

DIMERIZATION OF BENZOIC ACID IN SATURATED SOLUTION OF SUPERCRITICAL CARBON DIOXIDE

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Introduction

Supercritical fluids are desirable as new solvents in various processes. Over the past decade they have been extensively studied in terms of both fundamental and technological aspects. The characteristic features of supercritical fluids originate from intermolecular interactions in solutions. To date, solvent-solute interactions have been the main focus of a number of researchers while solute-solute interactions have been less studied, and scarcely considered for the prediction of thermodynamic properties. This is because the solute concentration in supercritical solutions is generally very dilute. Recently, Donohue *et al.*²⁰⁾ in a theoretical study insisted on the importance of chemical interactions in supercritical fluid. In experimental studies, the investigation of organized molecular assemblies has become a recent research topic pertaining to supercritical fluids. Smith *et al.* studied the micelle formation of surfactants in supercritical fluids, using a variety of techniques including UV-vis, IR, fluores-

cence spectroscopy, light-scattering and small-angle neutron scattering^{2,3,7,8,11,15-18}). This approach revealed that the phase behavior of micelles in supercritical fluid is mainly driven by the amphiphilic nature of surfactants. This group also reported that nonionic surfactants and alcohols aggregated due to inter- and intra-hydrogen bonding in supercritical carbon dioxide and ethane^{9,10}). These findings were based on FT-IR measurements. Prausnitz *et al.* reported the aggregation of cholesterol and fatty acid in supercritical CO₂, observing its dependence on pressure and role as a co-solvent¹²⁻¹⁴). Finally, excimer and exciplex formation in supercritical fluid has been investigated by Brennecke *et al.* via a fluorescent spectroscopic technique.⁴⁾

The purpose of this work is to investigate the dimer formation of benzoic acid via hydrogen bonding in supercritical CO₂. We used FT-IR spectroscopy to ascertain the stretching of the dimers. We could observe the dimerization of benzoic acid in supercritical CO₂ even in the very dilute concentration region where solute-solute interaction has usually been neglected in solubility calculations. The di-

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merization of benzoic acid in vapor phase was observed by Allen *et al.*¹⁾, while that in supercritical fluids has not been reported to date, although the possibility of dimerization of benzoic acid in supercritical CO₂ was suggested by DeBenedetti and Reid on the basis of their experimental results on diffusion coefficients⁶⁾.

2. Experiments

Benzoic acid (zone refined grade) from Tokyo Kasei Corp. was used without further purification. The carbon dioxide (>99.9%) was from Nihon Sanso K.K.

Infrared spectral data for benzoic acid in supercritical CO₂ were acquired with an apparatus¹⁹⁾ composed of an extraction section (Saturator), a high-pressure optical cell, and an FT-IR spectrometer (DigiLab. FTS-7R) purged with nitrogen gas. The optical cell was made of a stainless steel vessel with ZnS windows of 5 mm thickness. The optical path length was 5.25 mm. The optical cell had an internal volume of 0.103 cm³ and was equipped with a temperature control unit. The maximum working temperature of the cell was 150°C. Its pressure was 40 MPa.

The experimental procedure was as follows. CO₂ was liquefied and then pressurized to the desired pressures via a microflow pump system (a plunger-type pump with a flow controller and a pressure sensor; ISCO-SFC500). An excess of benzoic acid was loaded into a saturator column (100 mm long and 4.6 mm i.d.), then immersed in a constant-temperature air bath. Pressurized CO₂ was allowed to flow into the saturator and dissolved the benzoic acid. The saturated fluid was then introduced into the optical cell.

The temperature of the cell was monitored via a thermocouple and kept within ± 0.5 K of 45°C using a PID controller. The fluid pressure was measured with a pressure sensor having an accuracy of ± 0.05 MPa.

IR spectra were acquired with a deuterated-triglycine sulfate (DTGS) detector at 2 cm⁻¹ resolution with a coaddition of 16 scans. The spectra were recorded only after solubility equilibrium was attained. Among the IR-modes of benzoic acid we concentrated our attention on two carbonyl (>C=O) stretchings. One was a >C=O stretching of monomeric benzoic acid and the other was that of the hydrogen-bonded cyclic dimer of benzoic acid.

3. Results and Discussion

Firstly, the absorption spectra of supercritical CO₂ were measured at various pressures (8–30 MPa) at 45°C to acquire the background spectra of solvent. **Figure 1** shows an example of the IR-absorption

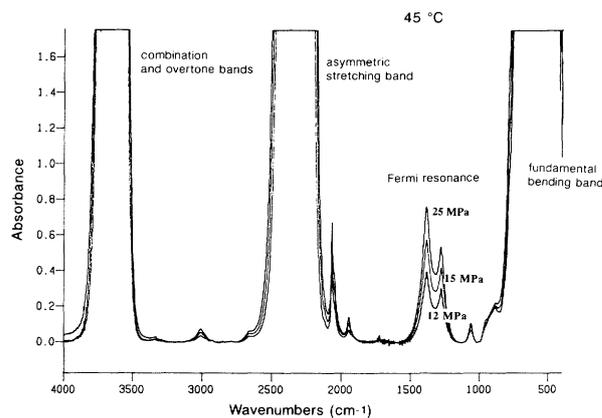


Fig. 1. Absorption spectra of supercritical carbon dioxide at 45°C

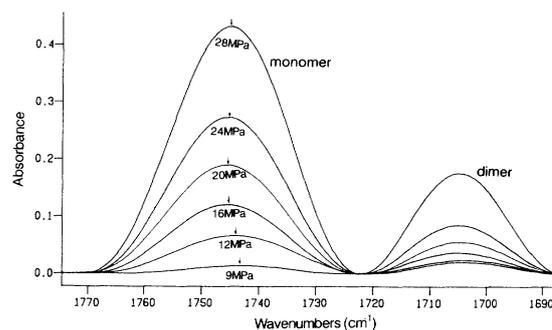


Fig. 2. Absorption spectra of benzoic acid in supercritical carbon dioxide at 45°C

spectra of CO₂. As suggested in the literature, three typical IR-bands appear: fundamental bending, asymmetric stretching, and combination and overtone. In addition, the prominent pressure dependence of Fermi resonance at 1282 and 1387 cm⁻¹ can be seen. Generally, the spectra of solutes in a solution are obscured by those of the solvent. However, two >C=O stretching modes of benzoic acid, which were focused on in the present study, were fortunately liberated from the IR-bands of CO₂. The absorption spectra of benzoic acid were obtained by subtracting the background spectra of CO₂ from those of the solution. **Figure 2** shows the absorption spectra of the >C=O stretching of benzoic acid in supercritical CO₂. The peak at 1705 cm⁻¹ is attributable to >C=O stretching of hydrogen-bonded cyclic dimer; the peak at 1745 cm⁻¹ is from >C=O stretching of free (non-associated) monomer⁵⁾. These results confirm the dimer formation of benzoic acid in diluted supercritical CO₂ solutions*. Both peaks were intensified as the fluid pressure increased, and their pressure dependences were slightly different.

Figure 3 shows the pressure dependence of the dimer and monomer absorption ratio at 45°C. The isothermal compressibility coefficient of CO₂ at 45°C

* mole fraction $\approx 10^{-3}$ – 10^{-4}

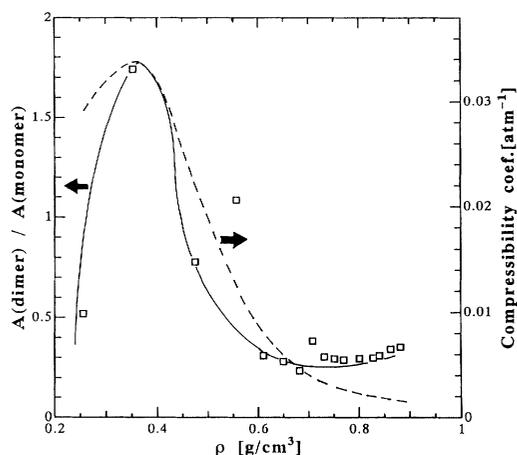


Fig. 3. Dimer and monomer absorption ratio at 45°C (—□—) and isothermal compressibility coefficient of CO₂ (-----)

is also plotted. The ratio reached maximum near the critical density and decreased with lessening density. Considering the experimental result that the absorption coefficient of the dimer is almost the same as that of the monomer in cyclohexane¹¹, the dimer and monomer absorption ratio seems to represent the molar ratio of the dimer and monomer. Therefore, the data in Fig. 3 suggest that dimerization equilibrium changes with solvent density. The increase in density shifted the dimerization equilibrium toward the monomer. This behavior may be explained as follows. It has been pointed out that solvent polarity originating from the quadrupole moment of CO₂ increases with density. At higher densities, the solvent polarity of supercritical CO₂ is so enhanced that CO₂ molecules of high density can solvate the dipole associated with the >C=O and -OH groups on the monomeric form of benzoic acid. Therefore, benzoic acid molecules become stable in monomeric forms at higher densities. As for the correlation with compressibility, such a finding suggests that the dimerization may be influenced by fluid density fluctuation. That is, a large fluctuation in density might promote the dimerization of benzoic acid at medium densities. What's more, we found that the peak wavenumber of the monomer shifted to higher values, while no spectral shift could be observed for the dimer. This observation might support our brief discussion of this solvation.

4. Conclusion

The dimerization of benzoic acid in supercritical CO₂ was ascertained by FT-IR spectroscopy. The absorption ratio of dimer and monomer was strongly dependent on solvent density and achieved maximum in the medium-density region, in which the isothermal

compressibility of the fluid was at its maximum. While further studies (equilibrium constant and its pressure dependence, heat of reaction, etc.) are necessary to identify the dimerization mechanism of benzoic acid and will be reported in the near future, the present study suggests that solute-solute interactions should be considered, even at very diluted concentrations, in developing a prediction model for the thermodynamic properties of supercritical solutions.

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