E_{6\text{C,vdW}}$
Benzaldehyde	-4.33	-0.14	-4.18	-1.57	-0.017	-1.56
Cinnamaldehyde	-5.77	-0.12	-5.65	-1.3	-0.015	-1.29

^a ΔE_{CHO} is the interaction energy of CO₂ with carbonyl group and atom group (CHO). $\Delta E_{6\text{C}}$ is the interaction energy of CO₂ above and below aromatic ring with atom group (6C). $\Delta E_{\text{CHO,vdW}}$ and $\Delta E_{\text{CHO,elec}}$ are averaged van der Waals and Coulomb energy contributions to the interaction energy (ΔE_{CHO}). $\Delta E_{6\text{C,vdW}}$ and $\Delta E_{6\text{C,elec}}$ are averaged van der Waals and Coulomb energy contributions to the interaction energy ($\Delta E_{6\text{C}}$). All energy values are in kJ/mol.

peak shape with $r_{\text{o-com,min}}$ at 0.76 nm and 0.67 nm (Fig. 5), respectively. The calculated results are shown in Table 2. We notice that the local interaction energy (ΔE_{CHO}) of cinnamaldehyde is larger than that of benzaldehyde, whereas the local interaction energy ($\Delta E_{6\text{C}}$) of benzaldehyde is larger than that of cinnamaldehyde. This explains the difference of the local density enhancement for carbonyl group and aromatic ring between benzaldehyde and cinnamaldehyde. Another important feature is that for the two interactions mentioned above, the electrostatic energies ($\Delta E_{\text{CHO,elec}}$ and $\Delta E_{6\text{C,elec}}$) are much smaller than the van der Waals energies ($\Delta E_{\text{CHO,vdW}}$ and $\Delta E_{6\text{C,vdW}}$). Therefore, the van der Waals interaction between CO₂ molecule and solute molecule controls the distribution of CO₂ molecule around the solute molecule.

4. Conclusions

In this work, the solvation structures of benzaldehyde and cinnamaldehyde were investigated. It is observed that spatial distribution of CO₂ molecule corresponds to the negative electrostatic potential of the solute molecules. The 2D solvent density distribution and the RDFs show that the solvent local density enhancement around the carbonyl group of cinnamaldehyde is higher than that of benzaldehyde, while it is opposite for the solvent local density enhancement above and below the aromatic ring of benzaldehyde and cinnamaldehyde. These features can be explained from the difference in the molecular interactions between CO₂ and carbonyl group and aromatic ring of benzaldehyde and cinnamaldehyde.

The interaction energies show that cinnamaldehyde has higher affinity to CO₂ than benzaldehyde. While the local interaction energies indicate the interaction between CO₂ and carbonyl group of cinnamaldehyde is stronger, but between CO₂ and aromatic ring is weaker compared to these of benzaldehyde, which explains the difference in the local density of benzaldehyde and cinnamaldehyde that mainly stem from the van der Waals contribution.

Finally, the apparent contradiction for the solubility of both solutes between our calculation and experiment is due to the fact that stronger solute–solute interactions, which is lacking in our calculations, play an important role in the solubility. This means that solute–solute interactions are important in governing the solubility.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.04.046.

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