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Hydrogen bonding of acetic acid in $CO_2 + n$-pentane mixed fluids in the critical region

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Abstract

Fourier transform infrared (FTIR) spectra and hydrogen bonding of acetic acid in CO_2 (1) + n-pentane (2) mixture were studied at 308.2 K up to 11 MPa. The experiments were conducted in the mixed supercritical (SC) and subcritical fluids near critical region and far from the critical region. The results demonstrated that the frequency of C=O stretching vibration of the monomer and dimer, the molar absorptivities of monomer and dimer, and the monomer–dimer equilibrium were very sensitive to pressure in the subcritical fluids and supercritical fluids in the critical region, especially as the pressure approached the phase boundary, while the effect of pressure on these properties outside the critical region was very limited.

Keywords: Acetic acid; FTIR; Cosolvent; Dimerization

1. Introduction

Supercritical fluids (SCFs) can be used in many application processes, such as extraction and fractionation, chemical reactions, and material processing. It is well known that SCFs have many unusual properties, which originate from special intermolecular interactions. In the past decade or so, different techniques have been used to study the intermolecular interactions in SCFs, such as spectroscopy [1–6], computer simulation [7], integral equation theory [8], EPR [9], small-angle X-ray scattering (SAXS) [10,11], partial molar volume (PMV) measurement [12,13], and calorimetry [14].

Fourier transform infrared (FTIR) spectroscopy has been used to investigate various properties of SCFs. For example, Kazarian and Poliakoff studied *trans*/*gauche* isomerism of hexafluoropropan-2-ol in supercritical (SC) SF_6 and CHF_3 and found that the effect of increasing density was small compared with the effect of increasing dielectric constant in the equilibria [15]. Wada et al. measured the IR spectra of substituted benzene compounds in SC CO_2 [16]. The results demonstrated that the molar absorption coefficient of substituent deformation stretch and C–C ring stretch varied with the system density. They estimated the local excess density of benzene derivatives in SC CO_2. A significant effect of solvent density on hydrogen

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bandings between methanol and triethylamine, and between perfluoro-*tert*-butyl alcohol and dimethyl ether was observed [2,17]. Lu et al. studied the monomer–dimer equilibrium of lauric acid in SC CO_2 and found that fluid density played an important role on the dimerization [18]. Study of Tsugane et al. revealed that benzoic acid could form a cyclic dimer by hydrogen bonding in SC CO_2 [19]. Yamamoto et al. [20] and Iwai et al. [21] studied the dimerization of acetic acid in SC CO_2 in the pressure range of 10–20 MPa.

Many application systems related with SCFs are mixtures. It is well known that the critical parameters and phase behavior of a mixture depend on its composition [22–28]. Therefore, the critical parameters of the systems should be considered [29]. However, compared with pure SCFs or dilute SC solutions, little is known about the intermolecular interactions of mixed fluids in the critical region. To explore the advantages of SCF technologies in various applications, the knowledge of mixed fluids in the critical region is necessary.

In previous work [29], we determined the constant volume heat capacity (C_v) of CO_2 + ethanol and $CO_2 + n$-pentane binary mixtures at 308.2 K in different phase regions. The results indicated that C_v is very sensitive to pressure near the critical point of the mixtures, indicating that the intermolecular interaction varies significant with pressure and composition in the critical region of the binary mixtures. In this work, the FTIR spectra of acetic acid in $CO_2 + n$-pentane binary mixtures were determined at 308.2 K in different phase regions. The molar absorption coefficients of the monomer and hydrogen-bonded dimer of acetic acid were determined and the equilibrium constants of dimerization were calculated on the basis of the FTIR spectra and the molar absorption coefficients. We focus on the effect of pressure on the monomer–dimer equilibrium, molar absorptivities of C=O stretching vibration, and the vibration frequency in different phase regions of the mixed solvent.

2. Experimental

2.1. Materials

CO_2 (99.995%) was supplied by Beijing Analytical Instrument Factory. *n*-Pentane (>99.5%) and acetic acid (99%) were produced by Beijing Chemical Reagent Factory. All of the chemicals were used as received.

2.2. Apparatus and procedures

The schematic diagram of the experimental set-up is shown in Fig. 1. A detailed description of the apparatus can be found elsewhere [30]. The apparatus consisted mainly of a FTIR spectrometer, a high-pressure sample cell, and a pressure gauge. Temperature fluctuation of the high-pressure cell was ±0.1 K, which was controlled by PID temperature controller (XMT, Beijing Chaoyang Automatic Instrument Factory) with a platinum resistance thermometer.

The IR spectrum was recorded using an Bruker IR spectrometer (TENSOR 27, RT-DLaTGS detector), and each sample was recorded with the average of 128 scans, the high-pressure cell was composed of a stainless steel body, two ZnS windows of 6 mm in thickness and the temperature controlling system. The optical path length of the cell was 0.9 cm and the inner volume of the cell was 1.89 cm^3. The high-pressure $CO_2 + n$-pentane mixture of desired composition was first prepared in a sample bomb of 60 ml. Then the IR sample cell was evacuated and purged with the mixture. Suitable amount of acetic acid was injected into the sample cell with a micro-syringe. The mixed fluid was carefully charged up to desired pressure. The absorption spectra were recorded every 10 min until it was independent of time, indicating equilibrium was reached. The absorption of the mixed solvent at the same condition was also determined as the background spectrum, although there was no obvious absorption in the range of interesting (1850–1650 cm^{-1}). All of the spectra were obtained by subtracting the background spectra from those of corresponding solutions.

3. Results and discussion

3.1. Phase behavior

In this work we focus on how the FTIR spectra and hydrogen bonding of acetic acid in SC CO_2 (1) + *n*-pentane (2) mixed solvent change with pressure in different phase regions. And the experiments were conducted at 308.2 K. The phase diagram (Fig. 2)

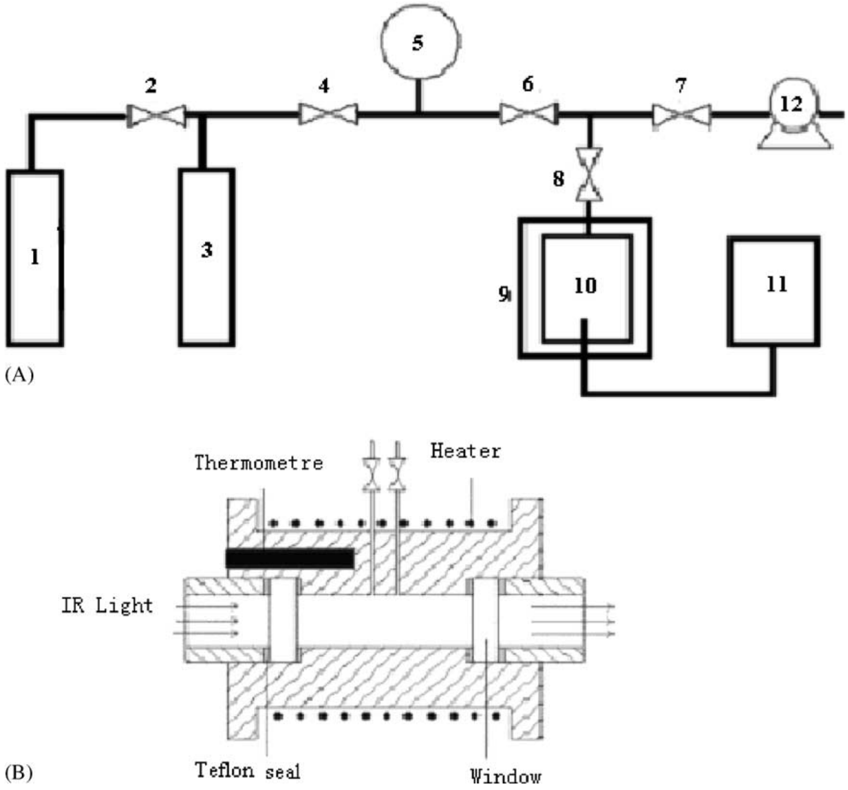


Fig. 1. Schematic diagram of the FTIR measurement system. A: (1) Gas cylinder; (3) pump; (5) digital pressure gauge; (9) FTIR spectrometer; (10) high-pressure IR cell; (11) temperature controller; (12) vacuum pump; (2, 4, 6–8) valves. B: Structure of the high-pressure IR cell.

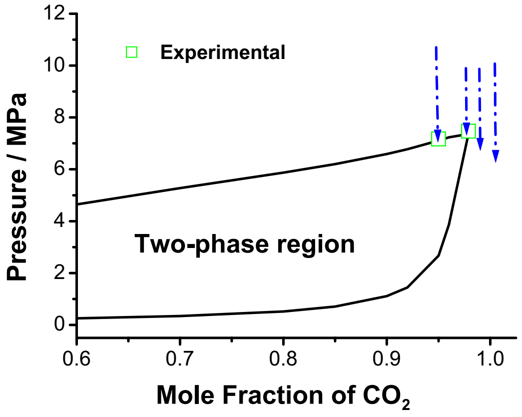


Fig. 2. Phase diagram of the $CO_2 + n$-pentane system at 308.2 K.

determined in our previous paper [29] allowed us to select suitable conditions of this work. The phase separation pressures at different compositions are given in Table 1. The critical composition of the binary solvent at this temperature is $X_2 = 0.021$. At the left side of the critical composition, a homogenous mixture can be regarded as compressed liquid or homogenous subcritical fluid when the pressure is higher than the bubble point pressure (BPP), and at the right side,

Table 1
Critical composition, critical pressure, and bubble point pressure (BPP) of CO_2 (1) + n-pentane (2) system at 308.15 K

X_2	BPP (MPa)
0.010	One phase[a]
0.021[b]	7.47[b]
0.050	7.17

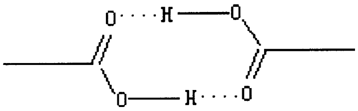
[a] One phase in the whole pressure range.

[b] Critical composition and critical pressure.

a homogenous mixture (in one phase region) is vapor or supercritical fluid. In this work all the experiments were conducted in one phase region.

3.2. FTIR spectra of acetic acid

The acetic acid can form hydrogen-bonded dimer in the following form [20,21,31]:



The FTIR spectra of acetic acid in CO_2 (1) + *n*-pentane (2) mixed fluid were measured. The experimental conditions are shown in Fig. 2 by the vertical lines, which can represent the SC and subcritical regions near the critical point of the mixed solvent. The densities of the solvents with different compositions are plotted in Fig. 3 as a function of pressure, which were determined in this work by gravimetric method [13].

In this work all the experiments were conducted in single-phase region, and the concentration of the solute was 2.07×10^{-3} mol/l. As an example, the spectra of the solute in the SC CO_2 determined at 10.1 MPa are demonstrated in Fig. 4. The band at 1772 and 1723 cm^{-1} can be attributed to the C=O stretching vibration of the monomer and the dimer, respectively. Figs. 5 and 6 shows the dependence of the frequencies of C=O stretching vibration of the monomer and dimer, respectively.

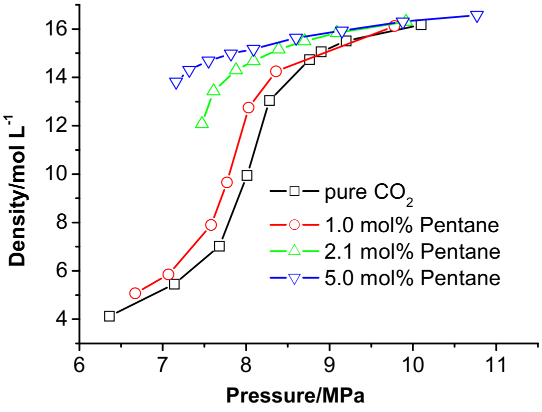


Fig. 3. Densities of CO_2 + *n*-pentane mixtures in different phase regions at 308.2 K.

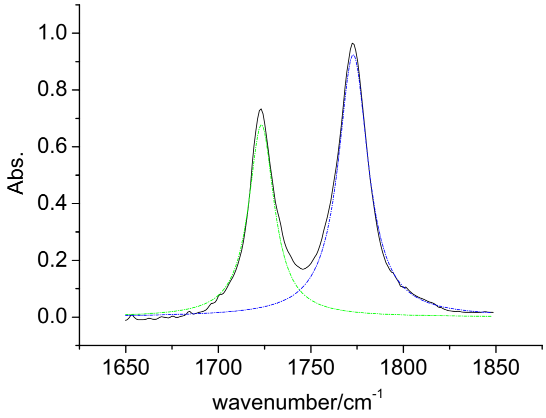


Fig. 4. Deconvolution of IR spectra for acetic acid in supercritical CO_2 at 10.1 MPa and 308.2 K. Molarity of acetic acid = 2.07×10^{-3} mol/l.

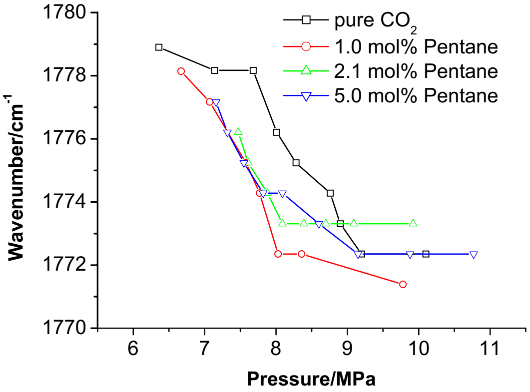


Fig. 5. The frequencies of C=O stretching vibration of acetic acid monomer as a function of pressure in pure and mixed fluids.

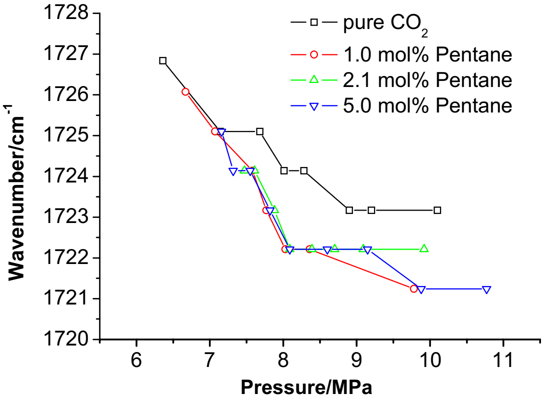


Fig. 6. The frequencies of C=O stretching vibration of acetic acid dimer as a function of pressure in pure and mixed fluids.

The results in Figs. 5 and 6 reveal that the effect of pressure on the frequency of C=O stretching vibration of the monomer and dimer is very limited in the solvent far from critical region. However, the frequency is very sensitive to pressure in the critical region of the mixed solvent, and increase rapidly as pressure approaches the critical point, bubble point of the mixed solvent. This suggests the sensitivity of the solvent properties to pressure in the critical region, especially as the pressure approaches the phase boundary. The vibrational frequencies of polar groups can be related with the semiempirical Kirkwood–Bauer–Magat model [3]

$$\frac{\nu_v - \nu_s}{\nu_v} = \frac{K(D-1)}{2D+1} \tag{1}$$

where ν_v and ν_s are the vibrational peaks of stretching vibration in gas phase (without solvent) and in the solvent, respectively. D denotes the dielectric constant of the solvent. K is a constant. The equation indicates that the frequency decreases as dielectric constant of the solvent increases. Considering the results in Figs. 5 and 6 and Eq. (1), one can see that the dielectric constant of the mixed solvent is more sensitive to pressure in the critical region of the mixed solvent, and at a fixed composition, the dielectric constant decreases rapidly as pressure approaches the phase separation points (critical point, bubble point) from high pressure, while the dielectric constant is not sensitive to pressure in the high-pressure region. The main reason is that the dielectric constant of a fluid increases with its density [20]. The density of the mixed solvent reduces significant when pressure approaches phase separation points from high pressure, and the effect of pressure on the density in high-pressure region is very limited, as is shown clearly in Fig. 3. Therefore, it can be deduced that dramatic change of solvent density with pressure in the critical region is the main reason for the sensitivity of the vibration frequencies of C=O.

3.3. Equilibrium constant

The dimerization equilibrium can be expressed as follows:

$$2\mathrm{HA} = (\mathrm{HA})_2 \tag{2}$$

$$K_2 = \frac{[(\mathrm{HA})_2]}{[\mathrm{HA}]^2} \tag{3}$$

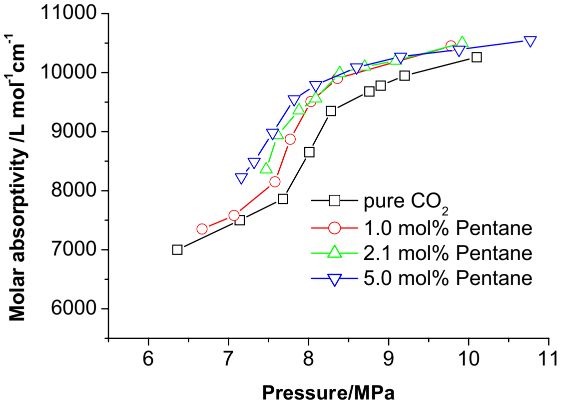


Fig. 7. Molar absorptivity of the monomer of acetic acid as a function of pressure.

where HA and $(\mathrm{HA})_2$ stand for acetic acid monomer and dimer, respectively. K_2 is the equilibrium constant. The total concentration of the acid, C, can be expressed as:

$$C = [\mathrm{HA}] + 2[(\mathrm{HA})_2] \tag{4}$$

If Lambert–Beer law holds for both carbonyl bands of the acid monomer and dimer, the maximum absorbances of the two bands, A_m, and A_d are given by

$$A_m = \varepsilon_m l[\mathrm{HA}] \tag{5}$$

and

$$\mathrm{A}_d = \varepsilon_d l[(\mathrm{HA})_2] \tag{6}$$

where l is the cell length and ε the molar absorptivity at the band maximum. Subscripts m and d denote the monomer and dimer, respectively.

To calculate K_2, the values of ε_m and ε_d are required. It is known that both ε_m and ε_d depend on the density of solvents [2,18]. It is expected that the molar absorptivity varies with pressure because, as shown in Fig. 3, the density of the solvent depends strongly on pressure, especially in the critical region. Therefore, in this work we determined the ε_m and ε_d values at different conditions using the method reported by Fujii et al. [31] The molar absorptivity ε_m and ε_d versus pressure curves are presented in Figs. 7 and 8. Both ε_m and ε_d change considerably with pressure or density of the solvent. The molar absorptivity of acetic acid monomer increases with increasing pressure, while that of the dimer decreases with pressure.

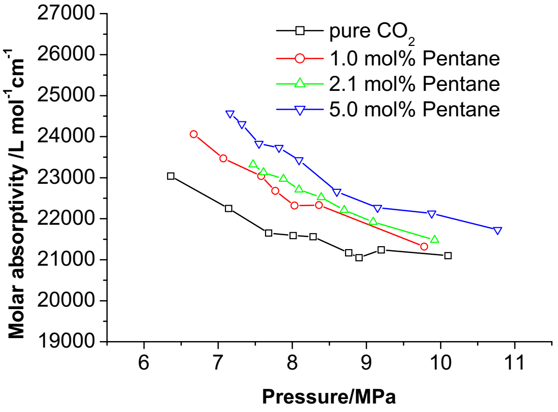


Fig. 8. Molar absorptivity of the dimer of acetic acid as a function of pressure.

This trend is similar to that reported by Yamamoto et al. [20] in SC CO_2. As expected, pressure has more pronounced effect on the molar absorptivity in the critical region of the mixed solvent because the density is more sensitive to pressure.

The dependence of the equilibrium constant of the dimerization on pressure is illustrated in Fig. 9. As can been seen from the figure, K_2 decreased with increasing pressure. This trend coincides with that reported by Yamamoto et al. [20] for the equilibrium constant of acetic acid in pure SC CO_2 in the pressure range of 10–20 MPa. The reason is that intermolecular hydrogen bonding is significantly disfavored by increased solvent density [15].

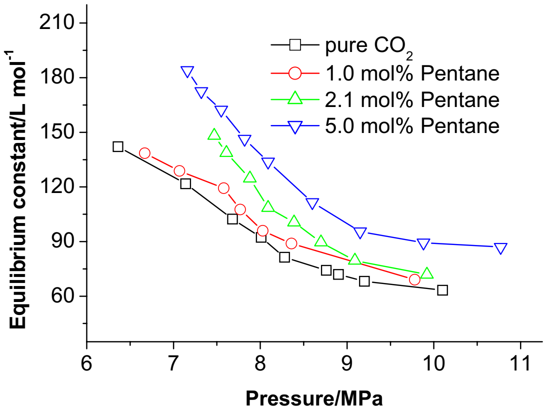


Fig. 9. Monomer–dimer equilibrium constant of acetic acid as a function of pressure.

Fig. 9 also indicates that K_2 changed considerably with pressure in the critical region. In the high-pressure region, where conditions are far from the critical point of the mixed solvent, K_2 was nearly independent of pressure. In other words, to adjust the equilibrium effectively, the mixed solvent should be in their critical region.

As discussed above, the critical composition at the experimental temperature is $X_2 = 0.021$. Fig. 9 also shows that K_2 is more sensitive to pressure in the critical fluid (with critical composition, $X_2 = 0.021$) and in the subcritical fluid or compressed liquid ($X_2 = 0.05$) in the critical region than in the supercritical fluids ($X_2 = 0$ and 0.01). This suggests that the properties of the critical fluid and subcritical fluid are more sensitive to pressure in the critical region because K_2 depends on the properties of the solvent. One of the advantages of SCF techniques is that the processes can be optimized to some degree by changing pressure due to the sensitivity of physical properties of SCFs to pressure. In fact, the dimerization of acetic acid can be regarded as a reversible reaction, and the reaction equilibrium in the mixed subcritical fluids can be adjusted by pressure. The results of this work hint that some processes can also be tuned effectively by pressure if mixed subcritical fluids in the critical region are used.

4. Conclusion

FTIR spectra and monomer–dimer equilibrium of acetic acid in $CO_2 + n$-pentane mixed solvent have been conducted in SC region and subcritical region of the mixed solvent. The frequency of C=O stretching vibration, the molar absorptivities of monomer and dimer, and the monomer–dimer equilibrium are very sensitive to pressure in the subcritical fluids and SCFs in the critical region. However, the effect of pressure on theses properties is very limited outside the critical region. Utilization of mixed solvents in the critical region may become an effective way to broaden the applications of SCFs.

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