Chromatography Theory: Application to Supercritical Fluid Extraction

The adsorption equilibrium constants for naphthalene on alumina have been measured in the presence of subcritical and supercritical carbon dioxide by the dynamic tracer response technique. The equilibrium constants decrease with increases in density, and the isochoric temperature dependency is very small at supercritical conditions. Through chromatography theory, an expression has been developed for the density dependency of the capacity factor, a quantity related to the adsorption equilibrium constant by the porosity and density of the particle and the porosity of the bed, in terms of the partial molar volume of the solute at infinite dilution in the fluid phase. The partial molar volumes extracted from the data agree well with the published data. Investigation of the dynamics of the bed shows that a model, including axial dispersion and effective diffusion into the pores, successfully represents the data. The effective diffusivities and the axial dispersion coefficients were also extracted from the second central moments of the response curves at each condition.

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Introduction

Supercritical fluids (SCFs) have received increased attention in the chemical, food, pharmaceutical and biochemical industries in the last decade. The solvent power of SCFs for dissolving nonvolatile substances approaches that of conventional solvents due to liquid-like densities. The low viscosity of SCFs and high solute diffusivities in SCFs result in superior mass transfer characteristics compared to traditional organic solvents. The high compressibility of SCFs near the critical point enables the separation of the extract by slight changes in temperature and pressure. As a result of these properties, extensive research and development work have been conducted in the last decade involving SCFs for development of new separation processes. The monographs by Stahl et al. (1988) and McHugh and Krukonis (1986) provide an excellent introduction to the field. Some important potential applications of SCF extraction from solid matrices include: removal of organic contaminants from soil (Dooley et al., 1987; Roop et al., 1989); removal of insoluble materials from coal extract (Adams et al., 1979); regeneration of catalysts (Tilscher et al., 1981); and adsorbents (Modell et al., 1980) and purification of polymers (McHugh and Krukonis, 1986).

In extraction from solid matrices, the adsorption isotherm for the solute in the presence of a SCF determines the thermodynamic extent of the extraction. Unfortunately, such studies are relatively few. Most of the research on SCFs have concentrated on phase behavior in SCF solutions. Kander and Paulaitis (1983) measured the adsorption isotherms for phenol adsorbed onto activated carbon in the presence of supercritical carbon dioxide (SCCO$_2$) at 309 and 333 K. For very dilute solutions, the adsorption isotherm behaves linearly, where the concentration in the SCF phase is proportional to that in the solid phase. The proportionality constant is defined as the adsorption equilibrium constant. Tan and Liou (1988) and Srinivasan et al. (1989) reported adsorption equilibrium constants for desorption of ethyl acetate from activated carbon using SCCO$_2$.

Supercritical fluid chromatography has been receiving increasing attention for separating high molecular weight and thermally labile compounds. The extent of the separation is mainly determined by the adsorption equilibrium constant. Since separation is achieved by temperature or pressure programming, the knowledge of the dependence of the equilibrium constant on temperature and pressure is a key factor in design of chromato-

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graphic columns. In addition, the rates of mass transfer, axial dispersion, adsorption and effective diffusion into the pores also contribute to the separation. These rate processes are also very important in designing commercial extractors and catalytic reactors involving SCFs as a reaction medium. At present, our understanding of these processes is limited due to lack of sufficient experimental data.

We have measured the adsorption equilibrium constants for naphthalene on alumina in the presence of CO_2 at 298.0, 308.4 and 318.0 K in the pressure range 77.7–308.6 bar using dynamic tracer response experiments. The partial molar volumes of naphthalene at infinite dilution in $SCCO_2$ were extracted from the isothermal density dependence of the equilibrium constants. The axial dispersion coefficients and the effective diffusivities were also measured at each condition.

Experimental Setup

A schematic diagram of the experimental setup is given in Figure 1. A syringe pump, ISCO LC-2600, modified for supercritical fluid chromatography, is filled with liquid CO_2 and compressed up to 80 bar using nitrogen. The pump is started and CO_2 starts to flow through the preheater, the stainless steel tube packed with alumina particles and the high-pressure UV detector with an internal volume of 500 μL (LDC Analytical). The internal diameter of the tube was determined by weighing the tube filled with distilled and deionized water. Constant mass flow rates are achieved by circulating water at a constant temperature through a copper coil wrapped around the cylinder of the pump.

The system pressure is established by a back-pressure regulator (Tescom Inc. 26-1722-24) placed after the detector. A second back-pressure regulator (Grove SD91-W), set at approximately 80 bar, enables CO_2 to go through a double-expansion process. The flow rate is monitored by a wet testmeter (Singer DTM-115) placed after the second back-pressure regulator. The pressure is measured by a factory-calibrated pressure transducer (Hydronic A 006220 TH-1V) placed after the detector with an accuracy of ±.7 bar.

The tube, the injection valve, and the backpressure regulators are immersed in a water bath. The temperature of the bath is controlled to ±0.2°C with an immersion circulator (Haake D1). A 20 μL pulse of naphthalene dissolved in CO_2 is introduced into the column through a high-pressure injection valve (Rheodyne Model 7010). The sample solution is prepared by passing high-pressure liquid CO_2 through a saturator packed with naphthalene. A metal filter placed at the bottom of the saturator prevents the entrainment of the solute. The response from the detector is recorded on a disk at equal time intervals for analysis.

Activated alumina (Alltech, Unibeads-A, spherical, 80/100 mesh) was used as the solid phase in the experiments. The particles were first sieved and washed with water to remove the fines and dried overnight in an oven at 383 K. After the drying was complete, the particles were sieved again to the desired particle size. The bed porosity was measured by weighing a known volume of particles. The density of alumina required for the calculation was measured by mercury porosimetry. The particle porosity was measured by dynamic tracer response experiments in a similar equipment by using argon as a

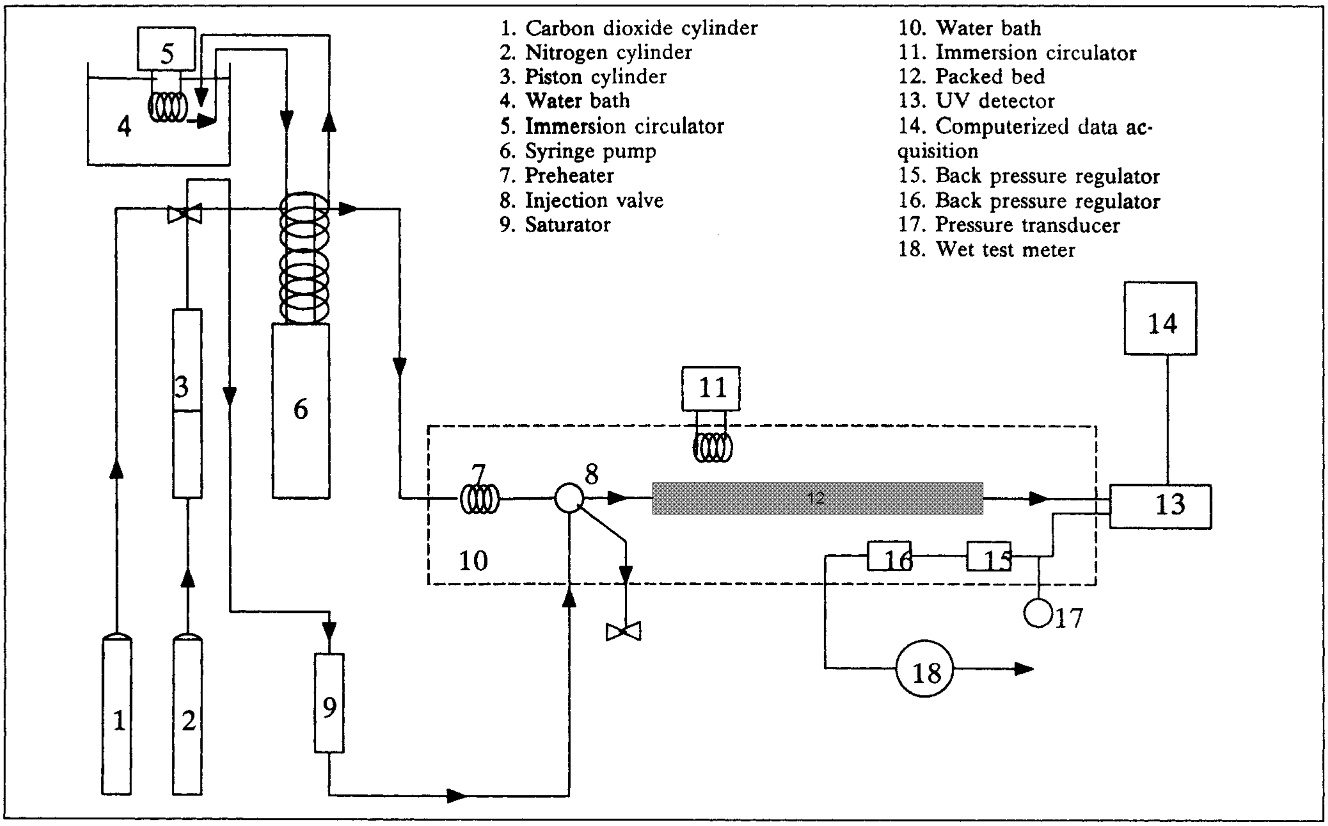

Figure 1. Experimental setup.

nonadsorbing tracer. In these experiments, heptane was used as the mobile phase and detection was performed with a differential refractive index detector (LDC/Milton Roy Refractomonitor III). The mean pore diameter and the specific surface area of the particles were determined by nitrogen adsorption. The particle pore volume obtained from nitrogen adsorption checks within 5% of the value determined by argon tracer. The specifications of the bed and the particles are given in Table 1.

Results

The system is governed by a system of coupled partial differential equations. The first and second moments of the response curve for the system are (Wakao and Kaguei, 1982):

$$t_R = \mu_1 - \mu_I = \frac{L}{U}(1 + \delta_0) \tag{1}$$

$$\sigma_m^2 = \mu_2' - \mu_{II} = \frac{2L}{U}\left[\delta_1 + D_{ax}(1 + \delta_0)^2 \frac{1}{U^2}\right] \tag{2}$$

where

$$\delta_0 = \frac{1 - \alpha}{\alpha}[\beta + \rho_p K_A] \tag{3}$$

$$\delta_1 = \frac{1 - \alpha}{\alpha}\left[\frac{\rho_p K_A^2}{k_a} + (\beta + \rho_p K_A)^2 \left(\frac{1}{5D_e} + \frac{1}{k_f R}\right)\frac{R^2}{3}\right] \tag{4}$$

where μ_I and μ_{II} are the moments for the input signal, obtained through experiments with the bed removed from the system. Such a subtraction procedure also helps to eliminate the effects of dispersion in the detector cell and in the connecting tubing on the measured parameters. The first and second moments are calculated by finite summation.

$$\mu_1 = \frac{\int_0^\infty C(t, L)\,t\,dt}{\int_0^\infty C(t, L)\,dt} \tag{5}$$

$$\mu_2' = \frac{\int_0^\infty C(t, L)(t - \mu_1)^2 dt}{\int_0^\infty C(t, L)\,dt} \tag{6}$$

Determination of adsorption equilibrium constants

K_A can be estimated from the slope of the straight line passing through the origin of a plot of t_R vs. L/U. The plots are presented in Figures 2, 3, and 4 for the three temperatures investigated in this study. The observed linearity confirms the assumption of linear equilibrium and the corresponding K_A values are presented in Table 2. A decrease is observed in K_A values with increases in density at a constant temperature. At a constant density, a significant reduction is observed when the temperature changes from subcritical to supercritical conditions. The isochoric temperature dependency, however, is small at supercritical conditions, at least in the pressure range investigated in this study.

Table 1. Properties of the Packed Bed

Bed length	0.2418 m
Bed diameter	0.00474 m
Bed porosity, α	0.38
Particle radius, R	75×10^{-6} m
Particle porosity, β	0.48
Particle density, ρ_p	2,140 kg/m^3
Mean pore diameter	80×10^{-10} m
Specific surface area	216 m^2/g

Determination of solute partial molar volumes at infinite dilution in SCF

Partial molar volume of the solute at infinite dilution in the supercritical fluid is a very important property for probing molecular interactions (Brennecke and Eckert, 1989). At the vicinity of the critical point, very large negative partial molar volumes are observed due to condensation of solvent molecules around the solute which results in a much greater local density than the bulk density of the fluid. This phenomenon, called clustering, is extremely important in SCF-phase equilibria since the degree of clustering is related to the solute–solvent interaction strength (Johnston et al., 1989), which in turn influences other macroscopic properties, such as solubilities. Such data are difficult to obtain at the vicinity of the critical point. This property also plays a major role in the pressure and temperature dependency of the capacity factors in supercritical fluid chromatography and has been used by various investigators for developing a thermodynamic description of solute retention (van Wasen and Schneider, 1980; Yonker et al., 1987; Yonker and Smith, 1988). In chromatography, solute retention is expressed as a dimensionless residence time called the capacity factor:

$$k = \frac{t_R - t_o}{t_o} = \frac{C^{sp}}{C^{mp}}\frac{V^{sp}}{V^{mp}} \tag{7}$$

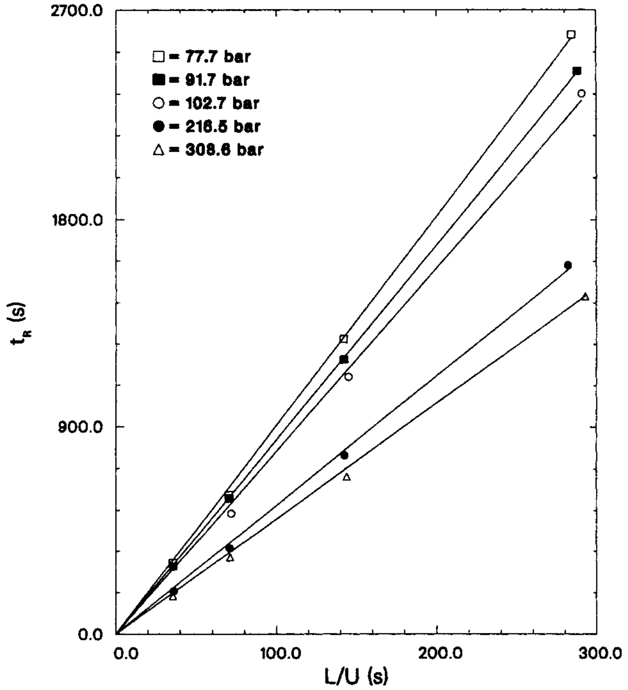

Figure 2. Variation of retention time with L/U at 298.0 K.

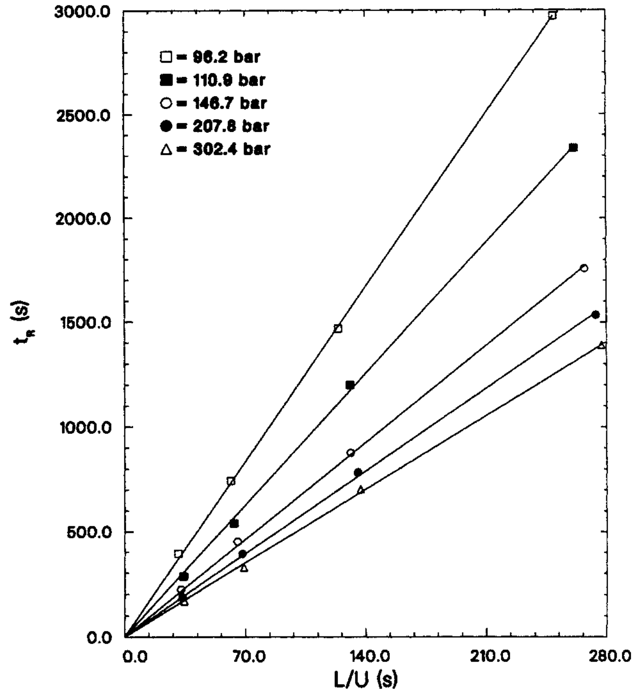

Figure 3. Variation of retention time with L/U at 308.4 K.

where t_o is the residence time for an unretained solute,

$$t_o = \frac{L}{U}\left[1 + \frac{(1-\alpha)}{\alpha}\beta\right] \tag{8}$$

C^{sp} and C^{mp} are concentrations of solute in the stationary phase and in the mobile phase, and V^{sp} and V^{mp} are the total volumes occupied by the stationary phase and the mobile phase.

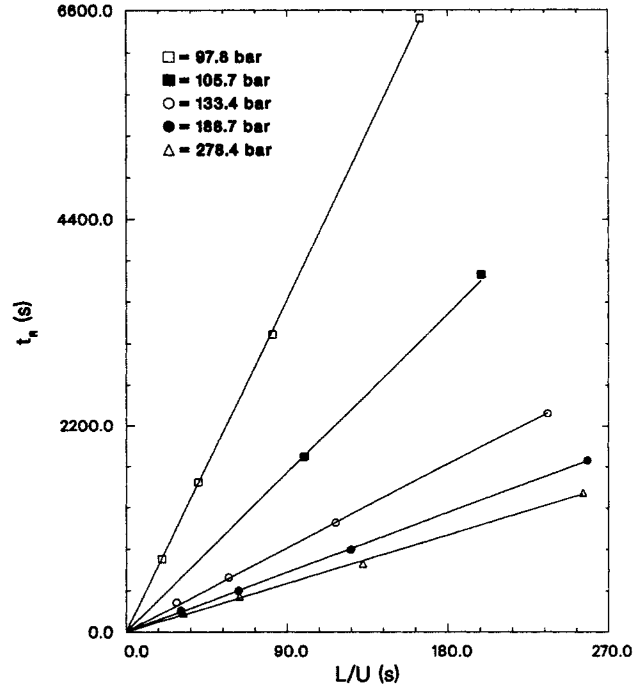

Figure 4. Variation of retention time with L/U at 318.0 K.

Table 2. Adsorption Equilibrium Constants for the Alumina-Naphthalene-CO_2 System

T(K)	P(bar)	$10^{-3}\rho$(kg/m^3)	10^3K_A(m^3/kg)
298.0	77.7	0.772	3.69
298.0	91.7	0.805	3.40
298.0	102.7	0.823	3.17
298.0	216.5	0.925	2.09
298.0	308.6	0.971	1.69
308.4	96.2	0.695	2.91
308.4	110.9	0.745	2.06
308.4	146.7	0.810	1.38
308.4	207.8	0.871	1.11
308.4	302.4	0.930	0.93
318.0	97.8	0.469	10.79
318.0	105.2	0.574	4.86
318.0	133.4	0.706	2.34
318.0	188.7	0.801	1.51
318.0	278.4	0.878	1.14

Recently, an expression was developed by Chimowitz and Kelly (1989) that relates the density dependence of the capacity factor in supercritical fluid chromatography to the partial molar volume of the solute at infinite dilution by the expressions:

$$\left(\frac{\partial \ln k}{\partial \ln \rho}\right)_T = -\left(1 - \frac{\overline{V}_1^{mp,\infty}}{R_g T K_T}\right) \tag{9}$$

where R_g is the gas constant and K_T is the isothermal compressibility of the fluid. The above expression was developed based on the experimental evidence given by Kumar and Johnston (1986) that $\overline{V}_1/K_T$ is nearly independent of density in the vicinity of the critical point. The above linearity was shown to hold even far away from the critical point. The linear variation of logarithm of density with that of capacity factor was also shown by van Wasen and Schneider (1980).

The following treatment provides an easy way of measuring partial molar volumes of solutes at infinite dilution near the critical point. The density dependence of the capacity factor is given by the expression (Yonker and Smith, 1988):

$$\left(\frac{\partial \ln k}{\partial \rho}\right)_T = \left(\frac{\partial P}{\partial \rho}\right)_T\left[\frac{\overline{V}_1^{mp,\infty} - \overline{V}_1^{sp,\infty}}{R_g T} - K_T\right] \tag{10}$$

Through the transformation $\partial\rho = \rho\partial \ln \rho$, the above expression reduces to:

$$\left(\frac{\partial \ln k}{\partial \ln \rho}\right)_T = \left[\frac{\overline{V}_1^{mp,\infty} - \overline{V}_1^{sp,\infty}}{R_g T K_T} - 1\right] \tag{11}$$

where (van Wasen and Schneider, 1980):

$$\overline{V}_1^{sp,\infty} = (V_m^{s1}/V_m^{smb})\,V_m^{mb} \tag{12}$$

where V_m represents molar volume, $s1$ the solute in the solid phase and smb the mobile phase in the solid phase. If there is a linear relationship between ln k and ln ρ, then the righthand side of Eq. 11 can be used to calculate the partial molar volume of the solute at infinite dilution. The above relation also reduces to Eq.

9, the expression developed by Chimowitz and Kelly (1989) for $\overline{V}_1^{sp,\infty}$ equals zero. In the vicinity of the critical point, where large negative partial molar volumes are observed, the contribution of the partial molar volume of the solute in the stationary phase is small. Therefore, Eq. 9 is qualitatively correct; however, it cannot predict the positive partial molar volumes above a certain density.

The data obtained in this study were used to calculate the partial molar volumes of naphthalene at infinite dilution in supercritical carbon dioxide to provide a comparison with the data of Eckert et al. (1986) obtained with the use of a high-precision densitometer. The adsorption equilibrium constant is related to the capacity factor by the expression through Eqs. 1, 3, 7, and 8:

$$k = \frac{(1 - \alpha)\rho_p K_A}{(1 - \alpha)\beta + \alpha} \tag{13}$$

The dependence of ln k on ln ρ for the three temperatures is shown in Figure 5. The partial molar volumes calculated from the slopes of these straight lines using Eqs. 11 and 12 are given in Figure 6 and compared with the data of Eckert et al. (1986). The densities and the isothermal compressibilities were calculated from an equation of state given by IUPAC (1976). The agreement is very good which indicates that the model developed is correct. Thus, two capacity factor measurements at two different densities would enable the calculation of partial molar volumes across a wide density range. Likewise, one measurement can be extended across a wide density range using an equation of state to calculate the partial molar volumes. However, at present there are no equations of state which can accurately predict the partial molar volumes near the critical point. The linearity also eliminates the need to know the solubility of the solute in SCF from which the binary interaction parameter is regressed. The above conclusions are also true for adsorption equilibrium constants since they are related to capacity factors through Eq. 13.

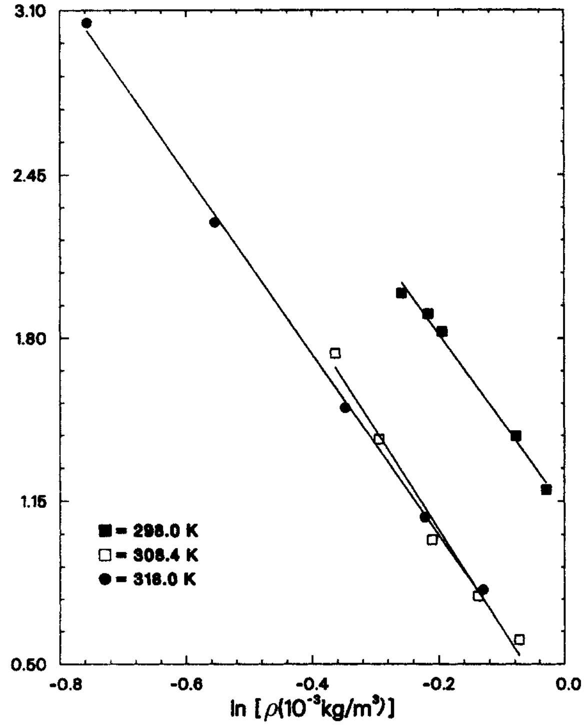

Figure 5. Variation of capacity factor with density.

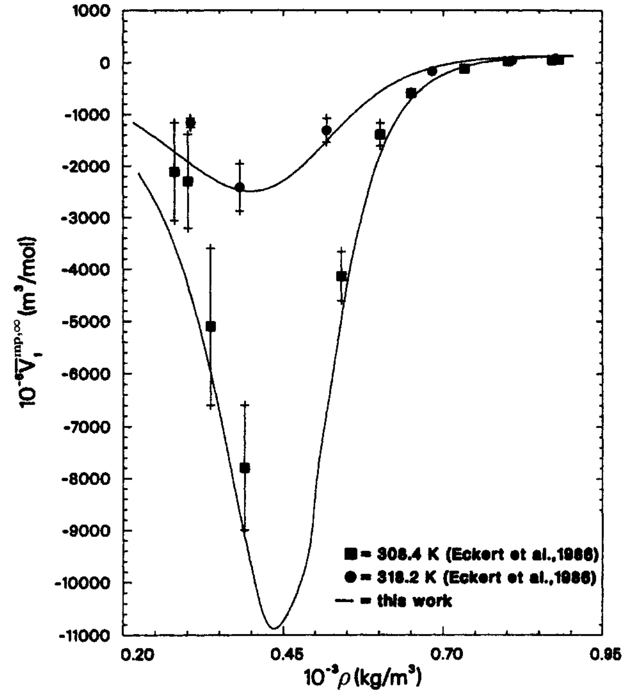

Figure 6. Partial molar volumes of naphthalene at infinite dilution in SCCO$_2$ as a function of density.

Determination of hydrodynamic and transport properties

The external mass transfer resistance was found to be very small compared to the intraparticle diffusion resistance for the Reynolds numbers employed in this study. The term $5/k_f R$ in Eq. 4 is much smaller than the term $1/D_e$ based on mass transfer coefficients calculated by a correlation developed by Lim et al. (1989) for solid-fluid mass transfer in a packed bed under supercritical conditions. Usually rates of physical adsorption are very fast, and the contribution of the rate to the second central moment can be neglected. The magnitude of the adsorption rate constants reported for ethyl acetate onto activated carbon in the presence of supercritical carbon dioxide also confirms this assumption (Srinivasan et al., 1989). D_{ax}/U can be considered constant for low Reynolds numbers in packed beds (Bischoff, 1960). This was also shown to be the case for liquid chromatographic separation of amino acids on silica gel (Uddin et al., 1990). Then, Eq. 2 reduces to:

$$\frac{\sigma_m^2 (1 + \delta_o)^2 L}{2 t_R^2} = \delta_1' U + \frac{D_{ax}}{U}(1 + \delta_o)^2 \tag{14}$$

where

$$\delta_1' = \frac{R^2 (1 - \alpha)(\beta + \rho_p K_A)^2}{15 \alpha D_e} \tag{15}$$

Therefore, a plot of the lefthand side of Eq. 14 vs. the interstitial

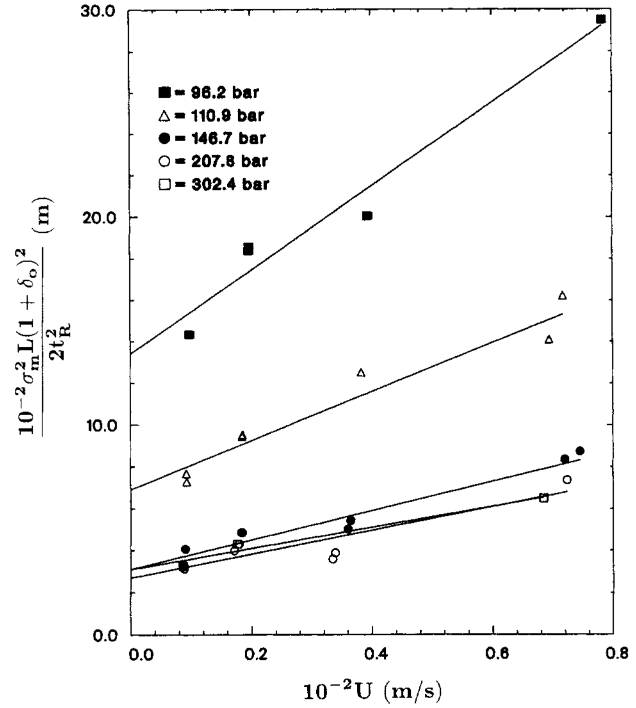

Figure 7. Variation of $\sigma_m^2(1 + \delta_o)^2\ L/2t_R^2$ with interstitial velocity at 308.4 K.

velocity should be linear, and from the slope and the intercept of such a line, the effective diffusivity and the axial dispersion coefficient can be estimated. This relation is shown in Figure 7 for 308.4 K. There is some scatter in the data, presumably due to the inaccuracies involved in the calculation of second central moments. The lines are reasonably straight showing that the model successfully describes the rate processes occurring in the system. The ratio of D_{AB}/D_e and the D_{ax}/U values measured at each condition is given in Table 3. The molecular diffusivities were calculated by a correlation given by Lamb et al. (1989), in which the experimental diffusivities of naphthalene are reproduced in SCCO$_2$ at 308 and 328 K with an average deviation of 5.5%. The correlation was assumed to hold at 298 K as well. Effective diffusivities are lower than bulk diffusivities, approximately by a factor of ten. Following the treatment by Satterfield et al. (1973) for liquids, the effective diffusivity is given by the expression:

$$D_e = \frac{D_{AB}\beta}{\tau} F(\lambda) \tag{16}$$

where τ is the tortuosity factor and $F(\lambda)$ is a factor that accounts for the restrictive diffusion effect given by (Beck and Schultz, 1972):

$$F(\lambda) = (1 - \lambda)^4 \tag{17}$$

where λ is the ratio of molecular diameter to pore diameter. The diameter of naphthalene was calculated as 6.06 A using the group contribution method of Bondi (1964), the average pore diameter was measured as 80 A by nitrogen adsorption method yielding a λ of 0.076. The average D_{AB}/D_e ratio in Table 3 indicates a value of 3.49 for the tortuosity factor which is reasonable considering that the tortuosity factors reported in the literature range from 2–5. This shows that Eq. 16 is also applicable for the determination of effective diffusivities in supercritical fluids.

Table 3. Effective Diffusivities and Peclet Numbers

T (K)	P (bar)	$10^5\eta$ (kg/m · s)	$10^9 D_{AB}$ (m^2/s)	D_{AB}/D_e	Pe
298.0	77.7	591.8	11.65	10.22	0.107
298.0	91.7	636.3	11.03	10.54	0.082
298.0	102.7	666.1	10.66	10.06	0.079
298.0	216.5	912.5	8.42	9.46	0.071
298.0	308.6	1,068.0	7.48	11.47	0.058
308.4	96.2	553.1	12.58	8.17	0.169
308.4	110.9	625.4	11.47	8.69	0.179
308.4	146.7	708.9	10.44	9.58	0.223
308.4	207.8	820.4	9.36	9.65	0.185
308.4	302.4	965.5	8.28	9.76	0.131
318.0	97.8	353.3	18.01	10.41	0.165
318.0	105.7	391.0	16.69	9.22	0.240
318.0	133.4	603.5	12.05	9.88	0.244
318.0	188.7	733.7	10.41	10.51	0.139
318.0	278.4	867.1	9.19	11.48	0.100
			Average:	9.94 ± 0.90	

The Peclet numbers were found to range from 0.058 to 0.244, which are lower than those reported for gases and liquids. The axial dispersion coefficients increase with increasing pressure suggesting that the dispersion process is controlled by convection and not by molecular diffusion at the low Reynolds numbers employed in this study.

Conclusion

A dynamic tracer response technique has been applied for simultaneous measurement of equilibrium and rate parameters in extraction from solid matrices using supercritical fluids. The adsorption equilibrium constants, the effective diffusivities, and the axial dispersion coefficients have been measured for the system naphthalene–alumina–CO$_2$. An expression was developed to extract partial molar volumes of the solute at infinite dilution in the fluid phase which relates the logarithm of density and capacity factors. The measured partial molar volumes of naphthalene in supercritical carbon dioxide were in good agreement with the data in the literature. The experimental technique is fast and reliable, and does not require calibration with its analysis being performed before expansion. The technique can also be expanded to obtain the whole adsorption isotherm.

Notation

C = concentration in the fluid phase, mol · m^{-3}
C^{mp} = concentration in the mobile phase, mol · m^{-3}
C^{sp} = concentration in the stationary phase, mol · m^{-3}
d_p = particle diameter, m
D_e = effective diffusivity, m^2 · s^{-1}
D_{AB} = molecular diffusivity, m^2 · s^{-1}
k = capacity factor
k_a = adsorption rate constant, m^3 · kg^{-3} · s^{-1}
k_f = mass transfer coefficient, m · s^{-1}
K_A = adsorption equilibrium constant, m^3 · kg^{-1}
K_T = isothermal compressibility, bar^{-1}
L = length of bed, m

P = pressure, bar
Pe = Peclet number, Ud_p/D_{ax}
R = particle radius, m
R_g = gas constant, $J \cdot K^{-1} \cdot mol^{-1}$
T = temperature, K
U = interstitial velocity, $m \cdot s^{-1}$
$\bar{V}_1^{sp,\infty}$ = partial molar volume of solute at infinite dilution in the stationary phase, $m^3 \cdot mol^{-1}$
$\bar{V}_1^{mp,\infty}$ = partial molar volume of solute at infinite dilution in the mobile phase, $m^3 \cdot mol^{-1}$
V_m = molar volume, $m^3 \cdot mol^{-1}$
V^{mp} = volume of the mobile phase, m^3
V^{sp} = volume of the stationary phase, m^3

Greek letters

ρ = fluid density, $kg \cdot m^{-3}$
ρ_p = particle density, $kg \cdot m^{-3}$
η = viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
β = particle porosity
α = bed porosity
μ_1 = first moment, s
μ_2 = second moment, s^2
λ = ratio of molecular diameter to pore diameter

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