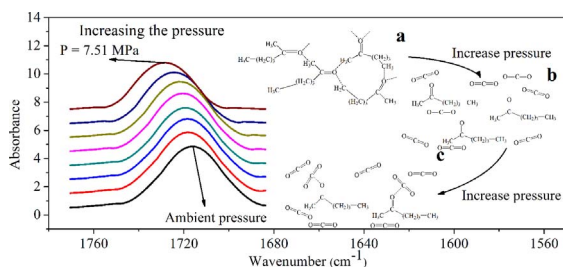# Dispersion properties of CO_2 and polar organic solvents with the same alkyl chain length mixtures using *in situ* FTIR spectroscopy

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GRAPHICAL ABSTRACT

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ABSTRACT

To investigate the microscale dispersion properties of CO_2 in polar organic solvents with equivalent alkyl chain lengths, the volume expansion coefficients and solubilities of CO_2 in 2-hexanone, hexanal, and 1-hexanol were measured at 318 K under different pressures. A modified Fourier-transform infrared spectroscopy technique was applied *in situ* to study the microcosmic mechanisms of volume expansion in the three mixtures, from ambient pressure to the supercritical state of CO_2 at 318 K. The results show that CO_2 and 2-hexanone/hexanal form 2-hexanone-CO_2 and hexanal-CO_2 aggregations, respectively, with increasing CO_2 pressure; the dispersion state of CO_2 molecules in the solvent is the primary factor causing the volume increase of the mixture and CO_2 solubility. During this process, the original microstructure of the liquid 2-hexanone and hexanal can be broken, and it becomes easier for CO_2 molecules to dissolve in the 2-hexanone and hexanal solvents.

1. Introduction

In recent years, supercritical CO_2 has been widely used in many industrial processes because of its special properties. Advantages include environmental protection [1], recyclability [2], and efficient processing effects [3]. Supercritical CO_2 can also act as an excellent solvent in material modification [4–6], dyeing [7,8], extraction [9–13], cleaning [14,15] processes, etc. As is well-known, the volume of an organic liquid will expand when CO_2 penetrates the liquid [16–18]; increasing CO_2 pressure enhances the volume expansion, as determined by the volume expansion coefficient and CO_2 solubility. This phenomenon arises from the intermolecular interaction of organic molecules, which when "weakened" causes the distance between the organic molecules to increase as CO_2 disperses into the organic liquid. Based on this characteristic, supercritical CO_2 offers significant advantages in many industrial fields. In enhanced oil recovery processes [19,20], supercritical CO_2 can be utilized as an oil-displacement agent, and this technology is known as CO_2-enhanced oil recovery (CO_2-EOR). With increasing CO_2 pressure, the volume expansion coefficient and CO_2 solubility in the crude oil mixture increase, and the viscosity of the crude oil decreases. Therefore, CO_2-EOR can be considered an efficient means of oil production enhancement in low-permeability reservoirs.

As mentioned above, CO_2 dissolution and oil volume expansion are two of the main mechanisms for improving oil recovery [21–25]. The higher solubility of CO_2 and oil volume expansion yields more oil recovery. In our previous work [26], the solubility of CO_2 in nonpolar organic solvents was found to be higher than that in polar organic solvents, and the volume expansion of CO_2 and a nonpolar organic solvent or polar organic solvent mixture also followed this tendency. Researchers have also shown that the existence of polar organic solvents in crude oil has a negative impact on CO_2 solubility and oil volume expansion, and consequently, on the performance of CO_2-EOR [27]. Since crude oil is composed of many different polar organic components, it is necessary to study the effects of volume expansion in supercritical CO_2 and polar organic solvent mixtures.

Volume expansions of CO_2 and some organic solvent mixtures have been reported, primarily from a thermodynamic perspective [28–30], for example, by the construction of phase diagrams of supercritical CO_2 and organic mixtures. Further investigation of the mechanism of volume expansion of CO_2 and an organic solvent at a micro-scale is required. In our previous work [31], the dispersion properties of CO_2 in oil were studied by measuring the volume expansion of the CO_2-oil mixture and CO_2 solubility in oil. Molecular dynamic simulation was used to measure the radial distribution function of molecules in the mixture. The results showed that the microcosmic dispersion state of CO_2 molecules in oil is the crucial control of volume expansion in the supercritical CO_2 and oil mixtures. Molecular dynamic simulation is a reliable way to investigate intermolecular interactions and the micro-scale dispersion properties of molecules in binary mixtures [32]; however, it cannot provide direct evidence of the microcosmic mechanisms. For technology development and engineering applications, there are still gaps between molecular dynamic simulation research and industrial requirements. Hence, a new method that can examine intermolecular interactions in supercritical CO_2 and organic solvent mixtures, from a microcosmic perspective using experimentation, will be significant.

Experimental methods used in modern optics have been used recently to study the structure of molecules under certain experimental conditions [33,34]. Fourier-transform infrared (FTIR) spectroscopy is one of the most common ways to detect the structure of molecules, especially to identify functional groups [35]. When the conditions of molecules change, the intermolecular interactions between the molecules will also change, and this is reflected in the FTIR spectra. *In situ* FTIR spectroscopy conducted under high pressure and temperature conditions has been used to investigate CO_2 and organic mixtures under supercritical CO_2 conditions [36–39]. Recently, this method has been used to investigate microcosmic mechanisms of volume expansion and absorption in supercritical CO_2 and polymer mixtures and supercritical CO_2 and powder mixtures [40,41]. The characteristic FTIR absorption peaks of functional groups of the polymer change regularly under different CO_2 pressures; this phenomenon reflects changes in the intermolecular interactions between molecules in the mixtures. For supercritical CO_2 and organic solvent mixtures, when the dispersion state of the molecules changes, the intermolecular interaction also changes, such that the *in situ* FTIR spectroscopy can be used to investigate the supercritical CO_2 and organic solvent mixtures.

In this study, the volume expansion coefficient and CO_2 solubility in 2-hexanone, hexanal, and 1-hexanol from ambient pressure to the supercritical state of CO_2 were measured using a visible high-pressure variable pressure-volume-temperature (*PVT)* device. The FTIR spectra of CO_2, 2-hexanone, hexanal, and 1-hexanol from ambient pressure to the supercritical state of CO_2 were detected using a modified *in situ* FTIR spectroscopic method. The effect of pressure on the volume expansion coefficient and CO_2 solubility in 2-hexanone, hexanal, and 1-hexanol is discussed. The effect of intermolecular interactions and the microstructure of the organic liquid on the volume expansion coefficient and CO_2 solubility in 2-hexanone, hexanal, and 1-hexanol are also discussed.

Table 1
CO_2 and organic solvents.

Chemicals	Purity (%)	Source
CO_2	99.99	Jing Gao Gas Plant, Beijing
2-hexanone	99.0	Shanghai Macklin Biochemical Co., Ltd
hexanal	97.0	Shanghai Macklin Biochemical Co., Ltd
1-hexanol	99.5	Beijing Chemical Works

2. Experiments

In this study, the volume expansion and CO_2 solubility were measured by a *PVT* device with a visible window. The FTIR spectroscopy approach was applied *in situ* to investigate the behaviour of the CO_2 and 2-hexanone, hexanal and 1-hexanol mixtures at different conditions.

2.1. Sample and material characterization

The CO_2 and organic solvents used in this study are given in Table 1.

2.2. Volume expansion coefficients and CO_2 solubility in 2-hexanone, hexanal, and 1-hexanol

A high-pressure variable *PVT* cell was used for the experiments. The total volume of the cell is 240 cm^3, which can be modified by a moving piston. The maximum working pressure and temperature of the cell are 150 MPa and 473.15 K, respectively. A sapphire glass window is installed in the front of the *PVT* cell. Through the window, the contents of the cell can be recorded by a digital camera, and the volume of the fluid phase can be measured under experimental conditions. The whole cell is heated by a heating-mixture. The temperature and pressure of the cell are measured by a temperature inductor and a pressure sensor, respectively. The uncertainties of the pressure and temperature measurements are 0.01 MPa and 0.1 K, respectively.

The procedures of the operation have been reported in our previous work [42], and the flow diagram of the experiment is shown in Fig. 1. The first step is to clean the instrument; the entire loop of the apparatus should be cleansed and evacuated several times by a vacuum pump. A known volume (V_0 = 30 mL) of the organic solvent is injected into the *PVT* cell, and CO_2 is pressurized into the cell. The whole apparatus is heated to the specific temperature. Using a magnetic stirrer, the CO_2 and organic solvent are mixed. After mixing, the pressure and temperature will be maintained at a fixed condition for at least an hour, until phase equilibrium is obtained. The volume (V_1) of the liquid phase can be calculated from the image captured by the charge coupled device (CCD) camera. Then the organic solvent is taken from the cell and charged into a small steel vessel that has already been vacuumed and weighed (M_0), and the pressure of the cell is kept constant by moving the piston when discharging the organic solvent out of the cell. The discharging process is performed slowly to avoid flashing, and the mass of CO_2 dissolved in the organic solvent is calculated using the weight-difference method: the mass of the steel vessel containing organic solvents and CO_2 (M_1) minus the mass of the vessel after releasing CO_2 to atmosphere (M_2). The solubility (mass ratio) of CO_2 is also calculated using these data. The volume expansion coefficient (N) in the CO_2 and organic solvent mixture is defined by Eq. (1):

$$N = V_1/V_0 \qquad (1)$$

The measurements are repeated three times, and the results are presented as the average of the replicates.

2.3. The design of the sample cell for in situ FTIR spectroscopy

To determine the infrared spectroscopy of the samples under experimental conditions, a sample optical cell was designed. These cells