

Local Excess Density about Substituted Benzene Compounds in Supercritical CO₂ Based on FT-IR Spectroscopy

N. Wada,* M. Saito, D. Kitada, R. L. Smith, Jr., H. Inomata,* K. Arai, and S. Saito

Department of Chemical Engineering, Research Center of Supercritical Fluid Technology, Tohoku University, Aoba Aza Aramaki, Sendai 980-77, Japan

Received: July 15, 1997; In Final Form: September 25, 1997[®]

IR spectra of substituted benzene compounds were measured in supercritical CO₂ with an apparatus capable of in situ measurement. An experimental procedure was developed which provided reliable data and allowed quantitative analyses. The molar absorption coefficient of substituent deformation stretch and C–C ring stretch were found to vary with the system density but their density dependence was different. A method for determining the local excess density of benzene derivatives in supercritical CO₂ is proposed. The expression obtained for the local excess density can be represented by a single function in terms of bulk density and exhibits a maximum just below the critical density.

Introduction

Supercritical fluids have attracted much attention as solvents for separation, material production, and reaction applications.¹¹ Previous works suggested that clustering/solvation in supercritical solutions is a key factor to understanding phenomena in the solutions and making a more efficient use of supercritical fluids. Clustering in supercritical solution can be defined as local density augmentation about a solute and has been studied through a variety of techniques: partial molar volumes,^{1,2} solvatochromic probes,³ UV/vis and IR spectra,^{4,5} X-ray diffraction,⁶ XAFS,⁷ fluctuation analyses,⁸ molecular simulation,^{9,10} and others.¹² Eckert et al.^{1,2} attributed the strongly negative partial molar volumes, \bar{v}_2^∞ , to the collapse of a large number of solvent molecules around a single solute molecule. They interpreted their results in terms of chemical theory in which n solvent molecules combine to form a solvent–solute complex, defined by an equilibrium constant, and named this phenomenon as “clustering”. Kim and Johnston³ found through UV/vis spectroscopic measurement with a solvatochromic probe, phenol blue, that the solvent clustered around the solute such that local solvent density exceeds the bulk density. Further, they showed that the local density to the bulk density is related linearly to the isothermal compressibility. Kajimoto et al.⁴ studied the charge transfer (CT) state formation for (*N,N*-dimethylamino)-benzonitrile in CF₃H and attributed the larger spectral shift to the occurrence of aggregation of solvent molecules around the solute. As the bulk density was increased, the bathochromic shift asymptotically converged to that observed in the liquid phase. Betts et al.⁵ reported on the local densities and cluster volume through the experiment on steady-state fluorescence and decay of a fluorescent probe, prodan, in supercritical N₂O. These works and others provide a strong basis for the spectroscopic interpretation of the clustering phenomena. Namely, solvent molecules tend to aggregate around solutes according to intermolecular attractive force, leading to a local density enhancement. The local density is determined by the balance between kinetic energy and intermolecular forces. Since intermolecular interactions are strongly dependent on the chemical structure of molecules, the local density around a solute in supercritical fluid should be strongly dependent on the functional groups of a solute as well. However, no studies have

reported on the effect of functional groups on the local density around a solute in a supercritical solvent, which we denote as the local excess density. In this work, we have made an attempt to discuss the relationship between the functional group of solutes and the local excess density by using Fourier transform infrared (FT-IR) spectroscopy, which is very sensitive to atomic structure and to the local environment. The previous works on FT-IR in supercritical solutions focused on intensive spectral shifts that are known to change with the solvency.⁵ However, it is difficult to extract quantitative information from the spectral shift in IR because of its smaller shift compared with that of UV or fluorescence spectra. This study has focused on an absorption coefficient derived from an absorbance to obtain quantitative information on local density about a functional group. The experiments have been carried out for several substituted benzenes so that the phenomenon can be clearly interpreted. A mathematical expression of local excess density around various substitutes is developed, which allows the quantitative description of the preferential clustering of the solvent about specific solute groups in supercritical fluids.

Experimental Section

Materials. Carbon dioxide solvent with a minimum specified purity of 99.99 mol % (Nihon Sanso) was used in all experiments. Solutes, C₆H₅X (X = –H, –NH₂, –OH, –OCH₃, –CH₃, –CH=O, –Cl) were used with the following minimum mol % purity: benzene, 99%; aniline, 99%; phenol, 99%; methoxybenzene, 95%; toluene, 99%; chlorobenzene, 99%; and benzaldehyde, 99%.

Apparatus. The experimental apparatus used in this study is shown in Figure 1. It consisted of a FT-IR spectrophotometer (Bio-Rad, FTS-60A), an optical cell with temperature control unit, a plunger pump (JASCO, 880-PU), a back-pressure regulator (TESCOM, Model 26-1721-24), a saturation column, and a magnetic circulation pump. The column and the magnetic pump were immersed in the constant temperature air bath. The optical path length of the cell was fixed at 5.25 mm and the cell volume was 0.103 cm³. The cell had ZnS windows that were 5 mm thick and was rated at 423 K and 40 MPa. The entire system volume was approximately 50 cm³. The temperatures of the cell and system were held constant by a proportional integral derivative (PID) controller. Pressure was

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1997.

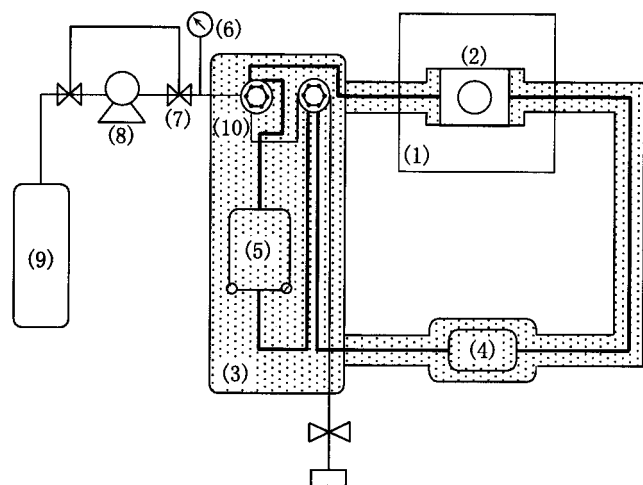


Figure 1. Schematic Diagram of the experimental apparatus: (1) IR spectrophotometer, (2) optical cell, (3) constant temperature bath, (4) saturation column, (5) magnetic circulation pump, (6) pressure gauge, (7) back-pressure regulator, (8) plunger pump, (9) gas cylinder, (10) six-way valve.

measured with a bourdon tube gauge which was accurate to 0.02 MPa. The full set up of the apparatus was installed in a temperature-controlled room. Further details are given in a recent publication.¹³

Method for FT-IR Measurements. Measurements at supercritical conditions were performed with the following procedure. After the system was thoroughly purged with CO₂, a preweighed solid or liquid sample was introduced into a saturation column. For liquid samples, glass wool was used to contain the liquid. After the liquid or solid sample was loaded, the system was brought to the desired pressure via the high-pressure pump (JASCO,880-PU). The contents were recirculated through the optical cell and the saturation column with a magnetic circulation pump for several hours until the steady state was attained. The IR spectra of the solutions were recorded with a deuterated triglycine sulfate (DTGS) detector at 2 cm⁻¹ resolution with 64 scans after the fluctuation of the absorbance diminished. Since the IR absorbance of water is very large and interferes with the spectra, the humidity was kept as low as possible. At the start of each experiment, the chamber of the spectrophotometer was purged with dry air to remove any residual traces of water and to reduce the noise level. The solute concentrations (2 ~12mM) used were well below the saturated solubility limits of each solute in the CO₂. At these low concentrations the solute-solute interactions could be safely neglected. Measurements were carried out at 318.2 K and over a pressure range of 7.0~26.4 MPa. Since IR absorption spectra are temperature and pressure dependent, the solute spectra were obtained by subtracting the spectra of pure solvent, CO₂, from the spectra of the solutions at the same temperature and pressure. The background spectra were recorded only when the baseline fluctuation was less than 0.02% in the wavenumber range of 400~4400 cm⁻¹, since quantitative discussion required the high reproducibility in absorption spectra.

Results and Discussions

IR spectra of all substituted benzenes in supercritical CO₂ at selected densities and constant solute concentrations are shown in Figure 2a-g. As shown in this figure, the absorptions of the substituents were easily distinguished. It should be noted that the absorbance of each vibrational peak increased with increasing density. This is expected according to the previous

paper¹³ and suggests that absorbance can be an index of solvent density. Here, we focused on two types of vibrational modes of the substituted benzene: the C-C ring semicircle stretch of the aromatic ring and the stretch of the substituent. The behavior of the C-C semicircle stretching vibration (1500 cm⁻¹) of benzene is shown in Figure 2a. For the case of aniline (Figure 2b), the C-C ring semicircle stretch and the NH₂ deformation stretch appeared at 1500 and 1620 cm⁻¹, respectively. Absorbances of the C-C ring stretch and the NH₂ deformation increased as the pressure (density) increased, but the density dependence of each mode was slightly different. Similar behavior was found for other substituted benzenes and is shown in Figure 2c-g. We used this density dependence of the absorbance to obtain quantitative information about the local density around the solute. Considering the Beer-Lambert law for quantitative analyses, the absorbance changes must be due to changes in the molar absorption coefficient because the path length and molar concentration are constant in our experiments. Molar absorption coefficients, E_p , were calculated from the Beer-Lambert law

$$A = E_p \cdot C \cdot l \quad (1)$$

where A , C , and l are absorbance, solute concentration, and optical path length, respectively. It has been reported that the E_p of the C-C ring stretch of naphthalene calculated from the Beer-Lambert law increases as the fluid density increases.¹³ However, as mentioned above, the density dependence of E_p of the C-C ring stretch was different from that of the NH₂ deformation stretch and other group substituents shown in Figure 3. Other solutes that involve the substituting functional groups (e.g., OCH₃, -Cl, -CHO, etc.) were analyzed similarly. According to quantum-chemical treatment,¹⁴ the molar absorption coefficient (E_p) is related to vibrational molecular properties.

$$E_p \sim \left(\frac{d\mu}{dq} \right)_{q=0}^2 \quad (2)$$

where μ and q are the dipole moment and the displacement coordinate, respectively. The dipole moment must be greatly affected by the solvent dielectric constant, which is also a function of the solvent density. Consequently, the change in the molar absorption coefficient (E_p) reflects the variation of the local density around the substituting functional groups, which results from solvent clustering around the solute. To discuss the density dependence of the solvation structure quantitatively, the concept of local excess density (ρ^{LE}) is used in this paper, which is defined as the difference between the local density (ρ^L) and the bulk density (ρ^B), $\rho^{LE} = \rho^L - \rho^B$. Considering the characteristic nature of the local excess density (ρ^{LE}), it should approach zero at low- and high-density limits where solutions can be regarded to have a uniform density distribution. Here consider a hypothetical homogeneous solution. The molar absorption coefficient of a solute (E_p^0) in such a hypothetical homogeneous solution varies directly with the bulk density (ρ^B) according to some function of density, because of $\rho^{LE} = 0$ for this solution. Since the dipole moment described by eq 2 must depend on temperature and density, it follows that (E_p^0) is a function of density:

$$E_p^0 \sim f(\rho) \quad (3)$$

If the function relating the molar absorption coefficient (E_p^0) of such a homogeneous solution with the bulk density (ρ^B) is known, then the local excess density (ρ^{LE}) can be evaluated by the relation of $E_p^0 \sim \rho^B$ and a measured molar absorption coefficient (E_p). Ideally, one would like to have a solute that

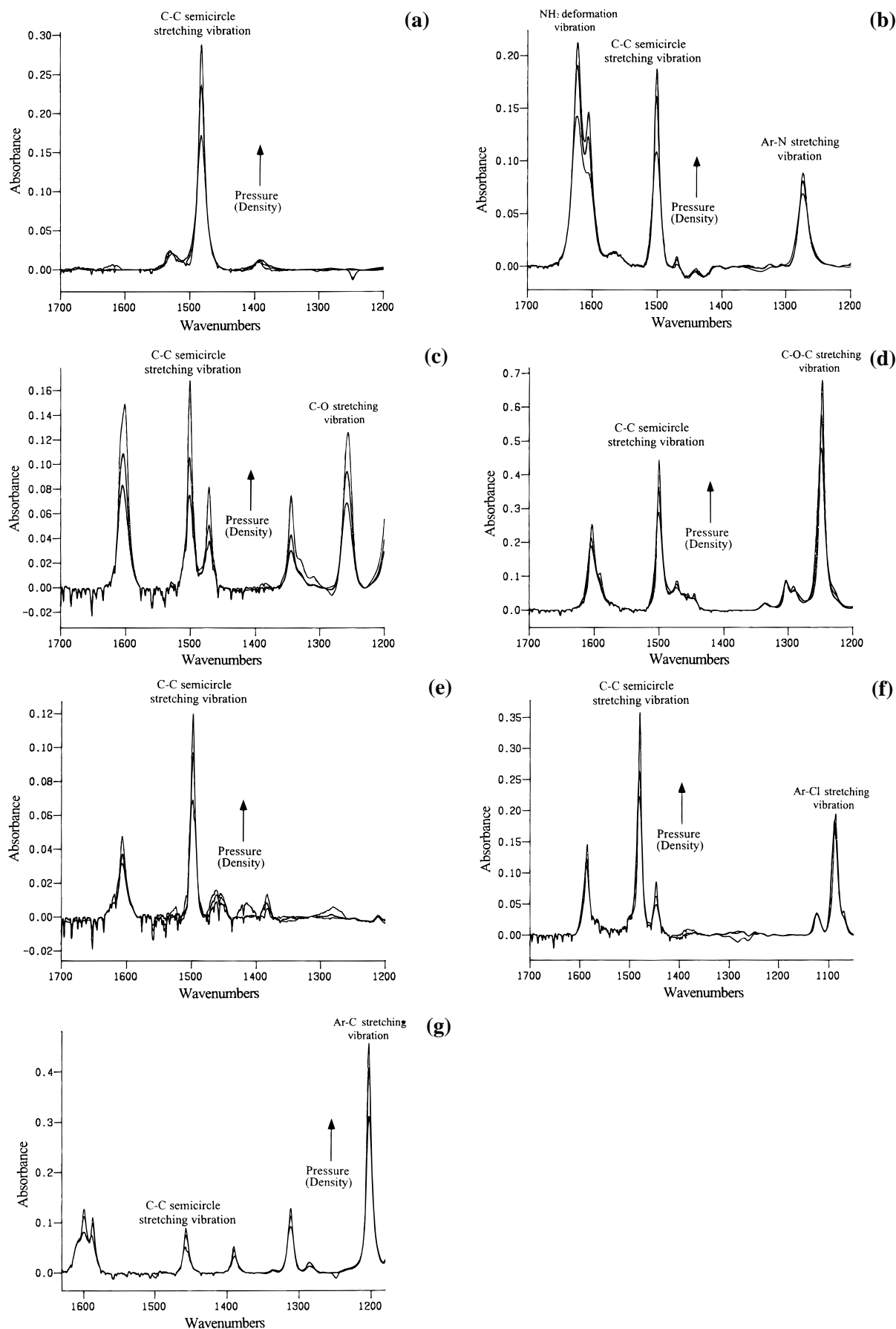


Figure 2. Infrared absorption spectra of the measured solutes in supercritical CO₂ (temperature = 318.2 K): (a) benzene (solute concentration 12 mM, density 0.47, 0.74, 0.87 g/cm³); (b) aniline (solute concentration 12 mM, density 0.18, 0.59, 0.74 g/cm³); (c) phenol (solute concentration 3 mM, density 0.18, 0.23, 0.47 g/cm³); (d) methoxybenzene (solute concentration 3 mM, density 0.18, 0.47, 0.87 g/cm³); (e) toluene (solute concentration 5 mM, density 0.23, 0.59, 0.77 g/cm³); (f) chlorobenzene (solute concentration 5 mM, density 0.18, 0.32, 0.77 g/cm³); (g) benzaldehyde (solute concentration 5 mM, density 0.32, 0.69, 0.87 g/cm³).

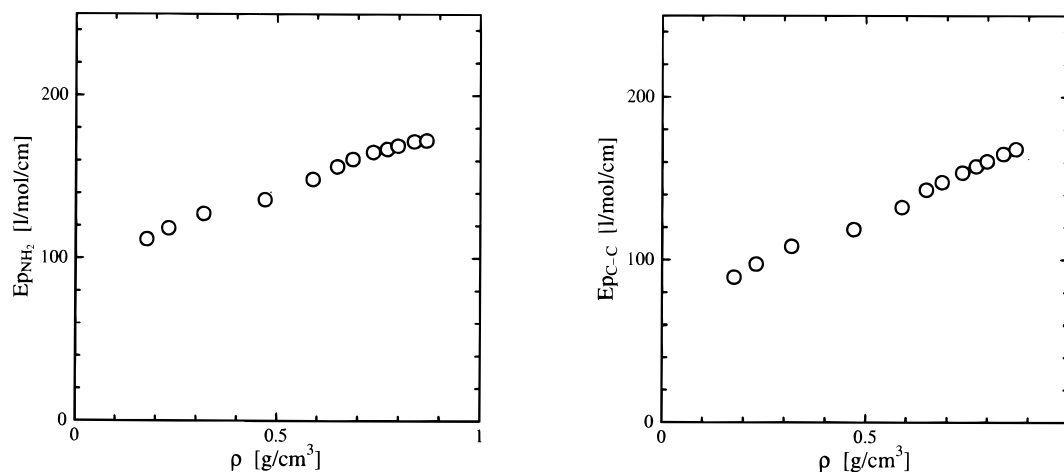


Figure 3. Density dependence of E_{pNH_2} , E_{pC-C} of aniline in supercritical CO₂ (temperature 318.2 K, solute concentration 2 mM).

would not perturb the solvent–solvent intermolecular interactions. Supercritical fluid mixtures, however, are well-known to have highly asymmetric and nonuniform density distributions. We used the following approach to develop a suitable functional relation of $E_p^0 \sim \rho^B$. The pure solvent behaves as a homogeneous fluid in the supercritical state even though local density fluctuations must exist (i.e., solvent–solvent clustering). This is because the cluster lifetimes are short-lived and tend to average out. According to eq 2, the molar absorption coefficient is directly related to solvent polarity because it influences charge distribution on a molecule. By examining various functions for solvent polarity, the following dielectric function was found to linearize the molar absorption coefficients of the Fermi resonance of CO₂.

$$f(\rho) = (\epsilon(\rho) - 1)/(2\epsilon(\rho) + 1) \quad (4)$$

where the dielectric constant, $\epsilon(\rho)$ is calculated from the correlation of Moriyoshi et al.¹⁵ In other words, the molar absorption coefficients of the Fermi resonance of CO₂ can be represented by eq 4 multiplied by a constant.

$$E_p^0 = C_1 f(\rho) \quad (5)$$

Equation 5 can be thought of as a universal function for molar absorption coefficients in homogeneous solutions and C_1 as a constant depending on each each vibration mode. In theory, eq 5 is applicable to all vibration modes. However, in practice, because of local clustering of the solvent, other vibration modes would be difficult to use. The molar absorption coefficients (E_p) measured in this work were correlated as a function of bulk density $f(\rho^B)$ for all systems, and E_p was expressed in terms of $f(\rho^B)$ as follows

$$E_p = C_2 f(\rho^B) \exp(-300 f(\rho^B)^2) + C_3 f(\rho^B) \quad (6)$$

where C_2 and C_3 are constants depending on each solute and each vibration mode. Here it should be noted that all molar absorption coefficients of various functional groups obtained in supercritical solutions were regressed using eq 6. Figure 4 shows a comparison between the molar absorption coefficient for the aromatic ring stretch of aniline (eq 6) with that of eq 5. Since the local excess density (ρ^{LE}) approaches zero at $\rho = 0$ and at high density, the constant C_3 should be equal to C_1 . Therefore, ρ^L at a certain bulk density ρ^B can be calculated from E_p (eq 6) at $f(\rho^B)$ is equal to E_p^0 (eq 5) at $f(\rho^L)$. The relationship between ρ^B and ρ^L is given by the dashed arrow, which shows the difference in dielectric function for the bulk density and

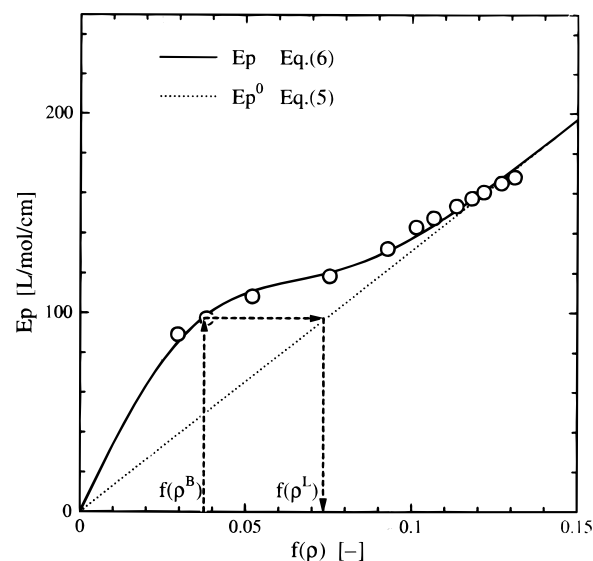


Figure 4. Relationship between $f(\rho^B)$ and ϵ of the aromatic ring stretch of aniline (temperature 318.2 K, solute concentration 2 mM).

TABLE 1: Parameters Determined (C_1 , C_2)

solute	vibration mode	C_1	C_2
benzene	C–C semicircle stretching vibration	430	334
aniline	C–C semicircle stretching vibration	1956	1295
	NH ₂ deformation stretching vibration	2760	1362
	Ar–N stretching vibration	1456	590
phenol	C–C semicircle stretching vibration	1304	1220
	C–O stretching vibration	1501	846
methoxybenzene	C–C semicircle stretching vibration	4296	2502
	C–O–C stretching vibration	8791	3781
toluene	C–C semicircle stretching vibration	466	373
chlorobenzene	C–C semicircle stretching vibration	1801	1169
	Ar–Cl stretching vibration	1912	616
benzaldehyde	C–C semicircle stretching vibration	554	498
	Ar–C stretching vibration	4062	2621

local density. Parameters $C_1 (= C_3)$ and C_2 in eqs 5 and 6 are shown in Table 1. Local density (ρ^L) at ρ^B can be calculated using eqs 4–6 with these parameters. The density dependencies of the local excess density (ρ^{LE}) about the benzene ring and substituted groups are shown in Figure 5 and Figure 6, respectively. From these results, the solvation structure changes according to the bulk density. In the dilute (gas) region, local excess density increases rapidly and approaches a maximum and then decreases with increasing density and asymptotically approaches zero at high densities. The relation between the local excess density (ρ^{LE}) and the bulk density (ρ^B) can now be

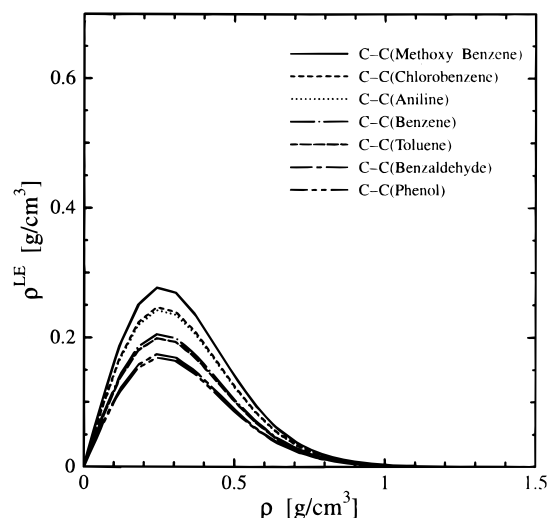


Figure 5. Density dependence of local excess density about C-C constituents (temperature 318.2 K, solute concentration 2 mM).

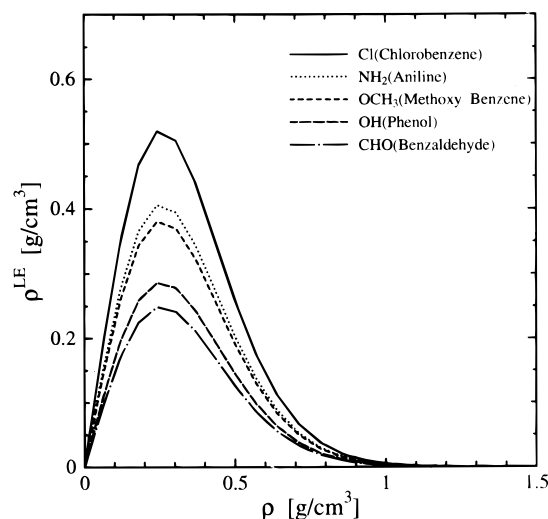


Figure 6. Density dependence of local excess density about substituted group constituents (temperature 318.2 K, solute concentration 2 mM).

defined by a single new function($g(\rho^B)$)

$$\rho^{\text{LE}} = \beta g(\rho^B) \quad (7)$$

where the function $g(\rho^B)$ is given as follows

$$g(\rho^B) = \frac{1}{\beta} \left[\frac{\sqrt{A^2 + \frac{12B g^L}{1 - 2g^L}} - A}{2B} - \rho^B \right] \quad (8)$$

$$g^L = \frac{C_2}{C_1} \left(\frac{A\rho^B + B(\rho^B)^2}{2A\rho^B + B(\rho^B)^2 + 3} \right) \times \exp \left(-300 \left(\frac{A\rho^B + B(\rho^B)^2}{2A\rho^B + B(\rho^B)^2 + 3} \right)^2 \right) + \left(\frac{A\rho^B + B(\rho^B)^2}{2A\rho^B + B(\rho^B)^2 + 3} \right)$$

Here, A and B are constants of the dielectric function of Moriyoshi et al.¹⁵ equal to 0.5099 g/cm³ and 0.1189 g/cm³, respectively. The constants C_1 and C_2 are the vibrational mode constants given in Table 1. Therefore, local excess density (ρ^{LE}) can be calculated with eq 7, IR spectroscopic data, and the bulk density. The functional form of $g(\rho^B)$ is independent

TABLE 2: Values of β of Solutes Studied

solute	vibration mode	β
benzene	C-C semicircle stretching vibration	0.21
aniline	C-C semicircle stretching vibration	0.24
	NH ₂ deformation stretching vibration	0.33
	Ar-N stretching vibration	0.41
phenol	C-C semicircle stretching vibration	0.17
	C-O stretching vibration	0.29
methoxybenzene	C-C semicircle stretching vibration	0.28
	C-O-C stretching vibration	0.38
toluene	C-C semicircle stretching vibration	0.20
chlorobenzene	C-C semicircle stretching vibration	0.25
	Ar-Cl stretching vibration	0.52
benzaldehyde	C-C semicircle stretching vibration	0.17
	Ar-C stretching vibration	0.25

of the substituting groups and dependent only upon ρ^B . The values of β tabulated in Table 2 provide the maximum of ρ^{LE} . The approach presented in this paper can be used to estimate the local density in supercritical solutions from IR spectroscopic measurements.

Conclusions

In this study, we developed a method for relating FT-IR spectra of solutes in supercritical CO₂ to the local excess density. For the vibration modes that we examined, the local molar absorption coefficient increased with increasing density. From the absorbance data obtained, the local excess density of substituted benzene rings could be evaluated. It was found that the local density of CO₂ solvent about the aromatic ring was different from that of substituents on the aromatic ring particularly in the supercritical state. The local excess density could be described by a single function. The local excess densities determined can be used to relate spectroscopic results to theoretical studies and thus to improve molecular simulations.

Acknowledgment. This work was partly supported by a Grant-in-Aid on Priority-Area-Research from the Ministry of Education, Science and Culture, Japan (08750863), for which the authors are grateful. The authors thank Mr. Mikio Kikuchi for skillful assistance in the construction of the experimental apparatus.

References and Notes

- (1) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Ellison, T. K. *Fluid Phase Equilib.* **1995**, *14*, 167.
- (2) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Kim, S. *J. Phys. Chem.* **1986**, *90*, 2738.
- (3) Kim, S.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 1206.
- (4) Kajimoto, O.; Futakami, M.; Kobayashi, T.; Yamasaki, K. *J. Phys. Chem.* **1988**, *92*, 1347.
- (5) Betts, T. A.; Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 8163.
- (6) Nishikawa, K.; Takematsu, M. *Jpn. J. Appl. Phys.* **1993**, *32*, 5155.
- (7) Murata, T.; Nakagawa, K.; Kimura, A.; Otoda, N.; Shimoyama, I. *Rev. Sci. Instrum.* **1995**, *66*, 1437.
- (8) Debenedetti, P. G. *Chem. Eng. Sci.* **1987**, *42* (9), 2203.
- (9) Petsche, I. B.; Debenedetti, P. G. *J. Chem. Phys.* **1989**, *91*, 7075.
- (10) Liew, C. C.; Inomata, H.; Saito, S. *Fluid Phase Equilib.* **1995**, *104*, 317.
- (11) Saito, S. *J. Supercrit. Fluids*, **1995**, *8*, 177.
- (12) Brennecke, J. F.; Eckert, C. A. *AIChE J.* **1989**, *35* (9), 1409.
- (13) Inomata, H.; Yagi, Y.; Saito, M.; Saito, S. *J. Supercrit. Fluids* **1993**, *6*, 237.
- (14) Barrow, G. M. *Introduction to Molecular Spectroscopy*; McGraw Hill: New York, 1982.
- (15) Moriyoshi, T.; Kita, T.; Uosaki, Y. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 589.
- (16) Yagi, Y.; Tsugane, H.; Inomata, H.; Saito, S. *J. Supercrit. Fluids* **1993**, *6*, 139.