

Solubility parameters of supercritical CO_2 and CO_2+H_2O fluids: A molecular dynamics study

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SPECIAL TOPIC — Structures and properties of materials under high pressure

Solubility parameters of supercritical CO_2 and CO_2+H_2O fluids: A molecular dynamics study

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Understanding the solubility of supercritical CO_2 and its mixtures with other fluids at various temperatures and pressures conditions is critical for their applications, such as extraction processes, material design, and carbon capture. In the present study, the solubility parameters of supercritical CO_2, H_2O, and their mixtures were calculated by molecular dynamics simulations. The results show that the solubility parameters decrease with increasing temperature and increase with increasing pressure and are linearly proportional to the density. Furthermore, the intermolecular interactions, including the hydrogen bonds, significantly affect the solubility parameter of the CO_2–H_2O system.

Keywords: molecular dynamics, solubility parameter, supercritical CO_2

PACS: 82.20.Wt, 82.60.–s, 82.30.Rs

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1. Introduction

Global warming, primarily attributed to excessive carbon dioxide emissions, has attracted extensive attention in recent years. Significant efforts have been made toward the development of carbon capture, utilization, and storage (CCUS) technologies to suppress the emission of carbon dioxide. It is important to understand the thermodynamic properties of carbon dioxide at various temperatures and pressures. Supercritical fluids usually have high diffusion coefficients, low viscosities, excellent mass transfer capabilities, and superior solubilities. Supercritical CO_2 (sCO_2), in particular, is widely utilized in extraction processes, material design, and carbon capture due to its advanced properties.[1] Therefore, it is important to understand the solubility properties of CO_2 at various temperatures and pressures.[2] On the other hand, water, as the most prevalent solvent on Earth, plays a significant role in geological carbon storage through its interaction with CO_2. Under underground temperature and pressure conditions, the solubility of CO_2 in water is important for understanding the global carbon cycle.[3,4] The solubility of the CO_2–H_2O–brine system has been extensively studied in previous experimental studies. These studies covered a temperature range from 323 K to 473 K and a pressure range from 0.5 MPa to 200 MPa.[5–15] In recent years, theoretical efforts have been conducted to calculate CO_2 and H_2O solubility under various temperature and pressure conditions. Hemmati-Sarapardeh *et al.*[16–18] utilized neural networks and deep learning to model CO_2 solubility in water at high temperatures and pressures. Portier *et al.*[19] proposed a thermodynamic model to calculate CO_2 solubility in pure water and NaCl solutions, ranging from 0 °C to 300 °C and 0.1 MPa to 30 MPa. Sorensen *et al.*[20] developed solubility models for CO_2 in pure water at 348–623 K and 1.6–140 MPa, as well as in NaCl solutions at 298–523 K and 0.1–138.2 MPa. Additionally, molecular dynamics simulations by Du *et al.*[21] suggested that the solubility parameters of sCO_2 can be enhanced by increasing the pressure or decreasing the temperature. The solubility parameter of sCO_2 is directly proportional to its density, and the addition of co-solvents further increases the solubility of the system. Similar temperature and pressure dependencies of the sCO_2 solubility parameters were also obtained from the molecular dynamic simulations by Zhang *et al.*[22] and Lu *et al.*[23]

Previous studies mainly focused on the solubility of CO_2 in other solvents. The effect of the intrinsic properties of the solute, solvent, and solution on the resulting solubility has been much less investigated. To understand the solubility of CO_2 and the influence of additional H_2O at various temperatures and pressures, molecular dynamics simulations were per-

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formed on the CO_2, H_2O, and CO_2–H_2O systems. The solubility parameters of these systems were calculated over a wide temperature range from 333 K to 1000 K and a pressure range from 20 MPa to 200 MPa. The relationship between the intrinsic solubility parameter of the CO_2–H_2O mixture and the solubility of CO_2 in H_2O was discussed.

2. Computational details

All molecular dynamics calculations were performed using the COMPASS force field implemented in Forcite.[24] The supercell of pure CO_2 contained 100 CO_2 molecules, the supercell of pure H_2O contained 150 H_2O molecules, and the supercell of the CO_2–H_2O mixed system contained 100 CO_2 molecules and 150 H_2O molecules (Fig. 1). The Velocity Verlet algorithm was utilized to solve the particle motion, and the NPT ensemble was employed to control the temperature and pressure of the system. Each molecular dynamics simulation ran for at least 500 ps with a timestep of 1 fs, and the trajectories were recorded every 1000 steps. The solubility parameter (δ) was calculated using

$$\delta = \sqrt{E_{\text{coh}}/V}, \tag{1}$$

where E_{coh} represents the cohesive energy of the total molecular system. It is the average energy required to separate all molecules from each other to infinity, and can be calculated as

$$E_{\text{coh}} = -\langle E_{\text{inter}} \rangle = \langle E_{\text{intra}} \rangle - \langle E_{\text{total}} \rangle, \tag{2}$$

where E_{inter} is the total energy between all the molecules, which is the total energy of the system E_{total} minus the intramolecular energy E_{intra}.

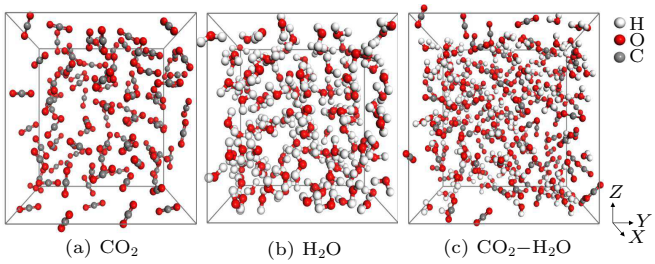


Fig. 1. Structural models. (a) Pure CO_2 with a supercell containing 100 molecules; (b) a supercell containing 150 H_2O molecules; (c) CO_2–H_2O mixed system with 100 CO_2 molecules and 150 H_2O molecules.

3. Results and discussion

3.1. The solubility parameter of sCO_2

To verify the validity of the present molecular dynamics simulations, the calculated densities of sCO_2 and H_2O at selected temperatures and pressures were compared with the previous experimental values[25,26] as shown in Table 1. The results show that the calculated densities agree well with the experimental data, with a maximum error of less than 6.2%.

Table 1. Comparison of calculated and experimental densities of CO_2 and H_2O.

Type	T (K)	P (MPa)	ρ (g·cm^{-3}) (present work)	ρ (g·cm^{-3}) (exp.)[25,26]	$\Delta\rho$ (%)
CO_2	313.15	15	0.786	0.78	0.77
CO_2	313.15	20	0.804	0.84	4.3
CO_2	323.15	15	0.692	0.700	1.1
CO_2	323.15	20	0.742	0.784	5.4
CO_2	333.15	15	0.601	0.604	0.50
CO_2	333.15	20	0.759	0.724	4.8
H_2O	423.15	10	0.886	0.922	3.9
H_2O	623.15	20	0.564	0.601	6.2

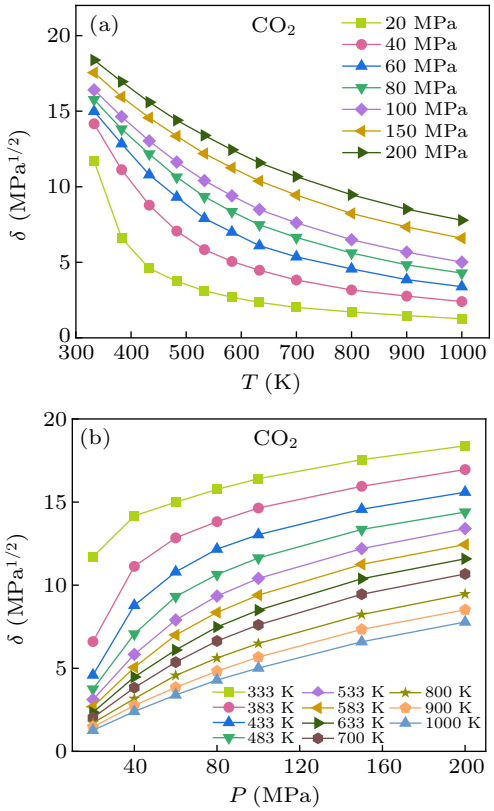


Fig. 2. (a) Variation of solubility parameters with temperature (300–1000 K) for the CO_2 mixed system at different pressures; (b) variation of solubility parameters with pressure (20–200 MPa) in CO_2 mixed system at different temperatures.

The temperature-pressure dependence of the solubility parameters of sCO_2 is shown in Fig. 2. Overall, the solubility parameter increases with pressure and decreases with temperature. These temperature and pressure dependencies are similar to those observed in previous studies. The evolution of the solubility parameter can be explained by changes in intermolecular interactions. With increasing temperature or decreasing pressure, the intermolecular interactions decrease and this results in reduced cohesive energy and a lower solubility parameter. At high pressures (e.g., 200 MPa), the molecular structures are much denser and the temperature effect on the intermolecular interaction becomes weaker. It can be seen that the solubility parameter is relatively less affected by the temperature at high pressure, and it is also less affected by pres-

sure at high temperature. In contrast, the solubility parameter is much more sensitive at low temperatures and pressures. For instance, at 20 MPa, the solubility parameter significantly decreases from 333 K to 500 K, followed by a linear temperature dependence at higher temperatures. Notably, the pressure dependence at 383 K is stronger than that at the lowest temperature of 333 K.

3.2. The solubility parameter of supercritical H_2O

The temperature/pressure-dependent of the solubility parameters of H_2O is shown in Fig. 3. The overall trend of the solubility parameters is similar to that of CO_2. However, it also shows some very different temperature and pressure dependencies. At low temperatures (below 583 K), the solubility parameter gradually decreases with temperature at all pressures. However, when the temperature increases to 700 K, the solubility parameter at 20 MPa dramatically decreases to a value of 8.27 $MPa^{1/2}$. Moreover, the pressure dependence also becomes much more sensitive at 700 K. Below 700 K, the solubility parameter is almost linearly proportional to pressure. At 700 K, it suddenly increases from 8.27 $MPa^{1/2}$ at 20 MPa to 20 $MPa^{1/2}$ at 40 MPa. The distinct solubility parameters at 700 K and 20 MPa indicate that H_2O transitions from a liquid state to a supercritical state.

3.3. The solubility parameter of CO_2–H_2O

Due to the differences in the intrinsic physical properties, H_2O and CO_2 exhibit different temperature and pressure dependencies of the solubility parameters. Therefore, it is interesting to study the influence of H_2O on solubility when mixed with CO_2, especially the relationship between the calculated solubility parameters and the experimental solubility of CO_2 in H_2O. The temperature/pressure-dependent solubility parameters of CO_2–H_2O are shown in Fig. 4. As expected, the overall temperature and pressure dependencies are similar. To understand the relationship between the solubility of CO_2 in H_2O and the solubility parameters of CO_2, H_2O, and CO_2–H_2O mixture, the experimental solubility results[15] and calculated solubility parameters are presented in Fig. 5. Experimental results in Fig. 5(a) show that the solubility increases with pressure, as expected. Regarding the temperature effect, the solubility initially decreases with temperature and then increases with temperature. For instance, such turning temperature for 20 MPa is around 400 K. It is known that the solubility of one solute in a solvent is usually higher when the solute and solvent have similar solubility parameters.[27] This is supported by the solubility difference between CO_2 and H_2O, as shown in Fig. 5(c). In particular, for low pressures such as

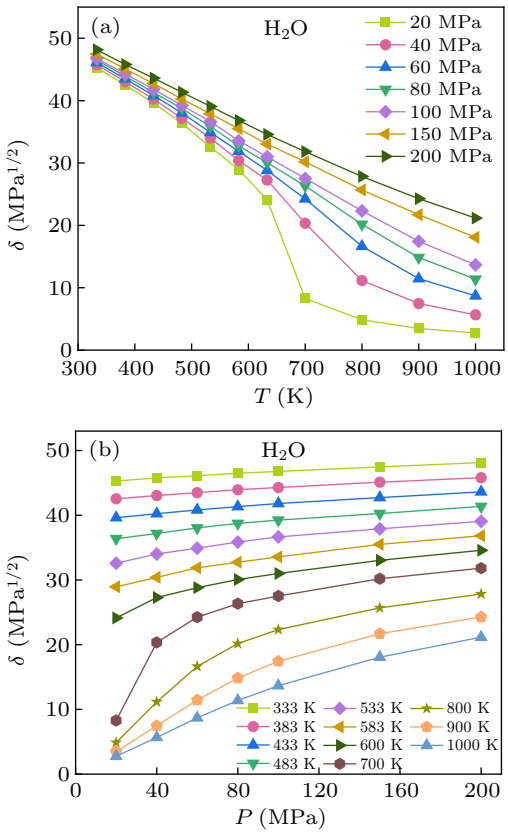


Fig. 3. (a) Variation of solubility parameters with temperature (300–1000 K) in H_2O mixed system at different pressures. (b) Variation of solubility parameters with pressure (20–200 MPa) in H_2O mixed system at different temperatures.

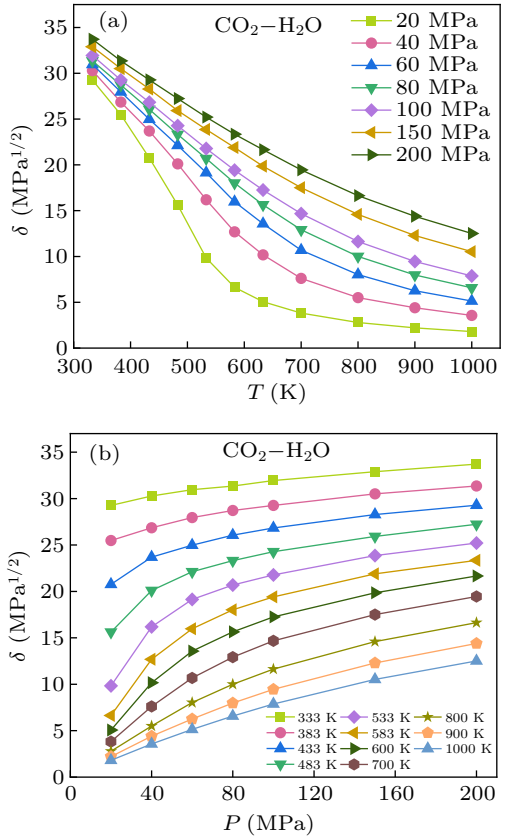


Fig. 4. Variation of solubility parameters with temperature (300–1000 K) in CO_2–H_2O mixed system at different pressures. (b) Variation of solubility parameters with pressure (20–200 MPa) in CO_2–H_2O mixed system at different temperatures.

20 MPa, the solubility parameter difference initially increased with temperature up to approximately 400 K. Above 400 K, the solubility parameter starts to decrease with temperature. This agrees well with the evolution of the experimental solubility results, indicating the underlying relationship between the solubility parameters and solubility. As mentioned above, the solubility parameter reflects the cohesive energy of the system. As shown in Fig. 5(b), the solubility parameter of the CO_2–H_2O mixture at 20 MPa decreases much faster with temperature. This indicates that the intermolecular interactions between CO_2 and H_2O are weaker at high temperatures. This is also consistent with the experiment in which the solubility at 20 MPa and 480 K is much smaller than the higher-pressure results. Nevertheless, the solubility parameter difference between CO_2 and H_2O at 20 MPa decreases much faster at higher temperatures. At 600 K, the solubility parameter of the CO_2–H_2O mixture at 20 MPa is much smaller than that at higher pressure, indicating that the mixture may transform into a supercritical state. However, there are no experimental solubility results at such high temperatures. The present results may trigger experiments to further verify the relationship between the solubility parameter and the real solubility.

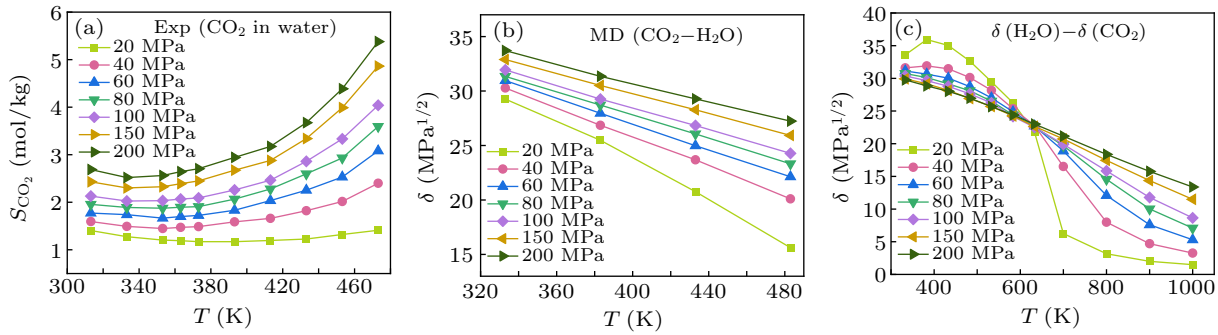


Fig. 5. (a) The experimental results[15] of CO_2 solubility in H_2O. (b) The calculated solubility parameters of the CO_2–H_2O mixtures from MD simulations. (c) The solubility parameter difference between H_2O and CO_2 fluids.

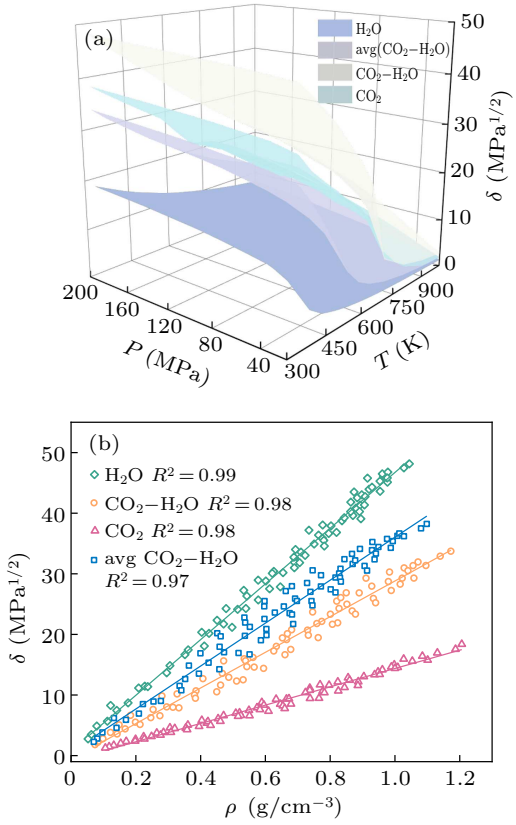


Fig. 6. (a) Solubility parameters of CO_2, H_2O, and CO_2–H_2O plotted as a function of the mathematical average. (b) Relationship between density and solubility parameters for CO_2, H_2O, CO_2–H_2O, and their mathematical average.

To investigate the influence of H_2O, the mathematically averaged solubility parameter of the CO_2–H_2O system which was calculated from Eq. (3) was compared with the calculated results, as shown in Fig. 6(a). Clearly, the calculated solubility parameter of the CO_2–H_2O system is different from the mathematical average. This indicates that the intermolecular interaction between CO_2 and H_2O changed the physical properties of the entire system, as well as the solubility parameter. A comparison of the CO_2, H_2O, and CO_2–H_2O systems at the selected temperatures and pressures is shown in Fig. 7. For the temperature dependence at 20 MPa, the mathematical average result also showed an abrupt change at 700 K in the CO_2–H_2O systems. In the calculated results, the solubility parameter significantly decreases from 333 K to 600 K, without an obvious kink during evolution. On the other hand, for the pressure dependence at 700 K, the calculated result for the CO_2–H_2O system is much less sensitive to the pressure than the mathematical average and the H_2O system.

From the abovementioned results, both high pressure and low temperature, which lead to high density, result in a higher solubility parameter. It is interesting to study the density dependence of the solubility parameter. As shown in Fig. 6(b), the density-dependent solubility parameters of these three systems were compared, together with the mathematically averaged density which was calculated using Eq. (4). The results for all three systems show a clear linear relationship. The solubility parameter of H_2O is higher than that of CO_2, and it also increases faster with density, while the value of the CO_2–H_2O system increases more slowly than the mathematical average. The linear relationship between the solubility parameter and density suggests that the solubility of these three systems can

be modulated by their density by adjusting temperature and pressure to control density.

$$\delta_{\mathrm{avg}(CO_2-H_2O)} = (N_{CO_2}\delta_{CO_2} + N_{H_2O}\delta_{H_2O})/(N_{CO_2} + N_{H_2O}), \quad (3)$$

$$\rho_{\mathrm{avg}(CO_2-H_2O)} = (N_{CO_2}\rho_{CO_2} + N_{H_2O}\rho_{H_2O})/(N_{CO_2} + N_{H_2O}), \quad (4)$$

where $\delta_{CO_2-H_2O}$ and $\rho_{CO_2-H_2O}$ are the average solubility parameter and average density of CO_2 and H_2O; N_{CO_2} and N_{H_2O} are the number of CO_2 and H_2O molecules in the system; δ_{CO_2} and δ_{H_2O} are the solubility parameters of CO_2 and H_2O; ρ_{CO_2} and ρ_{H_2O} are the densities of the CO_2 and H_2O systems.

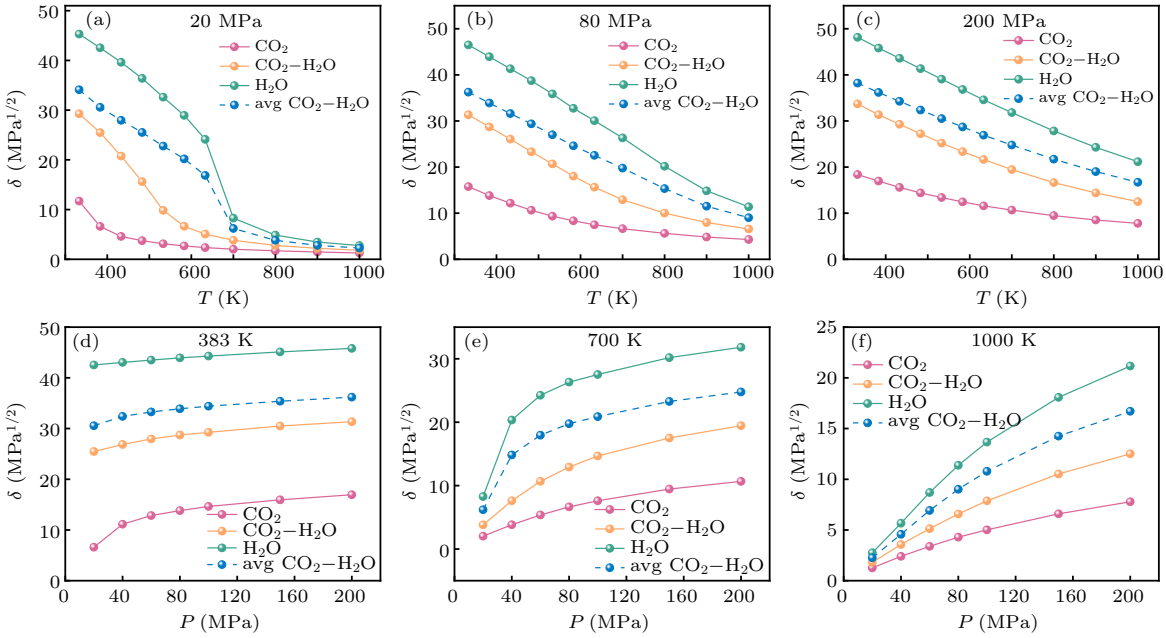


Fig. 7. Solubility parameters of CO_2, H_2O, and CO_2–H_2O plotted against their mathematical averages at selected temperatures and pressures.

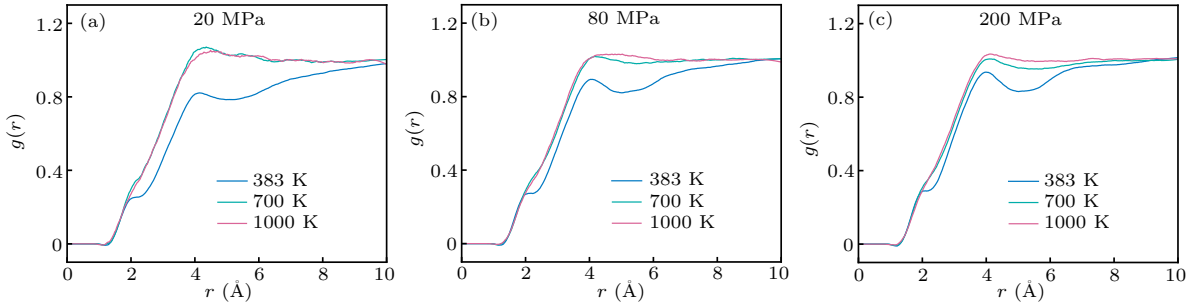


Fig. 8. The partial radial distribution function of H_{H_2O}–O_{CO_2} in the CO_2–H_2O system at selected temperatures and pressures.

To understand the evolution of the solubility parameters at various temperatures and pressures from a structural point of view, the partial radial distribution function (RDF) of H–O in the CO_2–H_2O system was analyzed at selected temperatures and pressures, as shown in Fig. 8. It should be noted that the partial RDF of H–O only includes H atoms from the H_2O molecules and O atoms from the CO_2 molecules. The results show a clear peak located at 2 Å at 383 K for all studied pressures. When the temperature increases to 700 K, the first peak located at 2 Å merges with the second peak. The first peak located at 2 Å corresponds to the hydrogen bond between the hydrogen atom and the oxygen atom in the neighboring molecule, as illustrated in the structural model shown in Fig. 9. It indicates that the disordered CO_2–H_2O structure has some short-range order due to the hydrogen bond.[28] When the temperature increases to 700 K, the weak hydrogen bonds are broken due to the highly diffusive motion of atoms, resulting in a more disordered structure.

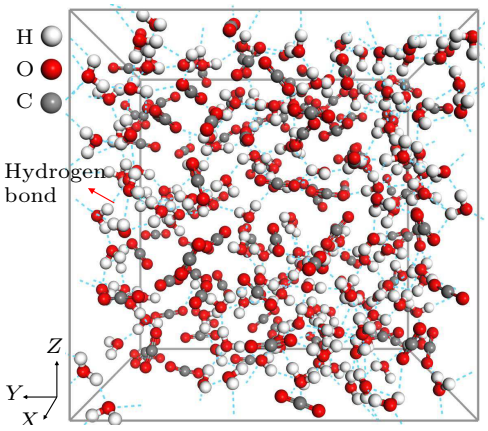


Fig. 9. Hydrogen bond model in the CO_2–H_2O mixed system.

4. Conclusions

In summary, the solubility parameters of the CO_2, H_2O, and CO_2–H_2O systems were calculated by molecular dynamics simulations. The overall results show that the solubility parameter increases with pressure and decreases with temperature. The solubility parameter shows a linear relationship with the density in all three systems. However, the pressure and temperature dependencies differ among the three systems. For instance, when the temperature increases to 700 K in H_2O, the solubility parameter at 20 MPa significantly decreases, indicating that H_2O transforms into a supercritical state. In contrast, in the CO_2–H_2O system, the solubility parameter also decreased rapidly at temperatures below 600 K at 20 MPa, but without an abrupt kink in the curve. The solubility parameter of the CO_2–H_2O systems is different from the mathematically averaged values of separate CO_2 and H_2O fluids. This suggests that the intermolecular interaction between CO_2 and H_2O molecules plays a role in determining the solubility of the system. The partial RDF analysis shows that the significantly decreased solubility parameter of CO_2–H_2O at high temperatures is due to the breakage of the hydrogen bonds, which help form a certain short-range order at low temperatures. A comparison between the calculated solubility parameters and the experimental solubility indicates a strong correlation between them. It would be interesting to extend the experiment to higher temperatures where the solution is in a supercritical state. The present results provide a systematic understanding of the solubility parameters of the CO_2, H_2O, and CO_2–H_2O systems at various temperatures and pressures. These findings can help to manipulate the solubility of a solvent system by controlling the temperature and pressure, which can be utilized in the extraction process and other applications.

Acknowledgements

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