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HIGH-PRESSURE ADSORPTION OF CARBON DIOXIDE ON SUPERCRITICAL-FLUID CHROMATOGRAPHY ADSORBENTS

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SUMMARY

Gibbs adsorption isotherms for sub- and supercritical carbon dioxide were measured on four common supercritical-fluid chromatography adsorbents, *viz.*, silica and octadecyl-, cyano- and diol-bonded silica, at 40°C from ambient pressure to 140 bar. All of the isotherms for supercritical carbon dioxide displayed maximum adsorption at pressures close to the critical pressure. Multilayer adsorption occurred at pressures close to the critical pressure in each system, and the type of bonded phase had little or no effect on the CO_2 adsorption isotherms. At subcritical pressures, multilayer adsorption of CO_2 occurred at relatively low pressures ($P_R \geqslant 0.4$). The adsorbed layer of "mobile" phase persisted to the highest experimental pressures (140 bar). Thus, at least a monolayer of adsorbed CO_2 will exist on the surface of adsorbent stationary phases under the conditions normally used for supercritical-fluid chromatography with CO_2 as the mobile phase. Both the density and dimensions of the adsorbed layer will vary with temperature and pressure.

INTRODUCTION

Adsorption isotherms of myriad systems have been measured at low pressures and temperatures for the investigation and interpretation of phase-transfer processes. Chromatographic adsorbents in particular have been extensively studied because of the unique duality of chromatographic systems in which the chromatographic performance is dictated by the characteristics of the phase distribution isotherm of the solutes and the mobile phase. As a consequence, the same chromatographic systems often provide an excellent means for measuring such phase distribution isotherms.

With the recently renewed interest in supercritical-fluid chromatography (SFC), the need for phase-distribution equilibria studies of the common SFC systems for the elucidation of the complex retention mechanism(s) has become apparent. However, adsorption isotherm measurements are difficult at the high pressures normally encountered with SFC. Consequently, relatively few quantitative investigations have been carried out for gas–solid *adsorption* or gas–liquid *absorption* equilibria under supercritical conditions.

In addition to the experimental difficulties, another problem is that at temperatures and pressures close to the critical point, the density of the fluid phase varies dramatically with pressure and ultimately approaches that of a liquid. In which case the amount of bulk fluid occupying the region adjacent to a surface will be significant even in the absence of a strong interfacial potential between the adsorbate and adsorbent (solid or liquid). This condition necessitates the use of the Gibbs adsorption model[1,2] in which the excess adsorption is defined in terms of the amount of adsorbate present at the surface in excess of the amount that would be present if the fluid density in this interfacial region were the same as the density of the bulk fluid. It is this "excess" quantity that is obtained by direct experimental measurements. "Absolute" adsorption is defined to be the total amount of adsorbate located within a layer of arbitrarily defined thickness adjacent to the adsorbent surface. The latter quantity clearly is influenced by the choice of the layer dimensions.

In spite of the difficulties, several authors have measured the equilibrium isotherms of some systems at conditions close to the critical point. Hori and Kobayashi[3] measured the adsorption of methane on Porasil over a range of sub- and supercritical conditions. An early review by Menon[4] cited several examples of adsorption equilibria studies for inorganic gases at supercritical conditions. More recently, Findenegg[5] also discussed the sub- and supercritical adsorption of propane and ethylene on graphitized carbon black adsorbents. However, none of these investigations involved systems commonly used for SFC.

Recently, however, a few fundamental phase-distribution studies of SFC systems have been completed. Selim and Strubinger[6,7] measured the uptake of supercritical pentane in capillary columns containing SE-30 and SE-54 polymeric stationary phases. Others[8] have measured stationary phase swelling (volume changes) of up to 400–500% under SC conditions for both butane and carbon dioxide in SE-30 by measurement of the changes in the void volume of capillary columns. In addition to the studies involving liquid stationary phases, the uptake of supercritical CO_2 by octadecyl-bonded silica has recently been determined by tracer pulse chromatography over a range of sub- and supercritical temperatures and pressures[9]. Yonker and Smith[10] also used tracer pulse chromatography to measure the uptake of a common SFC modifier, 2-propanol, from CO_2 by cross-linked SE-54 in a capillary column. Lochmüller and Mink[11] performed the same type of measurements with ethyl acetate adsorbed on silica from CO_2 using another chromatographic method, *viz.*, the peak maxima method.

In each case, the sorption isotherms of systems near the critical point of the adsorbate had an unusual shape. A maximum in the excess adsorption was observed at pressures close to the critical pressure (P_c) and temperatures slightly greater than the critical temperature (T_c) in the studies which covered both sub- and supercritical conditions[3,4,9]. The supercritical systems showed decreasing adsorption with increasing pressure (at fixed temperature) and decreasing temperature (at fixed pressure). The density isotherms, on the other hand, showed normal temperature dependence in every case, *i.e.*, the amount adsorbed decreased with increasing temperature at fixed density. For this reason, density isotherms are more meaningful than pressure isotherms for the comparison of supercritical adsorption isotherms.

Multilayer adsorption is commonly observed for gas–solid systems near the critical point of the adsorbate for both sub- and supercritical conditions. The maximum amount adsorbed decreases at temperatures and pressures higher and lower than T_c and P_c. If such multilayer adsorption occurs for supercritical CO_2, this modification of the stationary phase would have to be considered in any theoretical model for SFC retention mechanisms.

The objective of the present investigation was to determine the excess adsorption isotherms of carbon dioxide on several different types of common SFC adsorbents over a range of pressures in order to investigate the role of the stationary phase characteristics in the retention mechanism(s) observed in SFC.

EXPERIMENTAL

The experimental method used to determine the adsorption isotherms was mass spectrometric tracer pulse chromatography (MSTPC)[12,14]. Stable isotopes of CO_2 were used as the tracer probes with a mass spectrometric (MS) detection system[15,16]. The mass spectrometer was an HP-5985 gas chromatography (GC)–MS system operated in the selected ion monitor mode. The carrier gas stream was split into the GC–MS system through a short length of 5 μm I.D. fused-silica capillary tubing.

The carbon dioxide was SFC grade (Scott Specialty Gases), and $^{13}C^{18}O^{16}O$ (m/e = 47) (Merck & Co) was used as the stable tracer for the isotherm measurements. Neon, argon and krypton were used to determine the void volume of the columns. The tracer and inert gases were injected as a gaseous mixture via a gas-sampling valve that was pressurized with CO_2 to the operating pressure of the column prior to injection. More complete experimental details can be found in ref. 9.

The chromatographic columns and adsorbents are described in Table I. The surface areas for all four of the stationary phases were measured by BET adsorption of nitrogen at 77°K.

TABLE I

PHYSICAL CHARACTERISTICS OF THE CHROMATOGRAPHIC COLUMNS

Packing type	*Manufacturer*	*Column length (mm)*	*Packing weight (g)*	*Surface area (m^2/g)*
Silica	Scientific Glass Engineering	250	0.431	140
Octadecyl-silica	Scientific Glass Engineering	250	0.573	90
Cyano-silica	Keystone Scientific	100	0.214	120
Diol-silica	Keystone Scientific	100	0.192	210

RESULTS

The measured Gibbs (excess) adsorption isotherm for CO_2 on the silica adsorbent at 40°C is shown in Fig. 1, and the experimental data are given in Table II. The isotherm measurements included both sub- and supercritical conditions. At pressures of less than P_c for CO_2 (73.8 bar), the CO_2 mobile phase was a gas, and at higher pressures the mobile phase was a supercritical fluid with a density that varied from 0.32 to 0.67g/ml. In the subcritical regime, the density isotherm was nearly linear indicating relatively weak adsorbate-adsorbent and solute-solute interactions. However, the calculated monolayer capacity, assuming an area of 18 Å^2 for adsorbed

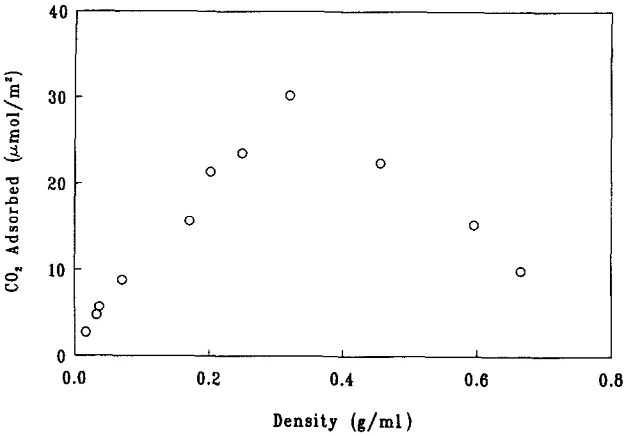

Fig. 1. Gibbs adsorption isotherm of CO_2 on Silica at 40°C.

CO_2, was only 9 μmol/m². Thus, at a reduced temperature of 1.03 (40°C), multilayer adsorption was observed at relatively low, subcritical pressures ($P/P_c \geqslant 0.6$). At pressures greater than P_c the *excess* amount of CO_2 adsorbed *decreased* with pressure. This apparent decrease in adsorption was actually due to the significant *increase* in the bulk density of CO_2 with pressure at pressures greater than P_c. Thus a point of maximum adsorption —about 3–4 layers— occurred at, or slightly below, the critical pressure. The unique shape of this isotherm is caused by several interrelated factors,

TABLE II

ADSORPTION ISOTHERM DATA FOR CO_2 ON SFC ADSORBENTS AT 40°C

Silica		*C_{18}-silica*		*Diol-silica*		*Cyano silica*	
Density (g/ml)	*Excess adsorbed (μmol/m²)*	*Density (g/ml)*	*Excess adsorbed (μmol/m²)*	*Density (g/ml)*	*Excess adsorbed (μmol/m²)*	*Density (g/ml)*	*Excess adsorbed (μmol/m²)*
Subcritical pressures							
0.017	2.7						
0.033	4.7					0.027	2.4
0.037	5.7	0.015	1.9	0.018	3.3	0.043	4.4
0.071	8.8	0.038	4.5	0.040	6.3	0.069	6.4
0.171	15.6	0.067	7.8	0.073	10.9	0.174	14.2
0.202	21.3	0.204	17.7	0.185	22.1	0.215	18.4
Supercritical pressures							
0.250	23.5	0.242	21.8	0.274	26.1	0.355	26.7
0.321	30.2	0.336	24.1	0.498	20.1	0.538	14.2
0.457	22.4	0.531	11.8	0.599	16.7	0.626	12.3
0.596	15.2	0.627	7.9			0.684	6.4
0.666	9.9	0.681	5.6				
		0.720	5.0				

viz., the high density and pressure of the adsorbate, temperatures close to the critical temperature, and the fact that only the excess amount of CO_2 adsorbed could be measured experimentally.

Very similar adsorption isotherms have previously been observed for supercritical propane and ethylene on graphitized carbon black[5]. With both of these adsorbates, the maximum adsorption occurred at pressures close to P_c and the adsorption observed at higher pressures decreased dramatically with pressure. The maxima in the adsorption isotherms were sharply peaked at temperatures close to T_c but more diffuse at higher temperatures. The formation of thick, adsorbed layers close to the critical point was suggested[5] to be a form of "prewetting" of the adsorbent by the supercritical adsorbate.

The exact effect of a thick layer of CO_2 adsorbed on SFC adsorbents on the retention of other solutes is uncertain. It is also unclear whether the adsorbed CO_2, which is in dynamic equilibrium with the bulk fluid phase, actually constitutes a part of the "stationary" phase. It has been shown in high-performance liquid chromatography that in some cases chromatographic solutes interact directly with an adsorbed solvent layer, particularly with bonded phases; whereas in other cases the solutes interact directly with the solid surface in a displacement process (polar solutes with silica)[17,18]. A similar mechanism may operate for SFC; however, the exact role of the stationary phase is presently unclear.

Almost all previous studies of SFC retention mechanisms have been carried out by studying the effect of physical and chemical parameters on the capacity factor (k') of different solutes. Unfortunately, this protocol gives only indirect evidence concerning the exact composition of different columns or packing types. Accurate knowledge of the packing weight, surface areas, flow-rates and void volumes, as well as k', is required for direct comparison of different columns, and very few studies of this type have been carried out with SFC systems.

The influence of the pressure drop across packed columns on the experimentally measured parameters such as k' and adsorption isotherms could possibly be significant, especially for systems near the critical point of the mobile phase[19]. A significant density (ρ) gradient may exist in a packed column even with a relatively small pressure drop across the column because of the large value of $(\partial\rho/\partial P)_T$ (where T = temperature) near the critical point. In order to evaluate the influence of the density gradient on the isotherm data in the present study, the inlet and outlet densities were calculated for each experiment. Table III contains the pressure and density data for the octadecyl-bonded silica column. The volume flow-rates used in the experiment ranged from 800 μl/min at low pressures to 50 μl/min at the highest pressures. Thus, the pressure gradients decreased with pressure and were negligible for all of the supercritical pressures. The density profiles and gradients are shown in Figs. 2 and 3. In no case was the density at the inlet significantly different from the outlet density, and there is no need for a correction applied to the experimental isotherm data.

These experiments were not typical of practical SFC conditions for two reasons: (i) the *molar flow-rate* was maintained constant, not the pressure, density or volume flow-rate, and (ii) the probe solutes were light gases, thus the flow-rates and consequently the pressure drops were much lower than those observed for SFC with high-molecular-weight solutes. However, the important point is that the experimental data obtained with the MSTPC technique do not require any correction for pressure or density gradients under the conditions used for this study.

TABLE III

PRESSURE AND DENSITY DATA FOR OCTADECYL-BONDED SILICA AT 40°C

Pressure (bar)		*Pressure Gradient*	*Density (g/ml)*		*Density Gradient*
Inlet	*Outlet*	$(\Delta P/<P>) \times 100$	*Inlet*	*Outlet*	$(\Delta \rho/<\rho>) \times 100$
10.3	7.0	38.1	0.018	0.012	39.7
21.2	19.0	10.6	0.040	0.038	11.8
33.1	32.5	1.9	0.070	0.066	6.0
60.9	60.0	1.5	0.157	0.155	2.5
69.1	68.4	1.0	0.198	0.196	2.0
84.3	83.9	0.41	0.339	0.337	1.6
96.6	96.2	0.43	0.533	0.531	0.78
110.8	110.4	0.31	0.628	0.627	0.26
124.7	124.4	0.22	0.682	0.681	0.13
138.1	137.7	0.25	0.720	0.720	0.12

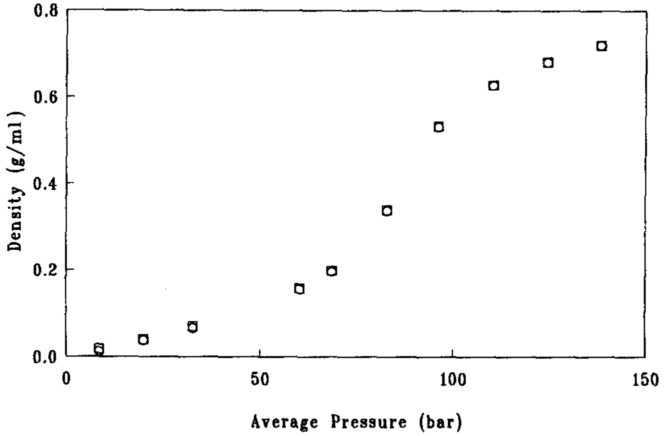

Fig. 2. Inlet and outlet densities for the C_{18}-bonded silica at 40°C. □ = Inlet; ○ = outlet.

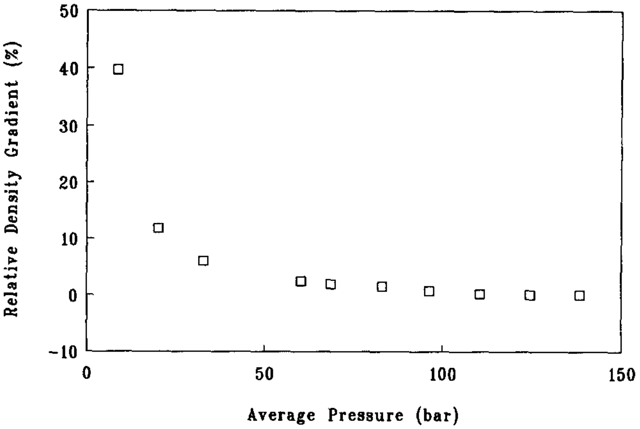

Fig. 3. Relative density gradients $100(\Delta\rho/<\rho>)$ for C_{18}-bonded silica at 40°C.

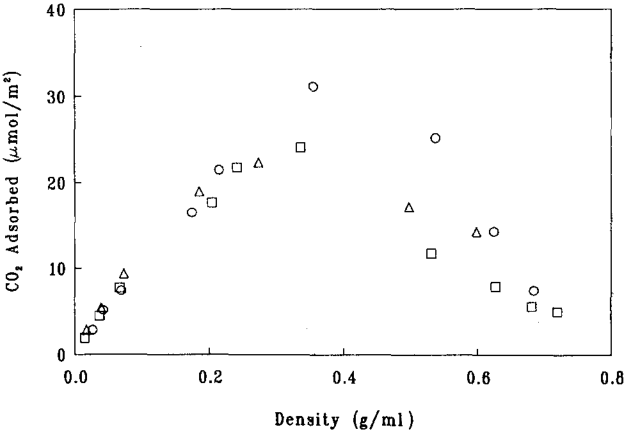

Fig. 4. Excess adsorption isotherms of CO_2 on several common SFC adsorbents at 40°C. □ = C_{18}-silica; ○ = cyano-silica; △ = diol-silica.

In order to determine the effect of different types of bonded stationary phase on the mobile phase uptake by SFC adsorbents, the adsorption isotherms of C_{18}-, diol- and cyano-bonded silica were also determined under the same experimental conditions. These isotherms are given in Table II and shown in Fig. 4. The isotherms are all very similar in shape and magnitude to the silica isotherm (Fig. 1), although there are differences especially at supercritical pressures.

The *subcritical* density isotherms for all four adsorbents were linear and nearly equivalent within experimental error. Thus, the bonded phases do not significantly affect the adsorption capacity for CO_2 (per unit surface area) of the support, and all of the SFC stationary phases studied acted as relatively inert adsorbents at subcritical pressures.

One difference in the supercritical isotherms is that the C_{18}-bonded silica appears to adsorb slightly less than the other adsorbents, including the untreated silica. This is a reflection of the non-polar character of this adsorbent compared to the others. However in every case, multilayer adsorption of CO_2 was observed at pressures greater than P_c, regardless of the surface characteristics. At high pressures (densities $\geqslant$ 0.7) the *excess* adsorption isotherms converged to a value of about 5 μmol/m^2 or approximately half of the low pressure monolayer capacity. Thus, at 40°C, the density of CO_2 in the surface layer was greater than the bulk density even at 140 bar.

CONCLUSIONS

High-performance liquid chromatography studies have shown that a monolayer of the strongest solvent component of the mobile phase commonly exists on the surface of the stationary phase; that the amount adsorbed does not depend upon the composition of the mobile phase; and that chemical modification of the adsorbent surface does not affect the monolayer capacity of the solid[17,18]. The studies reported here show that somewhat similar effects are observed for SFC with CO_2 as the mobile phase. That is, at temperatures slightly above T_c and pressures greater than P_c at least a monolayer of condensed mobile phase exists on the stationary phase adsorbent. At pressures only slightly above P_c, a thicker condensed layer of CO_2 of up to 3–4 molecular diameters is adsorbed under normal SFC conditions.

Our previous investigation[9] showed that multilayer adsorption of CO_2 was maximal at temperatures and pressures close to the critical point. The excess amount of CO_2 adsorbed decreased at higher pressures and temperatures, but never reached zero under conditions commonly employed for practical SFC. Thus, in SFC as in high-performance liquid chromatography, the stationary phase adsorbent is always "coated" by at least a monolayer of condensed mobile phase.

The effect of mobile phase "modifiers", such as alcohols, on the dimensions and composition of the adsorbed stationary phase film has not been determined. Lochmüller and Mink[11] have measured the adsorption of one such modifier, ethyl acetate, on Partisil-10 at 60°C. They observed typical Langmuir isotherms for this organic modifier —under conditions far from its critical point ($T_c = 25$°C)— on the SFC adsorbent. One unusual observation was that, at fixed concentration of the modifier in the mobile phase, the amount of modifier adsorbed on the stationary phase decreased with CO_2 pressure (density). This would indicate that the mobile phase and modifier competed for sites in the adsorbed layer. Yonker and Smith[10] measured the uptake of 2-propanol from supercritical CO_2 by a cross-linked polymer and found partition isotherms that were very similar to those shown in Figs. 1 and 4. The experimental protocol of the former study[11] mimicked the SFC technique of gradient programming at a fixed pressure, while the protocol of the latter study[10] was more relevant for the technique of density programming with a fixed mobile phase composition.

Thus, it is clear the stationary phases used for SFC *adsorb and/or absorb* both the supercritical mobile phase and polar modifiers. However, the effect of this stationary phase modification on the retention of SFC solutes is unclear. The exact effect of a polar modifier on the magnitude and composition of the adsorbed interfacial "phase" can best be determined by measurement of the binary adsorption isotherms of CO_2-modifier mixtures.

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