Equilibrium Constant and Enthalpy for the Hydrogen Bonding of Acetic Acid with Tetrahydrofuran in Supercritical CO_2

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FTIR spectroscopy was used to study the hydrogen bonding of acetic acid and tetrahydrofuran in supercritical (SC) CO_2 in the ranges of 100−160 bar and 308.15−323.15 K, and the concentration of tetrahydrofuran varied from 0 to 0.4 mol/L. The equilibrium constant K_c for the hydrogen bonding of tetrahdyrofuran with the monomer of acetic acid was calculated on the basis of the IR spectra determined. K_c is a strong function of pressure or the apparent density of CO_2 (moles CO_2 of per liter). The enthalpy of the hydrogen bonding was calculated on the basis of the relationship between K_c and temperature. In the lower isothermal compressible region of the fluid, both the enthalpy change (ΔH) and the entropy change (ΔS) of the hydrogen bonding process are negative and the hydrogen bonding is enthalpy driven. In the high isothermal compressible region, however, both ΔH and ΔS are positive, and the hydrogen bonding process becomes entropy driven.

1. Introduction

Supercritical fluids (SCFs) have some unique features.[1−10] In the past decade, studies on the intermolecular interactions (such as dipole−dipole, dipole−induced dipole, dispersion, hydrogen bonding) in SCFs have received much attention because of its importance to both pure and applied sciences.

It is well known that the isothermal compressibility becomes infinite when the critical point of a fluid is approached and SCF solvents exhibit anomalous behaviors, and all of these anomalous behaviors are connected with the large compressibility. Solvatochromic[11−17] and fluorescence spectroscopic[18−20] studies indicated that the local density of the solvents about probe molecules is much higher than the bulk density in highly compressible SCFs. Thermodynamic[21,22] and kinetic [23−27] investigations for the chemical reactions in SCFs documented that the solvent molecules are enriched in the vicinity of the reacting species, which results in the improved selectivity and enhanced rate constant. In addition, the partial molar volumes of solutes in SCFs are large negative values, which implies the clustering of solvent molecules about the solute molecules.[28−31]

Infrared spectroscopy has been used to study intermolecular interaction in supercritical fluids, and some interesting results have been observed. For example, a pronounced effect of solvent density on hydrogen bonding between methanol and triethylamine and between perfluoro-*tert*-butyl alcohol and dimethyl ether were observed in SF_6.[32−33] Benzoic acid in supercritical CO_2 can form cyclic dimer by hydrogen bonding.[34] Nonionic surfactants and alcohol aggregate in supercritical CO_2 and C_2H_6 because of inter- and intrahydrogen bonding.[35] Alcohol self associates in supercritical CO_2 and ethane.[36] Methanol and ethanol can hydrogen bond with benzoic acid and salicylic acid in supercritical CO_2,[37] which explains the fact that the solubilities of the solutes increase with the concentrations of the cosolvents. Poliakoff et al.[38] gave a review on the application of vibrational spectroscopy to the systems containing supercritical CO_2.

In this work, we studied the equilibrium constant of the hydrogen bonding of tetrahydrofuran and acetic acid in supercritical CO_2 ($T_c = 304.2$ K, $P_c = 73.8$ bar, $\rho_c = 10.6$ mol/L) using FTIR spectroscopy. Tetrahydrofuran was selected because it is a relatively weak base and the hydrogen bond is weak. Thus, the property of the hydrogen bond is more sensitive to the change of the properties of solvent, which can be used as a tool to probe the effect of temperature and pressure on the properties of supercritical fluids.

2. Experimental Section

Materials. CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.995%. The purity of acetic acid was 99.5% (A. R. grade), supplied by Beijing Chemical Reagent Plant. Tetrahydrofuran was also A. R. grade (99.0%), produced by Tianjin Chemical Agent Institute. All of the chemicals were used without further purification.

Apparatus. The experimental setup used was the same as that used previously,[37] and the schematic diagram is shown in Figure 1. It consists mainly of a gas cylinder (1), a high-pressure pump (3), a pressure gauge (5), an FTIR spectrometer (9), a high-pressure IR cell (10), a thermometer (11), a temperature controller (13), a vacuum pump (14), and valves and fittings of different kinds. A Bruker (model IFS-113v) FTIR spectrometer (9) was used in this work. The pressure gauge (5) consisted of a transducer (IC Sensors Co., model 93) and an indicator, which can be accurate to ±0.05 MPa in the range of 0−20 MPa. The high-pressure cell (10) was composed of a stainless steel body, ZnS windows of 6-mm thickness, and the temperature controlling system. The optical path length of the cell was 1.27 cm, and the internal volume of the cell was 1.32 cm^3. There was a stainless steel ball in the cell to stir the fluids in the cell before IR measurement, so that the equilibrium can be reached in a shorter period of time. The insulated cell was electrically heated to ±0.3 K of the desired temperature by using a controller with a platinum resistance temperature probe (model XMT, produced by Beijing Chaoyang Automatic Instrument Factory).

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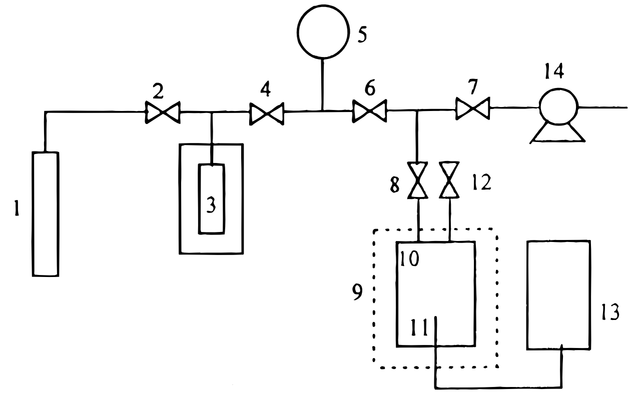


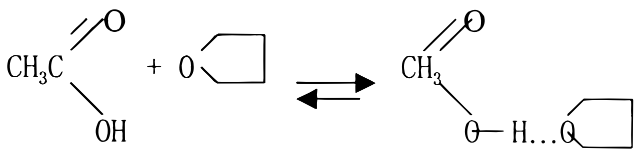
Figure 1. Schematic diagram of the FTIR measurement system: 1 gas cylinder; 3 pump; 5 digital pressure gauge; 9 FTIR spectrometer; 10 high pressure IR cell; 11 thermometer; 13 temperature controller; 2, 4, 6, 7, 8, 12 shut-off valves.

Experimental Procedures. The experimental procedure was similar to that described previously.[37] The IR cell was cleaned thoroughly with suitable solvents, dried under vacuum, and then purged with CO_2. The desired amount of tetrahydrofuran + acetic acid solution with a known concentration was introduced into the IR cell with a microsyringe through valve 12. Then valves 8 and 12 were closed immediately to prevent air getting into the cell by diffusion. The cell was connected to the system as shown in Figure 1. After thermal equilibrium had been reached, the air in the connecting line was removed by vacuum pump (14) with valves 4, 6, and 7 opened and valve 8 closed. Then valve 7 was closed and valve 8 opened. CO_2 was compressed into the cell (10) slowly using the high-pressure pump (3) until the desired pressure was reached. Valve 8 was then closed. The temperature and pressure of the cell remained constant for about 2 h before IR spectral measurement was conducted. Experiments showed that the equilibration time was long enough because the spectra with a longer equilibration time were the same. The concentrations of tetrahydrofuran and acetic acid were calculated from the weight, concentration of the solution injected, and the volume of the cell. It is worthwhile to mention that the mixture is homogeneous at all experimental conditions, which was known from the simulation experiments using an optical cell.

The IR spectra were acquired at 2 cm^{-1} resolution with the average of 256 scans. The absorption spectra of CO_2 with and without cosolvents were also recorded at various conditions. In this work, all of the spectra were obtained by subtracting the background spectra from those of corresponding solutions.

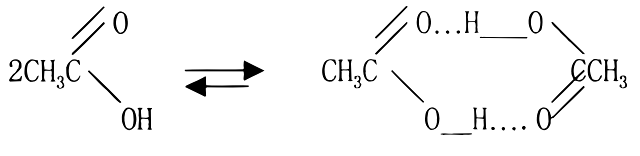
3. Results and Discussions

Equilibrium Constant of Hydrogen Bonding. Tetrahydrofuran is a base and can hydrogen bond with acetic acid to form 1:1 complex



I II

Acetic acid can form hydrogen-bonded cyclic dimer in the following form[34]



I III

In this work, IR spectra of a supercritical CO_2−acetic acid−tetrahydrofuran system were determined at 308.15, 313.15, 318.15, and 323.15 K. The concentration of tetrahydrofuran was up to 0.4 mol/L. The concentration of acetic acid was fixed at 1.0×10^{-3} mol/L.

For acetic acid in pure CO_2, two absorption bands can be observed in the 1600−1800 cm^{-1} range, as shown in Figure 2. On the basis of the papers for studying the hydrogen bonding of other organic acids in liquid and supercritical solvents by IR spectroscopy,[34] it can be concluded that the bands at 1772 cm^{-1} and 1729 cm^{-1} are attributable to $>C{=}O$ stretching of the monomer I and the dimer III of acetic acid, respectively.

As tetrahydrofuran is added, a new absorption band appears at 1760 cm^{-1}. Figures 3−5 give some examples of the spectra determined. The frequency of the new band is lower than that of the monomer I and higher than that of the dimer III of acetic acid. Odinokov et al.[39] studied the hydrogen bonding of benzoic acid with different bases in liquid CCl_4. The frequency of the $>C{=}O$ stretching shifts toward the lower side after hydrogen bonding. It is obvious that the new band at 1760 cm^{-1} is for the $>C{=}O$ stretching of the hydrogen bonded complex II formed from one acetic acid monomer and one tetrahydrofuran molecule. In this paper, we focus on how temperature, fluid density, and pressure affect the hydrogen bonding between acetic acid monomer and tetrahydrofuran, which can be expressed as

$$A+B \Leftrightarrow AB \tag{1}$$

where A, B, and AB stand for acetic acid, tetrahydrofuran, and the hydrogen-bonded complex II, respectively.

The IR spectra were separated into individual bands using a computer and the least-squares fitting method, and each band was represented by the Lorentzian function. The area under each individual band was obtained by numerical integration. On the basis of the Lambert−Beer law, the concentration of component i (C_i) can be expressed as follows

$$C_i = A_i/(\alpha_i L) \tag{2}$$

where α_i and L are absorption coefficient of component i and path length of the light, respectively. A_i is the area under the absorption band i. The equilibrium constant for eq 1 is defined by

$$K_c = C_{AB}/(C_A C_B) = \alpha_A A_{AB}/(\alpha_{AB} A_A C_B) \tag{3}$$

In eq 3, C_{AB}, C_B, and C_A are, respectively, concentrations of hydrogen-bonded complex, tetrahydrufuran, and acetic acid monomer. α_A and α_{AB} are, respectively, the absorption coefficients of $>C{=}O$ of the acid monomer I and in the hydrogen-bonded complex II.

In this study, the concentration of tetrahydrofuran is much higher than that of acetic acid (at least 110 times higher), and thus it can be assumed that C_B is equal to the original concentration, i.e., the concentration of tetrahydrofuran remains unchanged before and after hydrogen bonding. Thus, C_B in eq 3 is known, and as mentioned above, A_{AB} and A_A can be obtained from the IR spectra.

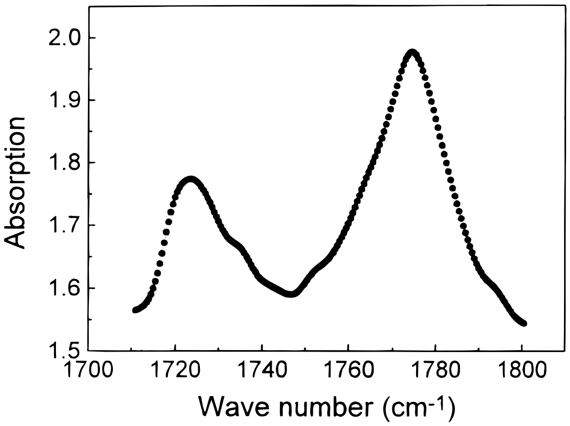


Figure 2. IR absorption spectrum of the acetic acid in pure CO_2 at 318.2 K and 100 bar.

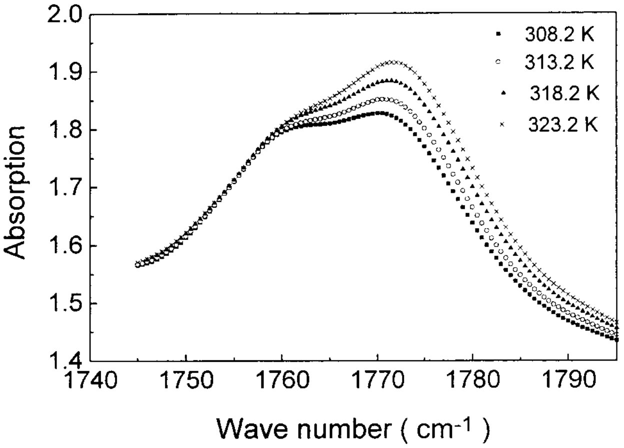


Figure 3. IR absorption spectra determined at different temperatures ($C_B = 0.112$ mol/L; $d_1 = 17.50$ mol/L).

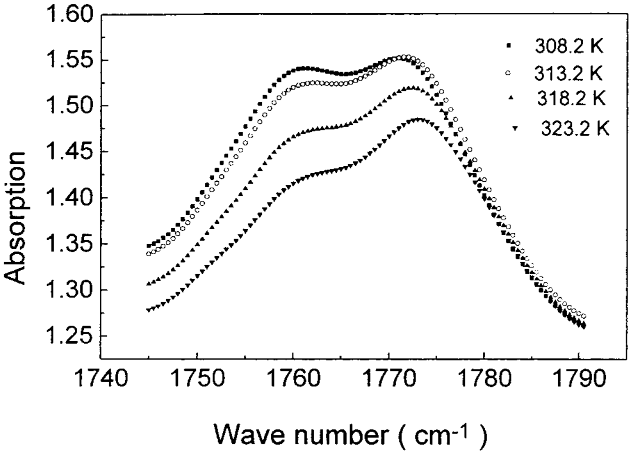


Figure 4. IR absorption spectra determined at different temperatures ($C_B = 0.224$ mol/L; $d_1 = 17.50$ mol/L).

To calculate K_c, the values of α_A/α_{AB} are required. Our experiments showed that at fixed acetic acid concentration and fluid density, the total area of the absorption bands was independent of temperature, although the area of each band is a function of temperature, which indicates that the effects of temperature and hydrogen bonding on the absorption coefficients are negligible, i.e., $\alpha_A/\alpha_{AB} = 1$. Allen et al.[40] studied the absorption spectra of benzoic acid in liquid CCl_4. They reported that the absorption coefficients of $>C{=}O$ in the monomer and in the hydrogen-bonded dimer are almost the same.

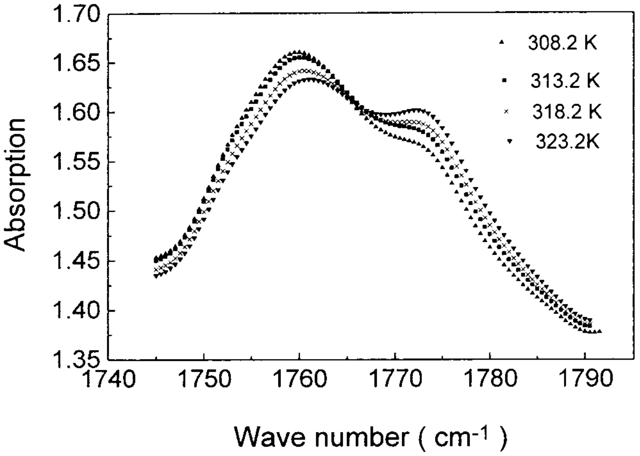


Figure 5. IR absorption spectra determined at different temperatures ($C_B = 0.392$ mol/L; $d_1 = 17.50$ mol/L).

On the basis of the discussions above, K_c can be calculated easily and the results are listed in Table 1. The densities of the mixtures at the same conditions as the spectra measurements were determined in this work using a gravimetric method,[31] and the apparent densities of CO_2 d_1 (moles of CO_2 per liter mixture) are also given in Table 1, which were calculated from the densities of the mixtures and the concentrations of tetrahydrofuran and acetic acid. The dependence of K_c on the apparent density of CO_2 d_1 is also shown in Figures 6−8 in which the concentrations of tetrahydrofuran are 0.112, 0.224, and 0.392 mol/L, respectively.

Enthalpy of Hydrogen Bonding. Equilibrium constants considering activity coefficients are defined as

$$K_a = K_c K_\phi \tag{4}$$

$$K_\phi = \phi_{AB}/(\phi_A \phi_B) \tag{5}$$

In eqs 5, ϕ_{AB}, ϕ_A, and ϕ_B are, respectively, the activity coefficients of hydrogen-bonded complex, acetic acid monomer, and tetrahydrofuran.

The standard enthalpy is related to K_a by[41]

$$d \ln K_a/dT = \Delta H^o/(RT^2) \tag{6}$$

where ΔH^o is the standard molar enthalpy for the hydrogen bonding process, T and R stand for temperature and gas constant, respectively.

For each species, the following expression should be obeyed[41]

$$(\partial \ln \phi_i/\partial T)_P = (H_i^o - \bar{H}_i)/(RT^2) \tag{7}$$

where H_i^o and $\bar{H}_i$ are the standard state molar enthalpy and partial molar enthalpy for component i. Combining of eqs 4, 6, and 7 yields[41]

$$(\partial \ln K_c/\partial(1/T))_P = -(H_{AB} - H_A - H_B)/R = -\Delta H/R \tag{8}$$

where ΔH is the molar enthalpy of the hydrogen bonding.

Discussion

The effect of temperature and pressure on d_1 is plotted in Figure 9 for $C_B = 0.112$ mol/L. The dependence of K_c on temperature and pressure is given in Figure 10, which was obtained from the data in Figures 6 and 9. At higher temper-

TABLE 1: The Values of K_c at Different Conditions

$C_B = 0.112$ mol/L			$C_B = 0.224$ mol/L			$C_B = 0.392$ mol/L		
T/K	d_1/(mol/L)	K_c	T/K	d_1/(mol/L)	K_c	T/K	d_1/(mol/L)	K_c
308.2	17.53	5.04	308.2	17.46	6.73	308.2	17.38	9.41
	16.66	4.93		16.64	7.00		16.62	6.15
	15.48	6.69		15.52	7.91		15.72	7.11
	14.39	8.04		14.62	11.59		14.99	9.73
	12.67	16.43		13.17	16.00		13.82	14.20
313.2	17.53	4.43	313.2	17.46	5.41	313.2	17.38	8.65
	16.66	4.35		16.64	5.81		16.62	5.34
	15.48	5.05		15.52	6.89		15.72	5.58
	14.39	5.90		14.62	9.59		14.99	8.48
	12.67	11.66		13.17	12.50		13.82	12.65
318.2	17.53	3.33	318.2	17.46	3.91	318.2	17.38	7.81
	16.66	3.55		16.64	4.38		16.62	4.61
	15.48	4.41		15.52	5.25		15.72	4.85
	14.39	4.90		14.62	6.01		14.99	7.40
	12.67	7.85		13.17	9.44		13.82	10.41
323.2	17.53	3.21	323.2	17.46	3.09	323.2	17.38	6.46
	16.66	3.15		16.64	3.53		16.62	3.29
	15.48	3.56		15.52	4.14		15.72	3.88
	14.39	3.28		14.62	4.90		14.99	5.09
	12.67	6.15		13.17	6.11		13.82	9.19

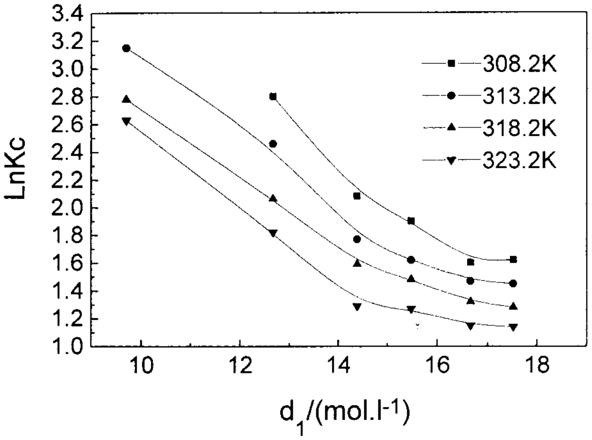


Figure 6. Dependence of $\ln K_c$ on d_1 at different temperatures (C_B = 0.112 mol/L).

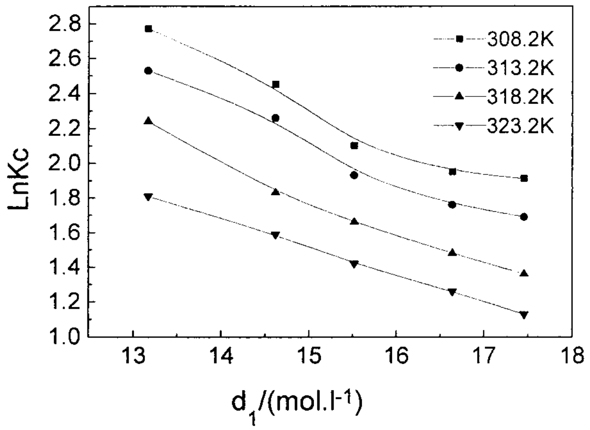


Figure 7. Dependence of $\ln K_c$ on d_1 at different temperatures (C_B = 0.224 mol/L).

atures, K_c is more sensitive to pressure because d_1 is more sensitive to pressure at higher temperature in the pressure range studied.

Figure 11 illustrates the variation of $\ln K_c$ with $1/T$ at different pressures, which was obtained from the data in Figure 10. Here, $\ln K_c$ is not a linear function of $1/T$, especially at the lower pressures. The dependence of $\ln K_c$ on $1/T$ is a strong function of pressure. At constant pressure, the data can be correlated using the following equation very well (the lines in the figure):

$$\ln K_c = a + b(1/T) + c(1/T)^2 \tag{9}$$

where a, b, and c are constants at constant pressure.

ΔH can be easily calculated using eqs 8 and 9, and the results are shown in Figure 12. At higher pressures, ΔH is negative,

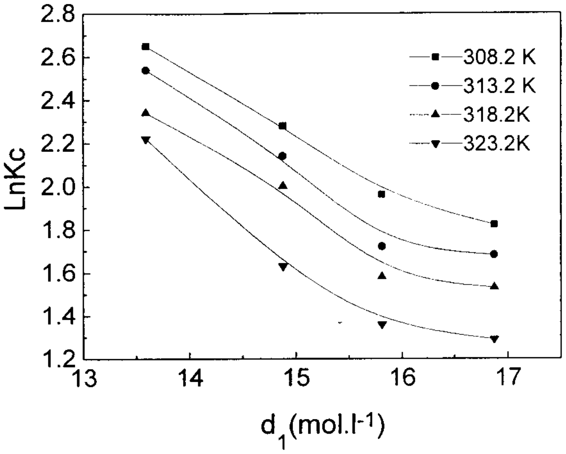


Figure 8. Dependence of $\ln K_c$ on d_1 at different temperatures (C_B = 0.392 mol/L).

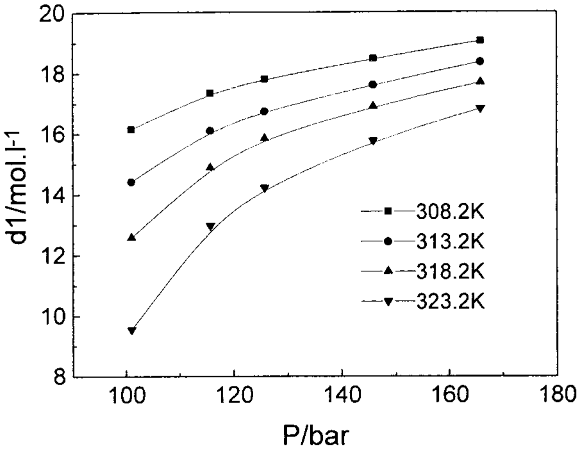


Figure 9. Effect of pressure on d_1 (C_B = 0.112 mol/L).

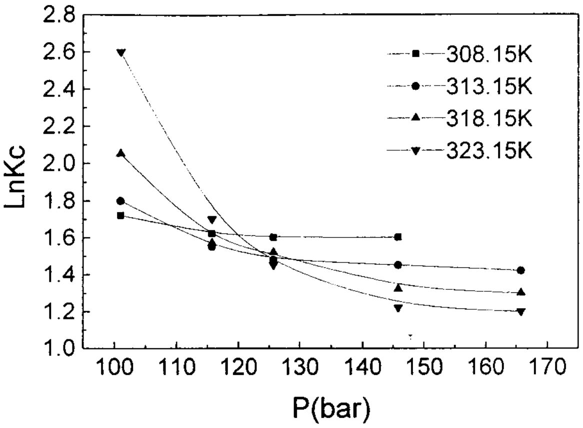


Figure 10. Effect of pressure on lnK_c (C_B = 0.112 mol/L).

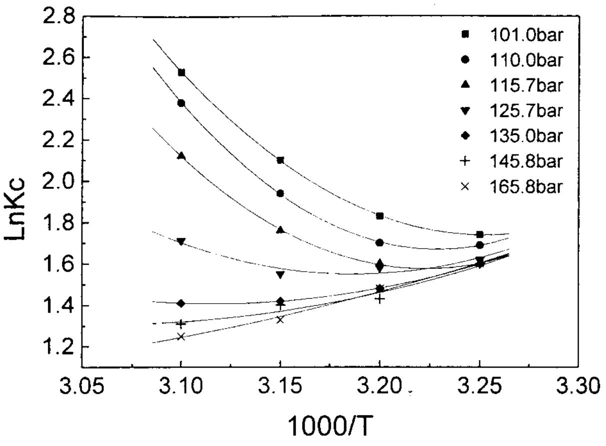


Figure 11. Dependence of lnK_c on 1000/T at different temperatures (C_B = 0.112 mol/L).

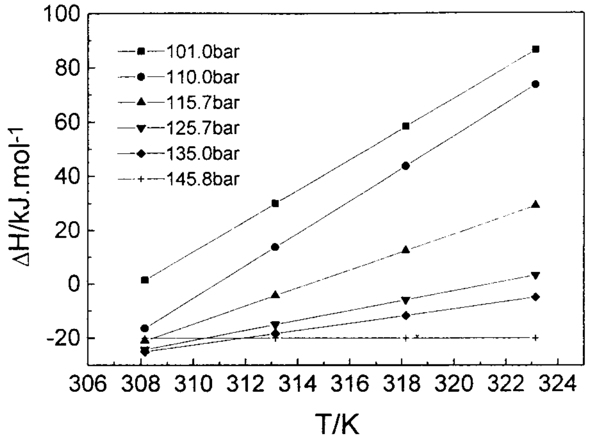
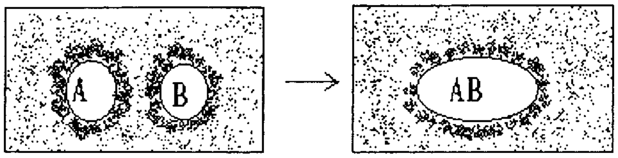


Figure 12. Dependence of ΔH on T at different pressures.

which is similar to the hydrogen bonding process in a vacuum or in liquid solvents. However, it is very interesting to notice that ΔH is positive and increases with temperature at lower pressures, i.e., the hydrogen bonding process is endothermic. This anomalous phenomenon can be attributed to the abnormal solvent effect in the system, which is discussed in the following.

The acetic acid and tetrahydrofuran are surrounded separately by CO_2 molecules before the hydrogen bonding process, and the hydrogen-bonded complex is surrounded by CO_2 molecules after the hydrogen bonding occurs. The process can be described by the following diagram:



Some of the CO_2 molecules surrounding tetrahydrofuran and acetic acid are removed during the hydrogen bonding process because the surface areas are reduced. We divide the hydrogen bonding process into two steps: (1) to remove the CO_2 molecules from CO_2−acetic acid and CO_2−tetrahydrofuran clusters necessary to form the hydrogen bond; (2) to form the hydrogen-bonded complex. The enthalpy change(ΔH) and entropy change(ΔS) can be divided into the two corresponding terms:

$$\Delta H = \Delta H_1 + \Delta H_2 \tag{10}$$

$$\Delta S = \Delta S_1 + \Delta S_2 \tag{11}$$

where ΔH_1 and ΔS_1 are the enthalpy change and entropy change of the first step. ΔH_2 and ΔS_2 stand for enthalpy change and entropy change of the second step.

The Gibbs free energy change ΔG is related to ΔH and ΔS

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

At equilibrium and at constant temperature and pressure, ΔG should be zero and eq 12 becomes

$$\Delta H/T = \Delta S \tag{13}$$

In eqs 10 and 11, ΔH_1 and ΔS_1 should be positive and ΔH_2 and ΔS_2 should be negative.

Other authors studied the clustering of CO_2 with other solutes and indicated that the highest augmented densities correspond reasonably with the highest isothermal compressibility.[2,18] At the lower pressures and higher temperatures studied in this work, the isothermal compressibility is high, which can be known from Figure 9. It can be expected that clustering of the solvent with the solutes is more significant. At these conditions ΔH and ΔS are positive from Figure 12 and eq 13. ΔH_1 and ΔS_1 in eqs 10 and 11 are dominant. It can be deduced that more CO_2 molecules are removed from the solute−solvent clusters to bulk solvent in the hydrogen bonding process and/or more energy is required for removing CO_2 molecules from the clusters. On the other hand, the bulk density is much lower than the local density surrounding the solutes at these conditions, and the CO_2 molecules in the bulk solvent are much more disordered, hence the entropy change for moving a CO_2 molecule from the clusters to the bulk solvent is larger, which is favorable to moving the CO_2 from the clusters to the bulk solvent. Thus ΔH_1 and ΔS_1 are dominant, and ΔH and ΔS are positive. The hydrogen bonding process is entropy driven.

At the higher pressures and lower temperatures studied in this work, the isothermal compressibility of the fluid is low and ΔH and ΔS are negative, i.e., ΔH_2 and ΔS_2 are dominant. It can be deduced that fewer CO_2 molecules are removed in the hydrogen bonding process and/or less energy is required for removing CO_2 molecules from the clusters. In the meantime, the difference between the local density and the bulk density is not considerable in the higher bulk density region, and the entropy of the CO_2 molecules surrounding the solutes is close to that of the bulk solvent. Both ΔS_1 and ΔH_1 are low, and ΔS_2 and ΔH_2 play main roles. ΔS and ΔH are negative, and the hydrogen bonding process is enthalpy driven.

4. Conclusion

In the ranges of 100−160 bar and 308.15−323.15 K, the equilibrium constant K_c for the hydrogen bonding of tetrahdyrofuran with the monomer of acetic acid in SC, CO_2 decreases with the apparent density of CO_2 (moles CO_2 of per liter). In the lower isothermal compressible region of the fluid, both the enthalpy change (ΔH) and the entropy change (ΔS) of the hydrogen bonding process are negative, and the hydrogen bonding is enthalpy driven. In the high isothermal compressible region, however, both ΔH and ΔS are positive, and the hydrogen bonding process become entropy driven.

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