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Fourier Transform Infrared Study on Hydrogen Bonding Species of Carboxylic Acids in Supercritical Carbon Dioxide with Ethanol

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Fourier transform infrared (FTIR) spectroscopy has been used to determine the equilibrium constants of the dimerization for carboxylic acid (acetic acid or palmitic acid) and the amount of hydrogen bonding species between carboxylic acid and ethanol in supercritical CO_2. Experiments were carried out at 308.2−313.2 K and 10.0−20.0 MPa. The noticeable band was the C═O stretching band for carboxylic acid. In the binary system (supercritical CO_2 + carboxylic acid), the equilibrium constants of the dimerization between the carboxylic acid monomer and dimer decrease with increasing pressure and temperature. The equilibrium constants of palmitic acid are larger than those of acetic acid. In a ternary system (supercritical CO_2 + carboxylic acid + ethanol), the amount of hydrogen bonding species between carboxylic acid and ethanol in supercritical CO_2 increases with the increasing mole fraction of added ethanol. Furthermore, the authors confirm that the solubility enhancement by ethanol used as an entrainer in supercritical CO_2 relates to the amount of hydrogen bonding species between carboxylic acid and ethanol.

1. Introduction

Supercritical fluid extraction has been given much attention recently as one of the new separation technologies in the chemical industry. Supercritical fluid extraction has the following advantages. Solvent recovery can be easily achieved by decompression or temperature change. Because of the high volatility of the supercritical fluid, the extracted products have no solvent contamination. Since supercritical fluid extraction has many advantages, the solubilities of high-boiling components in supercritical fluids have been measured by many researchers. The authors[1,2] measured the solubilities of fatty acids (myristic acid, palmitic acid, and stearic acid) and higher alcohols (cetyl alcohol, stearyl alcohol, and arachidryl alcohol) in supercritical CO_2. However, its solvent power is less than that of a liquid solvent. The addition of a small amount of an entrainer enhances selectively the solubility of certain components. Koga et al.[3] measured the influence of entrainer (ethanol or octane) on solubilities of fatty acids (palmitic acid and stearic acid) and higher alcohols (cetyl alcohol and stearyl alcohol) in supercritical CO_2. These results show that ethanol is more effective on the solubility enhancement for fatty acids in supercritical CO_2. On the other hand, the influence of octane on the solubility enhancement for higher alcohols in supercritical CO_2 is almost the same as that of ethanol. The mechanism of these entrainer effects has not yet been clarified. To consider the mechanism, it is effective to study the interaction between solute and entrainer in supercritical CO_2. A more reasonable choice of entrainer may be possible by understanding the microscopic structure in supercritical CO_2.

FTIR spectroscopy has been used by many researchers to study the microscopic structure such as solvation phenomena, clustering of solvent, and hydrogen bonding in supercritical fluids. In recent years, Fulton et al.[4] and Yee et al.[5,6] studied the intermolecular or intramolecular hydrogen bonding species of several alcohols (methanol-*d*, 1-butanol-*d*, dodecanol-*d*, etc.) in supercritical CO_2 and ethane. They reported the aggregation number of these alcohols in supercritical CO_2. Gupta et al.[7] studied a solvent effect on the hydrogen bonding species between methanol and triethylamine in supercritical SF_6. They approximated that the molar absorptivity of the free methanol monomer was linear with solvent density and determined the equilibrium constants between methanol and the triethylamine complex. Moreover, Gupta and Brinkley[8] measured the self hydrogen bonding in the 1-alkanol + *n*-alkane binary system and reported that the self hydrogen bonding could be represented by a function of concentration. Ikawa and Fujita[9] studied the intermolecular and intramolecular hydrogen bonding species of 4-hydroxy-4-methylpentan-2-one in supercritical xenon. They calculated the cluster size defined as the excess number of solvent molecules surrounding the solute molecule. Tsugane et al.[10] investigated the dimerization of benzoic acid in supercritical CO_2. Buback and Mahling[11] also studied the dimerization of acrylic acid and methacrylic acid in supercritical ethylene. Ke et al.[12] investigated the hydrogen bonding species of some organic acid (benzoic acid or salicylic acid) in supercritical CO_2 with a polar entrainer (methanol or ethanol). They confirmed that the hydrogen bonding species between solute and entrainer molecules increase with the increasing molarity of entrainer and suggested that the solubility enhancement by entrainer relates to the amount of hydrogen bonding species. However, they did not quantitatively consider hydrogen bonding species.

In this work, FTIR spectroscopy was used to determine the equilibrium constants of dimerization between carboxylic acid (acetic acid or palmitic acid) monomer and dimer, and the amount of hydrogen bonding species between carboxylic acid and ethanol in supercritical CO_2. Experiments were carried out at 308.2−313.2 K and 10.0−20.0 MPa. The noticeable band was the C═O stretching band for carboxylic acid. In the binary system (supercritical CO_2 + carboxylic acid), the authors

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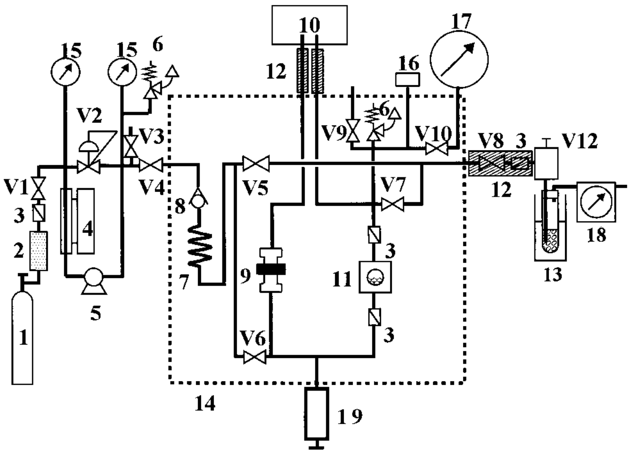

Figure 1. Experimental apparatus: (1) gas cylinder; (2) dryer; (3) filter; (4) cooling unit; (5) feed pump; (6) safety valve; (7) preheating coil; (8) check valve; (9) magnetic pump; (10) FTIR spectroscopy; (11) cell with glass windows; (12) flexible heater; (13) trap; (14) water bath; (15) pressure gauge; (16) digital pressure meter; (17) precision pressure gauge; (18) flow meter; (19) sample injector; V1 and V3-V11, stop valve; V2, back pressure regulator; V12, expansion valve.

considered the solvent effect based on the equilibrium constants of the dimerization between carboxylic acid monomer and dimer. Furthermore, in the ternary system (supercritical CO_2 + carboxylic acid + ethanol), the authors studied the amount of hydrogen bonding species between carboxylic acid and ethanol (entrainer) and the influence of ethanol on the solubility of carboxylic acid in supercritical CO_2.

2. Experimental Section

Acetic acid was supplied by Wako Pure Chemical Industries Ltd. The purity was 99.7%. Palmitic acid was supplied by Sigma Chemical Co. The purity was approximately 99%. Ethanol was supplied by Wako Pure Chemical Industries Ltd. The purity was 99.5%. High-purity CO_2 (more than 99.9%, Sumitomo Seika Co.) was used as received. High-purity N_2 (more than 99.9%, Sumitomo Seika Co.) was used as purge gas.

In this work, a circulation-type apparatus was constructed to measure the IR spectra of carboxylic acids in supercritical CO_2 with ethanol. The apparatus is shown schematically in Figure 1. The experimental procedure was as follows. CO_2 supplied from a gas cylinder (1) was liquefied through a cooling unit (4) and directed to a feed pump (5). A back-pressure regulator (V2) was used to maintain a constant pressure inside the system. The liquefied CO_2 was sent to a preheater (7), and it became a supercritical fluid. The valve (V6) was opened and supercritical CO_2 was introduced to a fluid circulation part. The circulation part consisted of a circulation pump (9), a cell with glass windows (11), and a FTIR spectroscope equipped with an optical cell (10). The inner diameter, length, and volume of the cell with glass windows were 15 mm, 256 mm, and 26.5 cm^3, respectively. Acetic acid was introduced by a sample injector (19). When the spectra of palmitic acid were measured, palmitic acid was previously introduced into the cell at low-pressure conditions because palmitic acid is solid at room temperature. The authors confirmed that solid palmitic acid was solved in supercritical CO_2 through the windows. The FTIR spectroscope (Herschel series FT/IR-350type, JASCO Co.) was purged with dry N_2 and then was used to obtain all IR spectra. The spectroscope was equipped with a germanium-on-KBr beam splitter and a mercury−cadmium−telluride (MCT) detector. The authors measured the IR spectra at 4 cm^{-1} wavenumber resolution to obtain the desired signal-to-noise ratio. The volume and optical path length of the optical cell were 9.8×10^{-2} cm^3 and 5 mm, respectively. The windows of the optical cell were made of ZnS. The thickness was 6 mm. The temperature of the optical cell was maintained by water pumped from a water bath (14), which was controlled within ±0.1 K. The pressure of the circulation part was measured by a digital pressure meter (HPO precision transducer, Heise Plant Dresser Industries Inc.) (16) and a precision Bourdon gauge (NKS type, GP35-141, Nagano Keiki Co.) (17). The uncertainty on pressure measurements is estimated to be less than ±0.01 MPa. The circulation pump was used to well mix a supercritical fluid in the circulation part. After the steady state was achieved, IR spectra were measured by FTIR spectroscopy. In the case of the ternary system, ethanol was introduced by the sample injector. The concentrations of carboxylic acid and ethanol were determined from the volume of the circulation part (0.109 L) and the weights of injected carboxylic acid and ethanol, respectively.

3. Results and Discussion

3.1. Supercritical CO_2 + Carboxylic Acid System. The IR spectra of the supercritical CO_2 + carboxylic acid system were measured in the ranges 10.0−20.0 MPa and 308.2−313.2 K. The C=O stretching bands of the acetic acid monomer and dimer appeared at 1772 and 1722 cm^{-1}, and those of palmitic acid monomer and dimer appeared at 1762 and 1716 cm^{-1}, respectively. Bulmer and Shurvell[13] reported that the C=O stretching bands were observed at 1767 (monomer), 1722 (linear chain), and 1715 cm^{-1} (dimer) in liquid CCl_4. In the present experimental conditions, no oligomer (more than trimer, linear chain) of carboxylic acids was considered to be formed, because the C=O stretching band of the oligomer was not observed between those of the monomer and dimer. Acetic acid contained no water as an impurity, because the O−H bending band of water at 1607 cm^{-1} was not observed. The peak of water was not observed in any experimental conditions of this work.

In this work, the equilibrium constant for the dimerization between carboxylic acid monomer and dimer, K_C, is defined by the following equation.

$$K_C = C_d/C_m^{\ 2} \tag{1}$$

where C_m and C_d are the molarities of the monomer and dimer of carboxylic acid, respectively. For the determination of C_m and C_d, the molar absorptivities of carboxylic acid monomer and dimer are required. These values were obtained at each pressure and temperature based on the method reported by Fujii et al.[14] These values are listed in Table 1. The results of the equilibrium constants of dimerization are listed in Table 2 and shown in Figure 2. They were determined at the molarities of carboxylic acids ranging from 1.30×10^{-3} to 1.2×10^{-2} mol L^{-1}. Literature values of the constants in organic liquid solvents[14,15] are listed in Table 3. The equilibrium constants in the organic liquid solvents are larger than those in supercritical CO_2, as shown in Tables 2 and 3. This fact indicates that monomeric form carboxylic acid is more stable in supercritical CO_2 than in the organic liquid solvents, because the interaction between CO_2 and carboxylic acid (quadrupole−OH group) is stronger than that between nonpolar or weakly polar organic solvents and carboxylic acid. As shown in Figure 2, the equilibrium constants for carboxylic acids decrease with increasing pressure and temperature. Similar phenomena are reported by Kimura and Yoshimura[16] in the supercritical CO_2 + 2-methyl-2-nitrosopropane system. When two carboxylic acid

TABLE 1: Molar Absorptivities of Carboxylic Acids Monomer and Dimer (Acid Molecule Basis)

		molar absorptivity ($L\ mol^{-1}\ cm^{-1}$)									
		10.0 MPa		13.0 MPa		15.0 MPa		18.0 MPa		20.0 MPa	
solute	temp (K)	monomer	dimer	monomer	dimer	monomer	dimer	monomer	dimer	monomer	dimer
acetic acid	308.2	10 200	24 600			10 300	22 300			10 100	21 600
	313.2	9 000	22 300			10 300	23 800			9 800	24 300
palmitic acid	308.2			11 300	19 500	12 000	20 200	11 700	20 000	11 700	20 400
	313.2			11 100	23 300	11 200	24 700	11 400	24 200	11 600	23 500

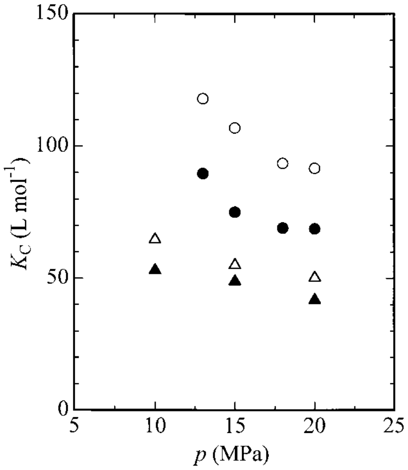

Figure 2. Equilibrium constants for carboxylic acids in supercritical CO_2: (○) 308.2 K; (●) 313.2 K, palmitic acid; (△) 308.2 K; (▲) 313.2 K, acetic acid.

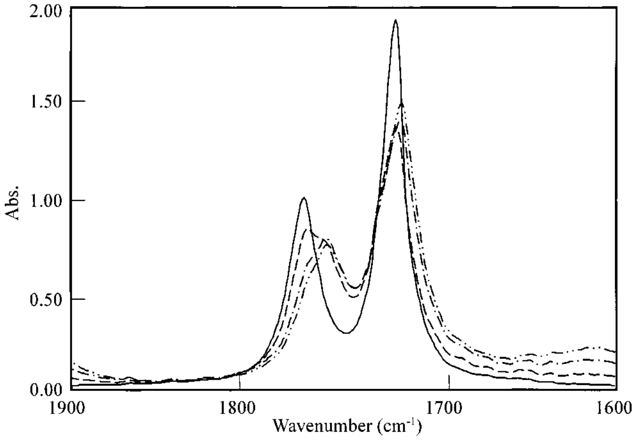

Figure 3. Stretching bands of $C=O$ for acetic acid in supercritical CO_2 with ethanol at 10.0 MPa at 308.2 K. Molarity of acetic acid = 9.855×10^{-3} mol L^{-1}. Mole fraction of ethanol: (—) 0; (– – –) 0.018; (–•–) 0.034; (–••–) 0.052.

TABLE 2: Equilibrium Constants K_C for Carboxylic Acids in Supercritical CO_2

		K_C ($L\ mol^{-1}$)				
solute	temp (K)	10.0 MPa	13.0 MPa	15.0 MPa	18.0 MPa	20.0 MPa
acetic acid	308.2	64.7		55.2		50.3
	313.2	53.1		48.9		41.8
palmitic acid	308.2		118.0	107.0	93.5	91.6
	313.2		89.7	75.1	69.1	68.8

TABLE 3: Equilibrium Constants K_C for Carboxylic Acids in Organic Liquid Solvents

solute	solvent	temp (K)	K_C ($L\ mol^{-1}$)
acetic acid	benzene	303.2	370[b]
		298.2	390 ± 70[a]
	toluene	298.2	390 ± 70[a]
	chlorobenzene	298.2	496 ± 80[a]
	chloroform	298.2	300 ± 50[a]
propionic acid	benzene	303.2	400[b]
n-butyric acid	benzene	303.2	435[b]

[a] Fuji et al.[14] [b] Pohl et al.[15]

monomers dimerize, a few CO_2 molecules, which interact with carboxyl group, become free. The total number of free molecules may increase by dimerization. So, the equilibrium constants for dimerization decrease with increasing pressure. Furthermore, the equilibrium constants of palmitic acid are larger than those of acetic acid. As shown in Table 3, the equilibrium constants of dimerization for carboxylic acids in benzene increase with increasing carbon numbers of carboxylic acids. These results indicate that the influence of the CH_2 chain length of acids on dimerization in supercritical CO_2 is similar in the organic liquid solvents.

3.2. Supercritical CO_2 + Carboxylic Acid + Ethanol Systems. *3.2.1. Supercritical CO_2 + Acetic Acid + Ethanol System.* The IR spectra of the supercritical CO_2 + acetic acid + ethanol system were measured in the range 10.0−20.0 MPa and 308.2 K under constant molarity of acetic acid. Figure 3 shows the experimental results of the $C=O$ stretching bands of acetic acid at 10.0 MPa and 308.2 K. This figure shows that the peak of acid monomer at 1772 cm^{-1} decreases with the increasing mole fraction of ethanol, and new peaks are observed at 1759 and 1728 cm^{-1}. On the other hand, the peak of acid dimer at 1720 cm^{-1} decreases with the increasing the mole fraction of ethanol and a new peak is observed at 1714 cm^{-1}. A typical deconvolution of the $C=O$ stretching bands is shown in Figure 4. Picquart et al.[17] reported that the difference between the peak positions of lauric acid monomer and that of lauric acid interacting with one molecule of methanol was 23 cm^{-1}. Moreover, the difference between the peak positions of lauric acid monomer and that of lauric acid interacting with two molecules of methanol was 48 cm^{-1}. The authors attempted to calculate the peak positions of the $C=O$ stretching band for acetic acid and acetic acid interacting with ethanol in a vacuum by MOPAC (MOPAC93). The calculated results are listed in Table 4. It is noted that the experimental data of Picquart et al.[17] are almost similar to the results calculated by MOPAC. The peak explained by the dot−dot−dashed line at 1759 cm^{-1}

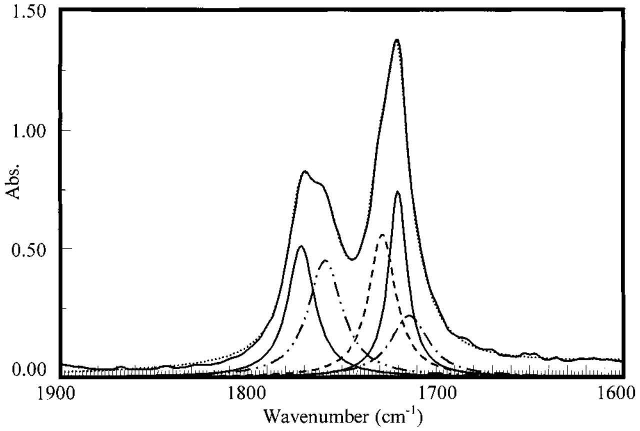

Figure 4. Deconvolution of IR spectra of acetic acid in supercritical CO_2 with ethanol at 10.0 MPa and 308.2 K. Molarity of acetic acid = 9.855×10^{-3} mol L^{-1}. Mole fraction of ethanol = 0.018. (···) Calculated IR spectra.

TABLE 4: Difference between Peak Positions for Species of Acetic Acid Calculated by MOPAC

species	$\Delta\nu$ (cm^{-1})
acid monomer−acid monomer interacting with one molecule of ethanol	23
acid monomer−acid monomer interacting with two molecules of ethanol	39
acid dimer−acid dimer interacting with one molecule of ethanol	6

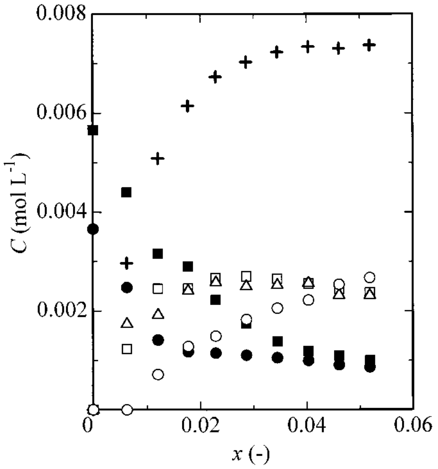

Figure 5. Molarities of species for acetic acid in supercritical CO_2 with ethanol at 10.0 MPa and 308.2 K: (■) acid monomer; (●) acid dimer; (□) acid monomer interacting with one molecule of ethanol; (△) acid monomer interacting with two molecules of ethanol; (○) acid dimer interacting with one molecule of ethanol; (+) total acid interacting with ethanol; acid molecule basis.

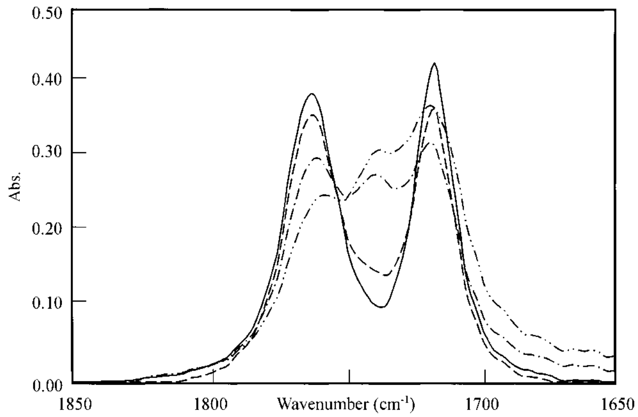

Figure 6. Stretching bands of C=O for palmitic acid in supercritical CO_2 with ethanol at 20.0 MPa and 308.2 K. Molarity of palmitic acid = 3.677×10^{-3} mol L^{-1}. Mole fraction of ethanol: (—) 0; (− − −) 0.005; (—·—) 0.015; (—··—) 0.024.

may be assigned to the C=O stretching band for the acetic acid monomer interacting with one molecule of ethanol because $\Delta\nu$ (acetic acid monomer−acetic acid monomer interacting with one molecule of ethanol) is 13 cm^{-1}. The peak shown by the dashed line at 1728 cm^{-1} is assigned to that for the acetic acid monomer interacting with two molecules of ethanol because $\Delta\nu$ (acetic acid monomer−acetic acid monomer interacting with two molecules of ethanol) is 44 cm^{-1}. The peak given by the dot−dashed line at 1714 cm^{-1} is assigned to that for the acetic acid dimer interacting with one molecule of ethanol because $\Delta\nu$ (acetic acid dimer−acetic acid dimer interacting with one molecule of ethanol) is 6 cm^{-1}.

Evaluation of the molarities of those species was attempted as follows. The molarities of acetic acid monomer (1772 cm^{-1}) and dimer (1720 cm^{-1}) in the ternary system were evaluated using the molar absorptivities of acetic acid monomer and dimer determined in the binary system, respectively, at the same pressure and temperature, because the molarity of ethanol is small. The molarities of hydrogen bonding species (1759, 1728, and 1714 cm^{-1}) were obtained using the molar absorptivities of the hydrogen bonding species, respectively. The authors used the following three assumptions to obtain these molar absorptivities. Namely, (1) the total molarity of carboxylic acid is constant in supercritical CO_2 with ethanol, (2) the areas of hydrogen bonding species obey the Lambert−Beer law and (3) the molar absorptivities of hydrogen bonding species are independent of the mole fraction of ethanol. These molar absorptivities were determined by solving the equations based on these assumptions. In this calculation, the nonlinear least-squares method was adopted. The values obtained are listed in Table 5. The absorptivities were also calculated by using MOPAC and are listed in Table 5. The relative magnitude of these absorptivities obtained by the experiment is quite similar to that by MOPAC. Figure 5 represents the molarities of those species in supercritical CO_2 at 10.0 MPa and 308.2 K. It is shown that the molarities of acetic acid monomer and dimer decrease with the increasing mole fraction of ethanol, and the molarity of hydrogen bonding species between acetic acid and ethanol increases. Moreover, the molarity of acetic acid interacting with one molecule of ethanol is the maximum among these hydrogen bonding species. The molarities of acetic acid interacting with ethanol at 10.0 MPa are similar to those at 20.0 MPa.

3.2.2. Supercritical CO_2 + Palmitic Acid + Ethanol System. Figure 6 shows the C=O stretching bands of palmitic acid in supercritical CO_2 with ethanol at 20.0 MPa and 308.2 K under

TABLE 5: Molar Absorptivities of Hydrogen Bonding Species between Carboxylic Acids and Ethanol at 308.2 K (Acid Molecule Basis)

	molar absorptivity (L mol^{-1} cm^{-1}), experiment		absorptivity (−), MOPAC
species	acetic acid (10.0 MPa)	palmitic acid (20.0 MPa)	acetic acid (vacuum)
acid monomer interacting with one molecule of ethanol	13 400	9 900	28.40
acid monomer interacting with two molecules of ethanol	13 300	10 700	28.32
acid dimer interacting with one molecule of ethanol	15 100	12 500	29.15

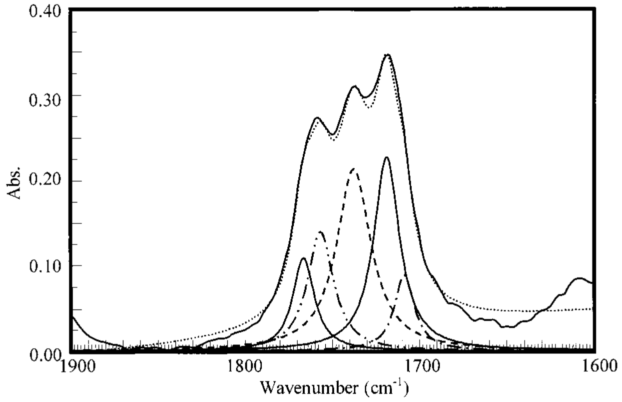

Figure 7. Deconvolution of IR spectra of palmitic acid in supercritical CO_2 with ethanol at 20.0 MPa and 308.2 K. Molarity of palmitic acid = 3.677 × 10^{-3} mol L^{-1}. Mole fraction of ethanol = 0.024. (···) Calculated IR spectra.

a constant molarity of palmitic acid. This figure shows that the peak of the acid monomer at 1766 cm^{-1} decreases with the increasing mole fraction of ethanol, and the new peaks appear at 1757 and 1738 cm^{-1}. On the other hand, the peak of the acid dimer at 1719 cm^{-1} decreases with the increasing mole fraction of ethanol and a new peak is observed at 1709 cm^{-1}. A typical deconvolution of the C=O stretching bands is shown in Figure 7. In this work, the peak shown by the dot−dot−dashed line at 1757 cm^{-1} may be assigned to the C=O stretching band for the palmitic acid monomer interacting with one molecule of ethanol because $\Delta\nu$ (palmitic acid monomer−palmitic acid monomer interacting with one molecule of ethanol) is 9 cm^{-1}. The peak shown by the dashed line at 1738 cm^{-1} is assigned to that for the palmitic acid monomer interacting with two molecules of ethanol because $\Delta\nu$ (palmitic acid monomer−palmitic acid monomer interacting with two molecules of ethanol) is 28 cm^{-1}, while the peak explained by the dot−dashed line at 1709 cm^{-1} is assigned to that for the palmitic acid dimer interacting with one molecule of ethanol because $\Delta\nu$ (palmitic acid dimer−palmitic acid dimer interacting with one molecule of ethanol) is 10 cm^{-1}.

Evaluation of the molarity of those species was attempted as well as of the case of acetic acid. The molar absorptivities for those species are listed in Table 5. Figure 8 shows the molarities of those species in supercritical CO_2 at 20.0 MPa and 308.2 K. It is noted that the changes of molarities of the palmitic acid monomer, dimer, and hydrogen bonding species between palmitic acid and ethanol are similar to those of acetic acid. However, the molarity of palmitic acid interacting with two molecules of ethanol is the maximum among these hydrogen bonding species.

The effect of ethanol as an entrainer on solubilities of palmitic acid in supercritical CO_2 was measured in the previous work.[3] Ethanol is effective on solubility enhancement of palmitic acid in supercritical CO_2. This result suggests that the solubility enhancement by an entrainer relates closely to the amount of hydrogen bonding species between the solute and the entrainer in supercritical CO_2.

4. Conclusion

In this work, the equilibrium constants of dimerization for carboxylic acids and the amount of hydrogen bonding species between carboxylic acid and ethanol in supercritical CO_2 were determined using FTIR spectroscopy. In binary systems, the equilibrium constants for carboxylic acids decrease with increasing pressure and temperature, and the equilibrium constants for palmitic acid are larger than those of acetic acid in supercritical CO_2. Moreover, it is shown that the equilibrium constants in supercritical CO_2 are smaller than those in organic liquid solvents. These results indicate that monomeric form carboxylic acid is more stable in supercritical CO_2 than in organic liquid solvents.

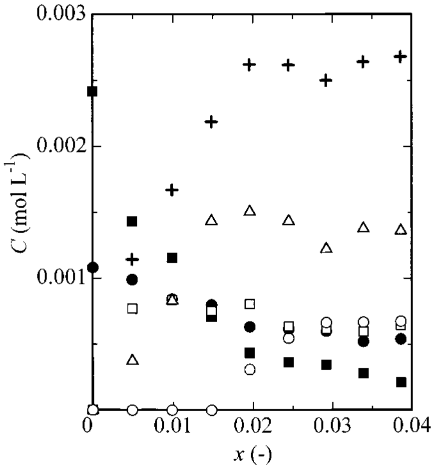

Figure 8. Molarities of species for palmitic acid in supercritical CO_2 with ethanol at 20.0 MPa and 308.2 K: (■) acid monomer; (●) acid dimer; (□) acid monomer interacting with one molecule of ethanol; (△) acid monomer interacting with two molecules of ethanol; (○) acid dimer interacting with one molecule of ethanol; (+) total acid interacting with ethanol; acid molecule basis.

In ternary systems, the amount of hydrogen bonding species between carboxylic acid and ethanol in supercritical CO_2 increases with the increasing mole fraction of ethanol. As shown in previous work,[3] ethanol is effective on solubility enhancement of palmitic acid in supercritical CO_2. From these results, it is noted that the solubility enhancement by an entrainer relates closely to the amount of hydrogen bonding species between the solute and the entrainer used in supercritical CO_2.

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References and Notes

(1) Iwai, Y.; Fukuda, T.; Koga, Y.; Arai, Y. *J. Chem. Eng. Data* **1991**, *36*, 430.

(2) Iwai, Y.; Koga, Y.; Maruyama, H.; Arai, Y. *J. Chem. Eng. Data* **1993**, *38*, 206.

(3) Koga, Y.; Iwai, Y.; Hata, Y.; Yamamoto, M.; Arai, Y. *Fluid Phase Equilib.* **1996,** *125*, 115.

(4) Fulton, J. L.; Yee, G. G.; Smith, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 8327.

(5) Yee, G. G.; Fulton, J. L.; Smith, R. D. *J. Phys. Chem.* **1992**, *96*, 6172.

(6) Yee, G. G.; Fulton, J. L.; Smith, R. D. *Langmuir* **1992**, *8*, 377.

(7) Gupta, R. B.; Combes, J. R.; Johnston, K. P. *J. Phys. Chem.* **1993**, *97*, 707.

(8) Gupta, R. B.; Brinkley R. L. *AIChE J.* **1998**, *44*, 207.

(9) Ikawa, S.; Fujita, Y. *J. Phys. Chem.* **1993**, *97*, 10607.

(10) Tsugane, H.; Yagi, Y.; Inomata, H.; Saito, S. *J. Chem. Eng. Jpn.* **1992**, 25, 351.

(11) Buback, M.; Mahling, F. *J. Supercrit. Fluid* **1995**, *8*, 119.

(12) Ke, J.; Jin, S.; Han, B.; Yan, H.; Shen, D. *J. Supercrit. Fluid* **1997**, *11*, 53.

(13) Bulmer, J. T.; Shurvell, H. F. *J. Phys. Chem.* **1973**, *77*, 256.

(14) Fujii, Y.; Yamada, H.; Mizuta, M. *J. Phys. Chem.* **1988**, *92*, 6768.

(15) Pohl, H. A.; Hobbs, M. E.; Gross, P. M. *J. Chem. Phys.* **1941**, *9*, 408.

(16) Kimura, Y.; Yoshimura, Y. *J. Chem. Phys.* **1992**, *96*, 3085.

(17) Picquart, M.; Lefevre, T.; Lacrampe, G. *Appl. Spectrosc.* **1995**, *49*, 1268.