

MEASUREMENT AND CORRELATION OF SOLUBILITIES FOR TRIFLUOROMETHYLBENZOIC ACID ISOMERS IN SUPERCRITICAL CARBON DIOXIDE

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The solubilities of 2- and 3-trifluoromethylbenzoic acids in supercritical carbon dioxide were measured at 308.2, 313.2 and 323.2 K by a flow-type apparatus. The pressure range of the measurement was from 9 to 23 MPa. The enhancements of solubility by fluorination were markedly observed. The experimental data were correlated by the Peng-Robinson equation of state. The correlated results show good agreement with the experimental data by adjusting binary interaction parameters. A molecular dynamics simulation was applied to investigate interactions between carbon dioxide and solutes. The interaction between carbon dioxide and 3-trifluoromethylbenzoic acid is larger than that between carbon dioxide and 2-trifluoromethylbenzoic acids. This fact coincide with the tendency of solubility enhancement.

INTRODUCTION

Supercritical fluid technology has been actively applied and used commercially in extraction, fractionation and purification processes. In particular, supercritical carbon dioxide is frequently used, because it can be used under relatively mild conditions. The supercritical carbon dioxide also has received much attention as a reaction medium. The enhancement of reaction rate is expected by adding of catalysts. However, the solubilities of catalysts usually used in organic solvents are very low in supercritical carbon dioxide. The recently studies have been reported that the solubilities are enhanced by fluorination[7, 12]. However, the solubility data of fluorinated compounds are very few and the mechanism for the enhancement of solubility has not been yet clarified. In this work, the solubilities of 2- and 3-trifluoromethylbenzoic acids in supercritical carbon dioxide were measured and discussed in comparison with non-fluorinated compounds. The experimental data were correlated by the Peng-Robinson equation of state. Further, the interactions between carbon dioxide and solutes were discussed by the molecular simulation results for pair correlation functions.

EXPERIMENT

Materials. Extra pure grade of 2-trifluoromethylbenzoic acid and guaranteed reagent grade of 3-trifluoromethylbenzoic acid (supplied by Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. The purities of 2- and 3-trifluoromethylbenzoic acids are more than 98 %. High-purity carbon dioxide (more than 99.9%, Sumitomo Seika Co.) was used as received.

Melting Temperature and Heat of Fusion. Before measuring the solubilities of 2- and 3-trifluoromethylbenzoic acids in supercritical carbon dioxide, the melting temperatures and heats of fusion were measured under atmospheric pressure by a differential scanning calorimeter (Shimadzu Co., Ltd., DSC-50).

Solubility. A flow-type apparatus was used to determine the solubilities of solid solutes in supercritical carbon dioxide. A detailed description of the equipment and operating procedures has been given elsewhere [5, 6]. From a cylinder, carbon dioxide was supplied and was liquefied through a cooling unit. The liquefied carbon dioxide was sent to a preheater by a high-pressure liquid chromatography pump. When carbon dioxide passed through the preheater, it became a supercritical fluid. Then supercritical carbon dioxide entered into equilibrium cells. The preheater and equilibrium cells were immersed into a water bath which was controlled within ± 0.1 K. The details of equilibrium cells are given in the previous paper [5, 6]. Solid solute was packed into the cell with glass beads to prevent channeling. When supercritical carbon dioxide passed through the equilibrium cells, supercritical carbon dioxide was in contact with solid solute under equilibrium pressure. The equilibrium pressure was measured by a Bourdon gauge which was calibrated against a strain pressure gauge. The supercritical carbon dioxide containing solute was decompressed through an expansion valve and then introduced into a U-shaped glass tube in which gaseous carbon dioxide and solid solute were separated. Usually 0.1-0.4 g of solute was trapped, and the flow rate of carbon dioxide at outlet of the apparatus was adjusted to be 1-12 cm³/s. The volume of carbon dioxide was measured by a wet gas meter. Then, any small amount of solute precipitated in the expansion valve was removed and trapped by using pure carbon dioxide gas. The amount of solute trapped was determined with an electric balance. The solubilities were determined from the weight of the solute and the volume of carbon dioxide.

CORRELATION

The following fundamental equation can be used to calculate the solubilities of high-boiling compounds in supercritical fluid.

$$y_2 = \frac{P_2^{\text{sub}}}{P} \cdot \frac{1}{f_2^{\text{G}}} \exp\left(v_2^{\text{S}} \frac{P - P_2^{\text{sub}}}{RT}\right) \quad (1)$$

where R is the gas constant. P and T denote the equilibrium pressure and temperature. P_2^{sub} and v_2^{S} are the sublimation pressure and solid-state molar volume of solute, respectively. The value of solid-state molar volume was estimated by the group contribution method of Immizi and Perini[4] and the sublimation pressure was calculated by the method proposed by Neau et al.[10]. Namely, the following equation was used to calculate the sublimation pressure.

$$\ln\left(\frac{P_2^{\text{sub}}}{P_2^{\text{t}}}\right) = -\frac{Dh_2^{\text{sub}}}{R} \left(\frac{1}{T} - \frac{1}{T_2^{\text{t}}}\right) \quad (2)$$

where Dh_2^{sub} is the heat of sublimation calculated by the sum of the heat of fusion and of vaporization. P_2^{t} and T_2^{t} denote the triple point pressure and temperature. The triple point temperature was approximated by the normal melting temperature. The melting temperatures and heats of fusion are listed in **Table 1**. The Peng-Robinson cubic equation of state (PR-EOS) was used to calculate the heat of vaporization by adopting the Clausius-Clapeyron equation.

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (3)$$

where a and b are the energy and size parameters that can be calculated with the critical properties P_C and T_C and acentric factor w .

The fugacity coefficient of solute in the pressurized gas phase f_2^{G} is usually evaluated by adopting an equation of state. The PR-EOS was also adopted to calculate the fugacity. In

order to apply eq.(3) to a binary system, the following mixing and combining rules for the constants a and b were used.

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij}) \sqrt{a_i \cdot a_j} \quad (4)$$

$$b_m = \sum_i x_i b_i \quad (5)$$

where k_{ij} denote the interaction parameter between unlike molecules i and j . The values of interaction parameter were adjusted by the experimental solubilities. The properties of pure components used to calculate the solubilities were listed in **Tables 2** and **3**.

Table 1 Melting temperatures and heats of fusion

Substance	T_m [K]	Dh^{fus} [kJ/mol]
Benzoic acid	395.5 ^{a)}	18.01 ^{a)}
2-Methylbenzoic acid	376.9 ^{b)}	20.17 ^{b)}
3-Methylbenzoic acid	381.9 ^{b)}	15.73 ^{b)}
2-Trifluoromethylbenzoic acid	380.7 ^{c)}	24.0 ^{c)}
3-Trifluoromethylbenzoic acid	376.8 ^{c)}	18.0 ^{c)}

a) Ginnings and Furukawa[3]

b) Andrews et al.[1]

c) This work.

Table 2 Properties of pure components

Substance	T_C [K]	P_C [MPa]	w [-]	v^S [cm ³ /mol]
Carbon dioxide	304.1 ^{a)}	7.37 ^{a)}	0.225 ^{a)}	-
Benzoic acid	751.8 ^{b)}	4.58 ^{b)}	0.619 ^{b)}	92.5 ^{c)}
2-Methylbenzoic acid	766.4 ^{b)}	3.99 ^{b)}	0.669 ^{b)}	107.4 ^{c)}
3-Methylbenzoic acid	766.5 ^{b)}	3.90 ^{b)}	0.672 ^{b)}	107.4 ^{c)}
2-Trifluoromethylbenzoic acid	681.6 ^{b)}	2.98 ^{b)}	0.658 ^{b)}	118.1 ^{c)}
3-Trifluoromethylbenzoic acid	681.8 ^{b)}	2.93 ^{b)}	0.661 ^{b)}	118.1 ^{c)}

a) Poling et al.[13]

b) Group contribution method of Marrero-Pardillo[8]

c) Group contribution method of Immizi and Perini[4]

Table 3 Sublimation pressures ^{a)}

Substance	P^{sub} [Pa]		
	308.2 K	313.2 K	323.2 K
Benzoic acid	0.491	-	-
2-Methylbenzoic acid	-	0.324	1.057
3-Methylbenzoic acid	-	0.375	1.167
2-Trifluoromethylbenzoic acid	2.497	4.428	13.00
3-Trifluoromethylbenzoic acid	4.007	6.850	18.75

a) Estimated by the method of Neau et al.[10]

MOLECULAR SIMULATION

NVT ensemble molecular dynamics simulation was applied to calculate the pair correlation functions. A single site model of carbon dioxide molecule and rigid all atom model of solute molecules were adopted in the simulation. The solute molecules were geometric optimized by PM3 method of WinMOPAC[14]. The Lennard-Jones (12-6) potential function was used as intermolecular potential. The corresponding state principle provides that all Lennard-Jones fluids for pure carbon dioxide obey the same reduced equation of state by using the reduced variables. The reduced critical constant values proposed by Nicolas et al.[11] were used to determine the size and energy parameters of carbon dioxide. The values of these parameters are $\sigma = 0.391$ nm and $\epsilon/k = 225.1$ K. The parameters for atoms in the solute molecules were adopted from the DREIDING force field[9]. The charge in the solute molecules was ignored. The arithmetic and geometry combining rules were used to calculate the size and energy parameters between carbon dioxide and solute, respectively.

A cubic cell with periodic boundary condition consisted of 200 particles of carbon dioxide and one particle of solute was adopted and the cut-off distance was set to 10 nm between every pair particles. The long range correlation for potential and virial for the influence of tail of the potential was estimated analytically. A scaling method was used for adjusting the temperature. The time step of the calculations was 1 fs. The number of equilibration steps was 1.0×10^4 steps and that of the production steps was 5.0×10^5 steps. The temperature and density were set to 313.2 K and 0.6 g/cm^3 . The pair correlation functions for carbon dioxide - carbon atom in fluorinated or non-fluorinated methyl group and carbon dioxide - carbon atom in carboxyl group of the solute molecules were calculated.

RESULTS AND DISCUSSION

It was ascertained that the solubilities obtained each experiments were independent of the flow rates. The solubilities are averaged by several data at each pressure. The experimental results for solubilities of 2- and 3-trifluoromethylbenzoic acids are shown in **Figures 1-3**. The solubilities of 2- and 3-trifluoromethylbenzoic acids are higher than that of benzoic acid as shown in **Figure 1**. The solubilities are enhanced by introducing the fluorinated methyl group. The enhancement of the solubilities of 3-trifluoromethylbenzoic acid is much higher than those of 2-trifluoromethylbenzoic acid. The solubilities of 2-trifluoromethylbenzoic acid are about two times higher than those of 2-methylbenzoic acid, and the solubilities of 3-trifluoromethylbenzoic acid are about ten times higher than those of 3-methylbenzoic acid as shown **Figures 2 and 3**. Solid phase was disappeared above the 14 MPa for 3-trifluoromethylbenzoic acid at 323.2 K.

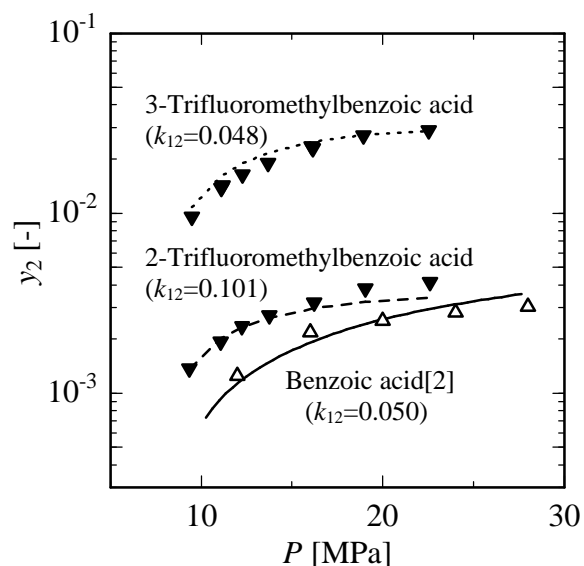


Figure 1 Solubilities of benzoic acid, 2-trifluoromethylbenzoic acid and 3-trifluoromethylbenzoic acid in supercritical carbon dioxide at 308.2 K.

The calculated results for the solubilities by PR-EOS are also shown in **Figures 1-3**. The correlations are in good agreement with experimental data. The interaction parameter for 2-trifluoromethylbenzoic acid is larger than those of other compounds. This fact indicates that the interaction between carbon dioxide and 2-trifluoromethylbenzoic acid is smaller than those of other compounds. The estimated sublimation pressures of fluorinated compounds are also ten times larger than those of non-fluorinated compounds. Thus, the enhancements of solubilities for 2-trifluoromethylbenzoic acid is small due to the weak interaction between carbon dioxide and 2-trifluoromethylbenzoic acid though sublimation pressure is large.

The simulated results for pair correlation functions are shown in **Figures 4-7**.

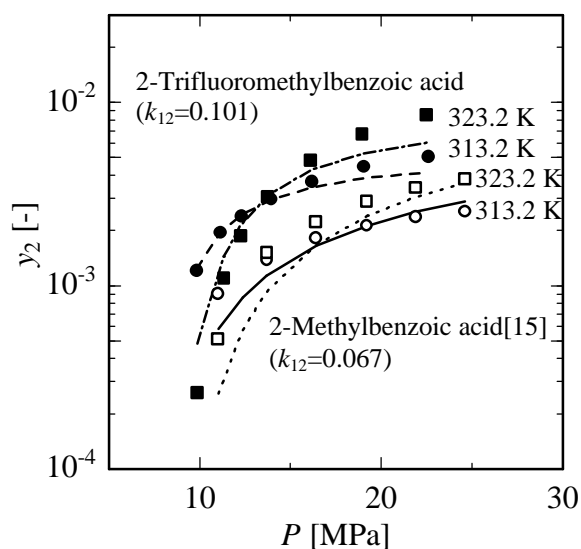


Figure 2 Solubilities of 2-methylbenzoic acid and 2-trifluoromethylbenzoic acid in supercritical carbon dioxide.

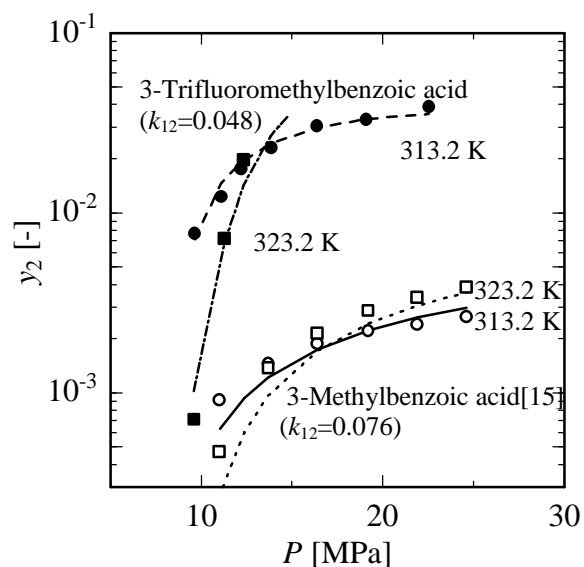


Figure 3 Solubilities of 3-methylbenzoic acid and 3-trifluoromethylbenzoic acid in supercritical carbon dioxide.

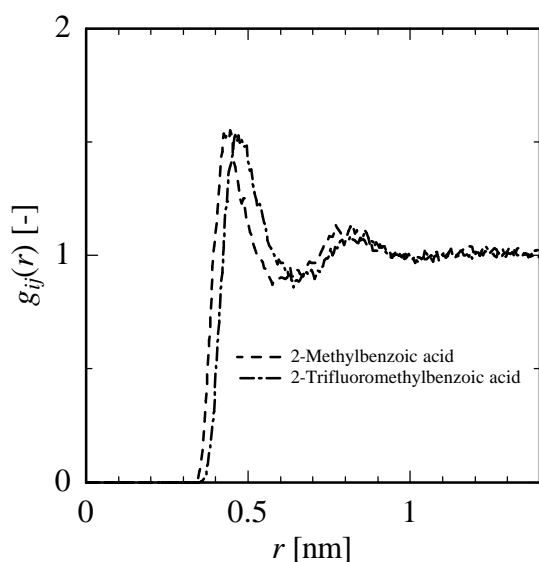


Figure 4 Pair correlation functions between carbon dioxide and carbon atom in methyl group at 313.2 K and 0.6 g/cm³.

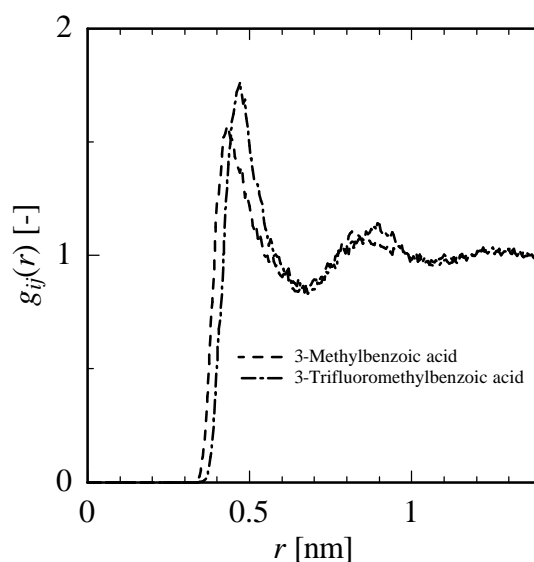


Figure 5 Pair correlation functions between carbon dioxide and carbon atom in methyl group at 313.2 K and 0.6 g/cm³.

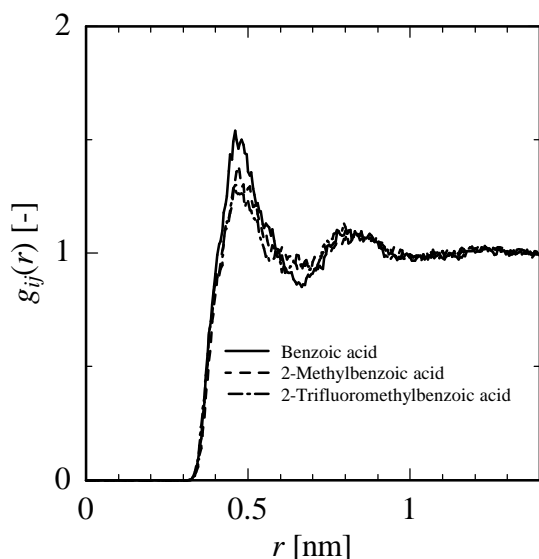


Figure 6 Pair correlation functions between carbon dioxide and carbon atom in carboxyl group at 313.2 K and 0.6 g/cm³.

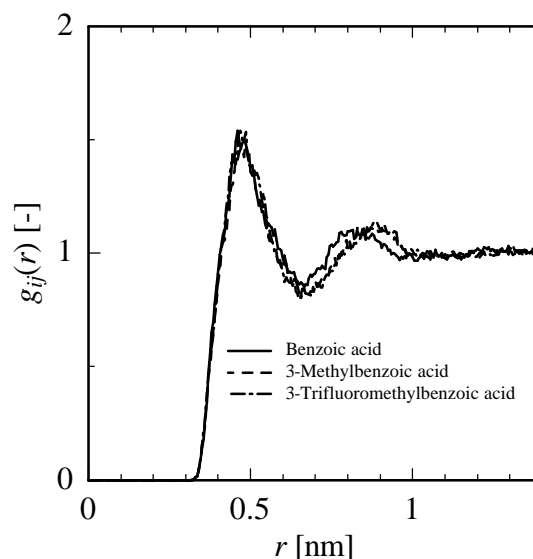


Figure 7 Pair correlation functions between carbon dioxide and carbon atom in carboxyl group at 313.2 K and 0.6 g/cm³.

The peak of pair correlation function between carbon dioxide and carbon atom in methyl group of 3-trifluoromethylbenzoic acid is higher than those of other compounds. The peak of pair correlation function between carbon dioxide and carbon atom in carboxyl group of 2-trifluoromethylbenzoic acid is lower than those of other compounds. It is shown that the interaction between carbon dioxide and 3-trifluoromethylbenzoic acid is larger than the interaction between carbon dioxide and 2-trifluoromethylbenzoic acid. This result agrees with the solubility data.

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