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A Study on the Adsorption Characteristics of Acetone and Benzene in Supercritical Carbon Dioxide Measured by Chromatography and IR Spectroscopy

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Chromatographic and FTIR techniques were applied to a study of the absorption characteristics of acetone and benzene on a silica gel (SG800) in supercritical CO_2 at 313.2 and 333.2 K. The chromatographic isotherms for acetone and benzene have a maximum at a pressure lower than the critical pressure of CO_2, and then decrease with increasing pressure. When the temperature increases, the adsorption isotherms decrease in the low-pressure region, and increase in the high-pressure region, providing a crossover at a relatively high pressure. The elution curves of acetone showed tailing, even at high pressures, while those of benzene showed quasi-Gaussian curves at high pressures. The tailing curves for acetone indicate the existence of heterogeneous sites; evidence of hydrogen-bonding formation with surface silanol groups has been provided by IR spectroscopy.

Supercritical fluids (SCF) are attractive solvents, since their solvent power and transport properties are dramatically changeable by changing the pressure as well as temperature. Adsorption phenomena in SCF have become important in potential SCF technologies, since many applications of SCF have involved adsorptions on solids; for example, SCF chromatography, SCF regeneration of activated carbons, and SCF drying or dewaxing.[1,2)]

Unique characteristics of adsorption in supercritical fluids are their dependences on the pressure and temperature. For example, Tan and Liou[3)] reported that the amount of toluene adsorbed on activated carbon in supercritical CO_2 *decreased* linearly with increasing pressure under a constant-concentration condition, and that the adsorption isotherms in the SCF region *increased* with increasing temperature. Recent work of Lee et al.[4)] has also shown that the adsorption equilibrium constants of toluene and naphthalene between silica gel and supercritical CO_2 decrease with increasing pressure, and that they increase with increasing temperature. Experimental adsorption data of Shojibara et al.[5)] covered a wide range of pressures and showed that the amount of benzene adsorbed on an activated carbon from a dilute solution of supercritical CO_2 had a maximum at a pressure below 1 MPa when the mole fraction of benzene was kept constant. Recently, we applied a molecular simulation technique[6,7)] to represent the experimental isotherms of Shojibara et al., and demonstrated that the unique behavior of adsorption in SCF could be ascribed to two factors: the enhanced solubility in SCF and the competitive adsorption of SCF; the two factors simultaneously play a role toward decreasing the adsorption of a solute with increasing pressure.

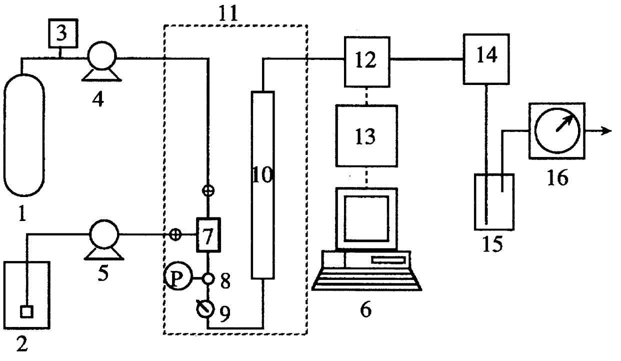
Recently, we used a Fourier transform infrared (FTIR) spectroscopic technique to investigate physical adsorption in SCF;[8,9)] the experimental systems which we used were a dilute organic solvent $+CO_2$/silica gel (SG800: pore size=80 nm) and the pressure range was from atmosphere to 15 MPa. The pressure dependence of the integral absorbance of hydrogen-bonded OH bands adsorbed by a solute (methanol, acetone, acetonitrile, tetrahydrofuran, and diethyl ether) was found to be similar to the adsorption isotherms of benzene adsorbed on activated carbon in supercritical CO_2[5)] and those calculated from Monte Carlo simulations.[6,7)] An inquiry was raised, however, concerning the relationship between the IR absorbance curve and the adsorption isotherm curve, since the integral absorbance reflects only the amount of hydrogen-bonded OH of surface-silanol groups adsorbed by the solute molecules.

In the present study we used a chromatographic technique to determine the adsorption isotherms of organic solvents diluted in supercritical CO_2 on silica gel (SG800), which were the same systems as those used in FTIR measurements of the adsorption in SCF. The adsorption isotherms obtained by chromatography are considered to be controlled by two interactions: hydrogen bonding and the van der Waals interaction, while the adsorption isotherms previously obtained by the FTIR method are regarded to be adsorption due to hydrogen bonding. Acetone and benzene were chosen as the organic solvents, since acetone fairly forms hydrogen bonding with silanol groups, while benzene does so only slightly. Experiments concerning the adsorption isotherms were performed up to 15 MPa at two temperatures (313.2 and 333.2 K) to obtain a temperature effect upon adsorptions in SCF. Therefore, the objective of the present work was to compare two adsorption isotherms of acetone and benzene obtained by different methods, chromatography and IR spectroscopy, and to discuss different intermolecular interactions for determining the adsorption equilibrium in SCF.

Experimental

Experimental Method. Figure 1 shows a schematic diagram of the experimental apparatus. The liquid CO_2 pump (4) is a Consta Metric 3200 (Thermo Separation Products; USA) cooled at -5 °C. CO_2 gas flows through a column (10) and a UV detector (12) with 8 μL high-pressure flow cell having a 10 mm optical path. The volumetric flow rate of CO_2 gas was measured using a dry gas flow meter (16). The absorbance measured by the UV detector was automatically collected by a computer (6). A column packed with silica gel (SG800) was placed in an air thermostat (11) (Shimadzu Model CTO-10AC) kept at 313.2 or 333.2 K. The column-inlet pressure (P_{in}) was monitored with a pressure transducer (8), while the column-outlet pressure (P_{out}) was controlled and monitored by a back pressure regulator (14) (Model 880-81 (JASCO; Japan)). In a low-pressure region up to 5.0 MPa, the inlet pressure was controlled by a pressure regulator (3). The dead volume (V_0) of the column was measured by an elution methods; that is, the retention volume of benzene on SG800 injected in a liquid methanol flow was regarded as V_0.

The column-outlet concentration ($C_{2,\mathrm{out}}$) was determined from the UV absorbance measured at 280 nm (acetone) or 250 nm (benzene) multiplied by the extinction coefficients of each solute. We prepared several sample gases of known concentrations of acetone and benzene diluted in CO_2, and measured the absorbance of each sample gas at pressures up to 15 MPa, from which the extinction coefficients of each solute were determined, and also the Lambert–Beer law was confirmed in the two cases. The silica gel (SG800) packed in columns [(4.46 mm (i.d.)×50 mm) and (4.60 mm (i.d.)×250 mm)] was of the large-pore type powder used in the previous IR experiments (pore size = 80 nm, particle size = 10μm, Fuji-Davison Co., Ltd.). The CO_2 was an ultra-high purity grade (99.99%) gas purchased from Iwatani Carbonics Co., Ltd. Acetone and benzene were extra-pure-grade reagents from Wako Chemical Co., Ltd. They were used without further purification.



1 : Gas cylinder
2 : Solvent bottle
3 : Pressure regulator
4 : Gas pump
5 : Organic solvent pump
6 : Computer
7 : Mixer
8 : Pressure transducer
9 : Injector
10 : Column
11 : Air thermostat
12 : UV detector
13 : Data analyzer
14 : Back pressure regulator
15 : Collector
16 : Gas flow meter

Fig. 1. Schematic diagram of experimental apparatus.

Theory

The adsorbed amount of solute (q_2) was determined by two methods: the conventional retention peak method and the ECP (Elution by Characteristic Point) method[10] according to the obtained chromatogram. The net retention volume (V_{N}) is defined as the retention volume (V_{R}) subtracted by the dead volume (V_0), where V_{R} is defined as the volumetric flow rate (F_{V}) at the column pressure (P_{col}) multiplied by the retention time (t_{R}),

$$V_{\mathrm{N}} \equiv V_{\mathrm{R}} - V_0. \tag{1}$$

The arithmetic average of the inlet pressure (P_{in}) and the outlet pressure (P_{out}) is used for P_{col}, and the value of F_{V} is determined by converting the flow rate measured at an atmospheric pressure to that at P_{col}.

When the shape of the chromatogram is Gaussian or quasi-Gaussian, V_{N} is related to the distribution coefficient (K_{d}) of the solute between the stationary phase and mobile phase through

$$V_{\mathrm{N}} = K_{\mathrm{d}} m, \tag{2}$$

where m is the mass of the absorbent packed in the column. The adsorbed amount of solute per unit mass of adsorbent is then calculated from

$$q_2 = K_{\mathrm{d}} y_2 / V_{\mathrm{m}}, \tag{3}$$

where y_2 and V_{m} are the mole fraction of the solute and the molar volume of pure CO_2, respectively, at P_{col}. The value of y_2 is evaluated from the mole fraction at the column-outlet, $y_{2,\mathrm{out}}$ $(=C_{2,\mathrm{out}} V_{\mathrm{m,out}})$, multiplied by $V_{\mathrm{m}}/V_{\mathrm{m,out}}$, a correction factor converting the mole fraction at P_{out} to that at P_{col}.

When chromatograms of varying concentration have peak maxima lying virtually on the common envelope formed by the coincident diffuse boundaries, the ECP method may be applicable to calculate q_2. The ECP method is based on the assumption that during migration of the diffuse boundary through a column the derivative of q_2 with respect to the concentration of solute ($\partial q_2/\partial C_2$) is constant when the mobile-phase concentration C_2 is kept constant. Integration of the mass-balance equation in a column subject to the condition of constant C_2 gives the relation between V_{N} and the derivative $\partial q_2/\partial C_2$ at C_2 and P_{col} as

$$V_{\mathrm{N}} = m\left(\frac{\partial q_2}{\partial C_2}\right)_{P=P_{\mathrm{col}}}. \tag{4}$$

The derivation of the above Equation 4 is given elsewhere.[10] The adsorbed amount of solute (q_2) is then calculated by integrating the derivative as

$$q_2 = \int_0^{C_{2,\mathrm{out}}} \left(\frac{\partial q_2}{\partial C_2}\right) \mathrm{d}C_2. \tag{5}$$

The mole fraction of solute (y_2) at P_{col}, corresponding to q_2 evaluated through Eqs. 4 and 5, is calculated as $y_2 = C_{2,\mathrm{out}} V_{\mathrm{m}}$, as mentioned in the above paragraph.

Results and Discussion

Adsorption of Acetone. Figure 2 shows the elution behavior of acetone on SG800/CO_2 at 313.2 K and different pressures ((A) 2.2, (B) 5.6, (C) 10.0, and (D) 15.0 MPa) for different amounts of injection. Each elution curve in Figs. 2A, 2B, 2C, and 2D has a common envelope formed by the coincident rear diffuse boundaries. The common rear diffuse side indicates that there exist energetically heterogeneous sites on silica gel SG800 for acetone; that is, acetone molecules adsorbed on more stable sites are delayed in desorption until the concentration of the fluid phase becomes low. The ECP method was applied to determine the adsorption isotherms of acetone at each column pressure.

Figure 3 shows the experimental adsorptions of acetone, q_2, at constant total pressure, P, against the partial pressure of acetone, y_2P. The numbers in the Fig. 3 denote the total pressure in MPa. If the adsorption of acetone is solely determined by the partial pressure, all of the curves should coincide; however, the adsorption curves decrease along with an increase in the total pressure, which suggests two factors determining the adsorption at high pressures: (1) the vapor-phase non-ideality, or the enhanced solubility in CO_2, and (2) the competitive adsorption of CO_2 suppressing the adsorption of acetone. The adsorption curves at low pressures show a sharp bend at a relatively low partial pressure, and then increase with increasing partial pressure with a slightly decreasing gradient. The sharp bend reflects the existence of strongly active sites for acetone.

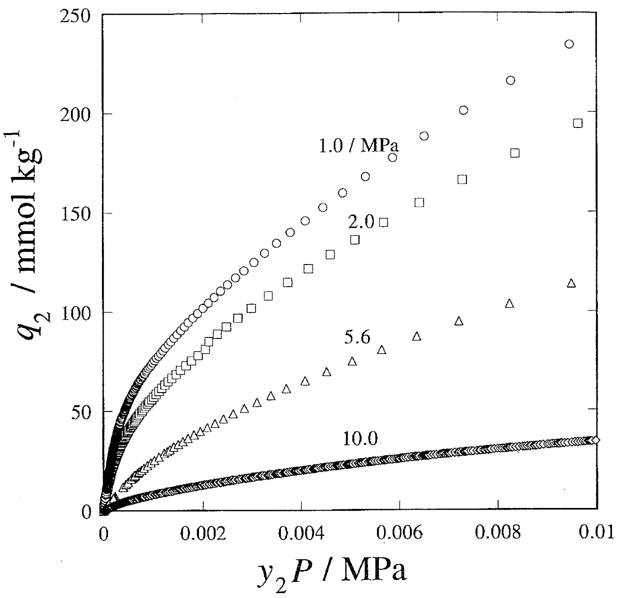


Fig. 3. Adsorption isotherm of acetone on SG800/CO_2 at 313.2 K.

It is noted here that the tailing curves observed at high pressures in Figs. 2C and 2D indicate that acetone molecules have become adsorbed on active sites under competition with CO_2 molecules. Evidence for this competing adsorption between acetone and CO_2 was observed in previous experiments in-

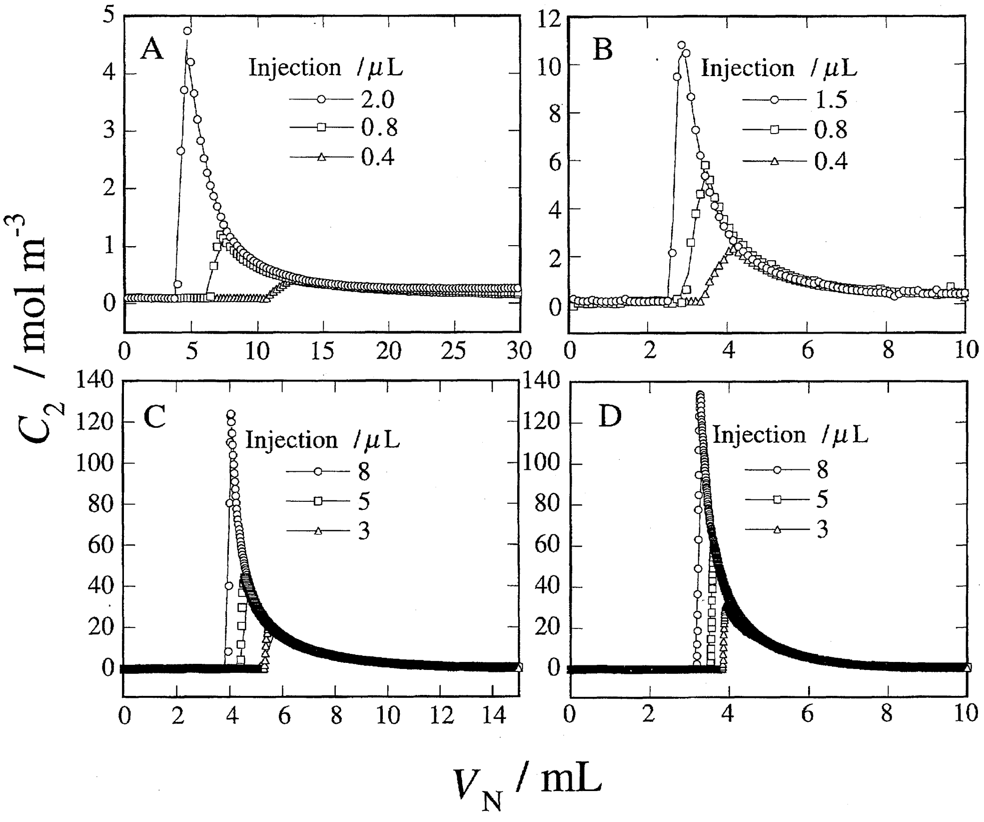


Fig. 2. Elution behavior of acetone adsorbed on SG800/CO_2 at 313.2 K: (A) 2.2 MPa, (B) 5.6 MPa (4.46 mm (i.d.)×50 mm (L)), (C) 10.0 MPa, and (D) 15.0 MPa (4.60 mm (i.d.)×250 mm (L)).

volving FTIR spectroscopy;[8] that is, the C=O stretching vibration band at approximately 1700 cm^{-1} gradually shifted downward (red-shift) with increasing pressure due to the formation of hydrogen bonding with OH groups on silica gel. The gradual red-shifts occurred simultaneously along with a decrease in the absorbance of the difference spectra of the hydrogen-bonded C=O group, which might be evidence indicating that acetone molecules adsorbed on more active sites (more red-shifts) could compete with CO_2 molecules having a higher adsorption potential at an increased pressure.

Figure 4 shows the pressure dependence of the amount of acetone adsorbed from fluid mixtures of constant y_2 at 313.2 K. The two solid lines represent the chromatographic adsorptions at $y_2=0.002$ and 0.004, respectively, which were determined from the adsorption isotherms shown in Fig. 3, while the two broken lines represent the integral absorbance of the hydrogen-bonded OH band at $y_2=0.002$ and 0.01 measured by the FTIR technique.[8] The chromatographic adsorption isotherms (solid lines) show a maximum at a pressure ranging from 2 to 6 MPa, and then decrease with increasing pressure until 15 MPa. The spectroscopic isotherms (broken lines) show a maximum at about 2 MPa, and then decrease with increasing pressure. We may conclude that the chromatographic and spectroscopic data provide similar characteristic curves for the adsorption equilibrium of acetone against the pressure, though we observe two different features: (a) the pressures corresponding to the maximum adsorption are different and (b) at high pressures the chromatographic lines decrease more sharply than do IR spectroscopic lines.

The spectroscopic isotherms indicate the amount of OH groups that are hydrogen-bonded with C=O groups, while the chromatographic isotherms include contributions of two interactions: the hydrogen bonding and the van der Waals interaction. The former is strong and specific, while the latter is weak and non-specific. Therefore, the relative contribution of the weak van der Waals interaction to the chromatographic adsorption decreases in the high-pressure region where the adsorption potential of CO_2 increases, which may result in a larger decrease in the chromatographic adsorption isotherms than the decrease in the spectroscopic ones.

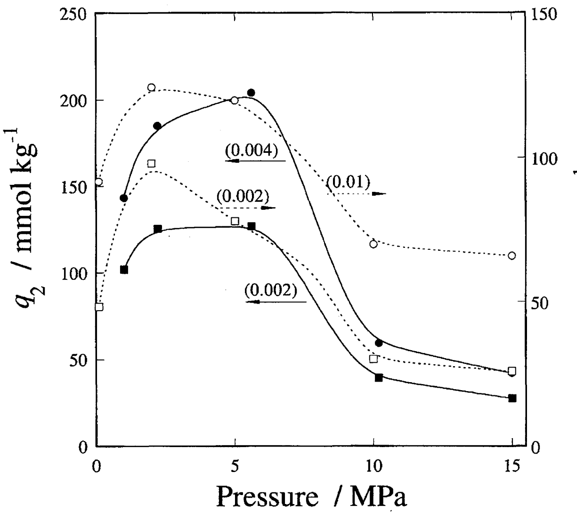


Fig. 4. Adsorbed amount and integral absorbance of acetone on SG800/CO_2 at 313.2 K; The numbers in parenthesis indicate mole fraction of acetone in a fluid, y_2: solid lines and broken lines represent the chromatographic adsorption and integral absorbance, respectively.

Figure 5 shows the pressure dependence of the amount of acetone adsorbed on SG800 for two compositions, $y_2=0.002$ and 0.004, at 313.2 K (solid lines) and 333.2 K (broken lines). It is noted that the solid and the broken lines for each composition coincide at approximately 7.3 MPa; that is, in the low-pressure region the adsorbed amount of acetone decreases with increasing temperature, while it increases in the high-pressure region. This crossover phenomenon may be called the fluid density effect, since in the supercritical fluid region and under the constant-pressure condition, the fluid density decreases significantly along with an increase in the temperature, and that the decrease in density causes decreases in the solvent power (solubility of solutes) so as to overcome the increase in escaping tendency of the solute from the surface due to the temperature increase. As a whole, the adsorption of the solute increases along with temperature under the condition of constant pressure. Tan and Liou[3] reported that the crossover of the equilibrium adsorption loading occurred when the bulk concentration of toluene in supercritical carbon dioxide was fixed. Though we fixed the mole fraction of the fluid, and their experimental system is different from ours, the crossover phenomenon was observed, which may be one of the important adsorption characteristics in SCF.

Adsorption of Benzene. Figure 6 shows the elution behavior of benzene on SG800/CO_2 at 313.2 K and different pressures ((A) 1.0, (B) 2.0, (C) 5.5, and (D) 10.0 MPa) with different amounts of injection. In Figs. 6A and 6B, the elution behavior of benzene is similar to that of acetone, showing the common rear envelope formed by the coincident diffuse boundaries, which indicates that the surface of SG800 is en-

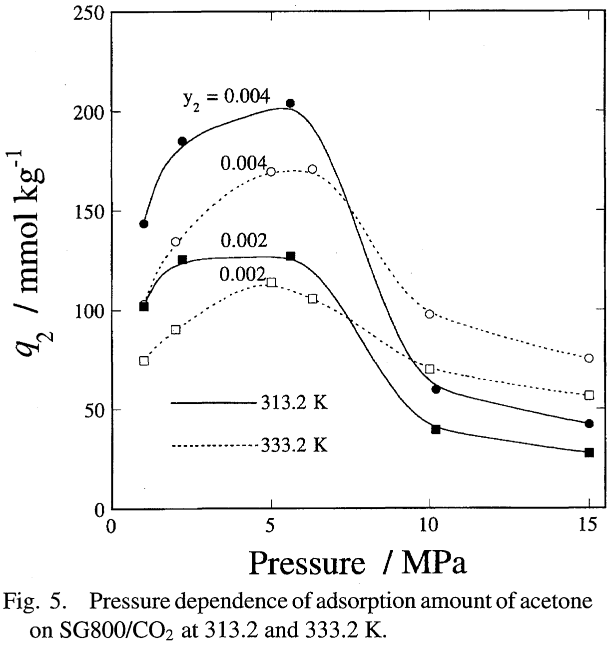


Fig. 5. Pressure dependence of adsorption amount of acetone on SG800/CO_2 at 313.2 and 333.2 K.

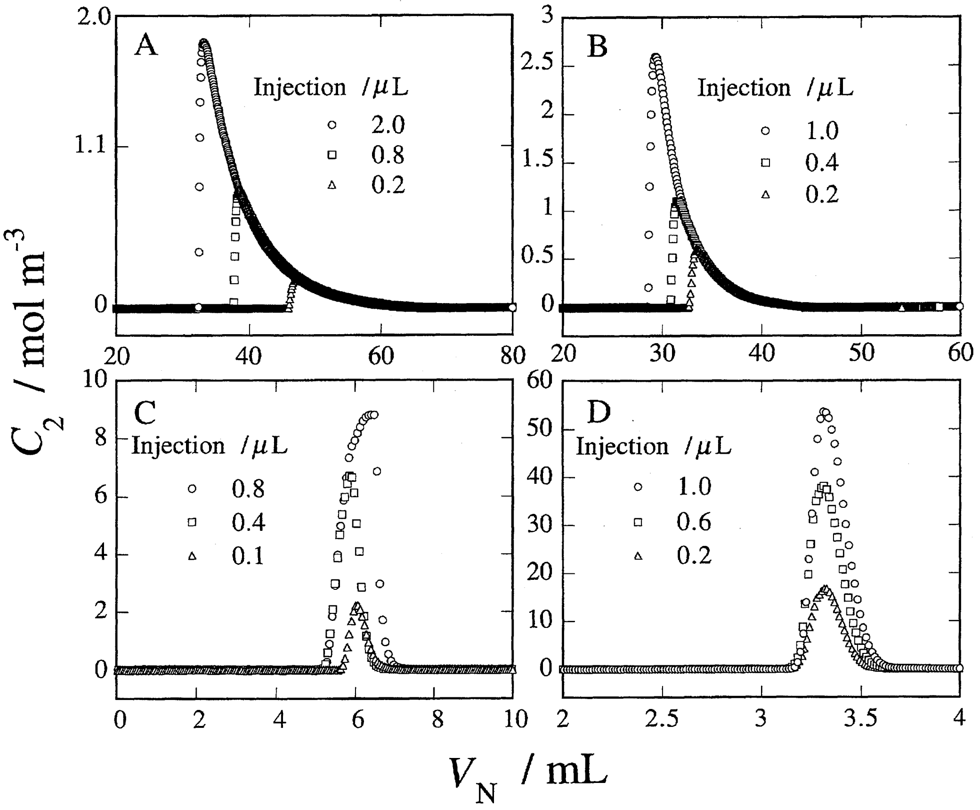


Fig. 6. Elution behavior of benzene adsorbed on SG800/CO_2 at 313.2 K: (A) 1.0 MPa, (B) 2.0 MPa, (C) 5.5 MPa, and (D) 10.0 MPa.

ergetically heterogeneous for benzene molecules. On the other hand, at pressures greater than 5.5 MPa, the elution curves of benzene appear to be nearly Gaussian, as shown in Figs. 6C and 6D, except for the curve of the largest injection in Fig. 6C, where overloading behavior is observed. The change in the elution behavior, from common rear envelopes to near-Gaussian curves, may suggest the following explanations for the adsorption of benzene: (1) most of the silica gel surface, including the active sites for benzene, may be covered with CO_2 molecules at high pressures; (2) the frequency of exchange of the adsorbed CO_2 molecules by benzene molecules may become low, since the major interaction of benzene with the silica surface is the van der Waals force, and it is not so strong as that of acetone; and (3) the overloading profile in Fig. 6C may be ascribed to the curvature of the adsorption isotherm, being concave upward ($\partial^2 q_2/\partial C_2^2 > 0$) at a high concentration of benzene, though this type of isotherm is not common for adsorption equilibria. One possibility of concerning this type is due to the solubility limit of benzene in the fluid phase; that is, the amount of benzene in the mobile phase at the column inlet might have exceeded the saturated mole fraction of benzene in the vapor phase. At pressures higher than 7 MPa, no overloading elution behavior was observed, since the solubility in CO_2 increases dramatically. The above explanation seems to be supported by vapor–liquid equilibrium data for binary mixtures of CO_2 and benzene at 313.15 K measured by Ohgaki and Katayama.[11] In determining the value of K_d through the elution peak method, we limited the concentration of benzene to be lower than 0.002 in y_2, where no overloading was observed.

Figure 7 shows the pressure dependence of the amount of benzene adsorbed on SG800 for two compositions, y_2 = 0.001 and 0.002, at 313.2 K (solid lines) and 333.2 K (broken lines). At first glance, the adsorbed amount of benzene is much smaller than that of acetone; it is about one fourth the

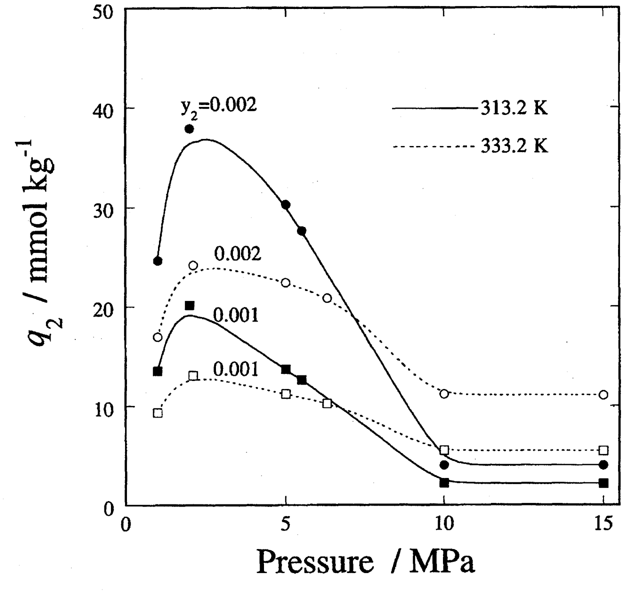


Fig. 7. Pressure dependence of adsorption amount of benzene on SG800/CO_2 at 313.2 and 333.2 K.

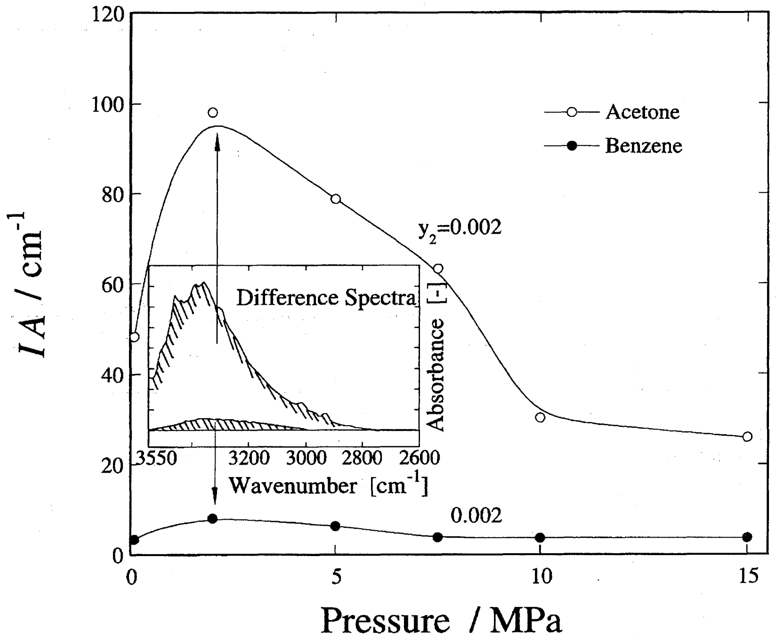


Fig. 8. Integral absorbance vs. pressure for hydrogen-bonded OH stretch band on SG800 (10 mg) for acetone and benzene (y_2=0.002) diluted in CO_2 at 313.2 K.

adsorption of acetone. All of the adsorption curves have a maximum at about 2.0 MPa, and the curves at 313.2 K show a rapid decrease with increasing pressure, which may be ascribed to the weak van der Waals interaction of benzene with the silica gel surface. The crossover phenomenon occurred at approximately 6.5—7.3 MPa, which is almost the same as in the case of the adsorption of acetone.

IR Spectroscopy. Figure 8 shows the pressure dependence of the integral absorbance determined from the difference spectra of hydrogen-bonded OH stretching vibration adsorbed by acetone and benzene from a dilute solution (y_2=0.002) in CO_2 at 313.2 K. The experimental apparatus and procedures have been reported elsewhere.[8] The difference spectra at 2 MPa for acetone and benzene are shown in the small inside figure, where the hatched lines are drawn to indicate the absorbance area integrated. The maximum integral absorbances are observed at about 2 MPa for the two solutes; the pressure dependence of the two curves are similar in shape, though the integral absorbance of benzene is very weak compared with that of acetone. It may be concluded that the adsorption characteristic of benzene in supercritical CO_2 is controlled by the van der Waals interaction, while that of acetone is affected by the two interactions, the hydrogen bonding and the van der Waals interaction, which result in slightly different curves for the adsorption isotherms of acetone and benzene.

Conclusions

The physical adsorptions of acetone and benzene on a silica gel (SG800) in supercritical CO_2 have been measured at 313.2 and 333.2 K and at pressures up to 15.0 MPa using a chromatographic technique. The elution curves of acetone showed typical tailing with a common diffuse boundary, which indicated that the SG800 surface was heterogeneous. On the other hand, the elution curves of benzene showed typical tailing at low pressures and semi-Gaussian behavior at high pressures, which indicated that the surface was also heterogeneous for benzene, and that at high pressures the strong active sites were almost covered by CO_2 molecules. It is suggested that the adsorption potential of benzene was weak due to the van der Waals interaction.

The chromatographic and the spectroscopic isotherm curves of acetone and benzene showed almost the same feature, having a maximum (P_{max}) at a pressure lower than P_c of CO_2, and decreasing with increasing pressure over the high-pressure region, though some different features were observed in isotherms of acetone obtained from the two techniques. The two isotherm curves at 313.2 and 333.2 K showed a crossover point at a relatively high pressure close to P_c of CO_2; that is, in the SCF region, the adsorption isotherm curves at a higher temperature were higher than the curves at a lower temperature, which is an unusual characteristic for adsorption in SCF, mainly due to the so-called fluid density effect with changing the temperature.

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References

1) M. McHugh and V. Krukonis, "Supercritical Fluid Extraction," 2nd ed, Butterworth-Heinemann, USA (1994).

2) "Supercritical Fluid Chromatography," ed by R. M. Smith, The Royal Soc. Chem., England (1988), Chaps. 1 and 3.

3) C.-S. Tan and D.-C. Liou, *Ind. Eng. Chem. Res.*, **29**, 1412 (1990).

4) C-H. Lee, S. H. Byeon, and G. D. Holder, *J. Chem. Eng. Jpn.*, **29**, 683 (1996).

5) H. Shojibara, Y. Sato, S. Takishima, and H. Masuoka, *J. Chem. Eng. Jpn.*, **28**, 245 (1995).

6) T. Nitta and J. Yoneya, *J. Chem. Eng. Jpn.*, **28**, 31 (1995).

7) T. Shigeta, J. Yoneya, and T. Nitta, *Mol. Simul.*, **16**, 291 (1996).

8) D. W. Jin, K. Onose, H. Furukawa, T. Nitta, and K. Ichimura, *J. Chem. Eng. Jpn.*, **29**, 139 (1996).

9) D. W. Jin and T. Nitta, *J. Chem. Eng. Jpn.*, **29**, 708 (1996).

10) J. R. Conder and C. L. Young, "Physicochemical Measurement by Gas Chromatography," New York (1979), Chap. 9.

11) K. Ohgaki and T. Katayama, *J. Chem. Eng. Data.*, **21**, 53 (1976).