Journal of Chromatography, 505 (1990) 139–146
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 22 260

Sorption isotherms of mobile phase components in capillary supercritical fluid chromatography

CLEMENT R. **YONKER*** and RICHARD D. SMITH
Chemical Methods and Separations Group, Chemical Sciences Department, Battelle, Pacific Northwest Laboratories, Richland, WA 99352 (U.S.A.)

SUMMARY

Tracer pulse chromatography-mass spectrometry (TPC-MS) was used to study the sorption isotherms of carbon dioxide with a bonded and cross-linked SE-54 stationary phase in capillary supercritical fluid chromatography. These data were compared and contrasted with previously reported absorption isotherm studies for 2-propanol in 2-propanol–CO_2 binary solvents using TPC-MS. Isotherms were determined as a function of density (pressure) and temperature. Results for CO_2 demonstrate an initial increase in the surface excess isotherm with increasing pressure, a maximum being reached, followed by a decrease in the amount adsorbed with further increases in pressure.

INTRODUCTION

The experimental study of stationary phase solvation by supercritical fluids has been limited. Pioneering studies by Sie et al.’ in 1966 demonstrated that CO_2 was soluble in squalane and slightly soluble in glycerol-coated stationary phases at 40°C. The study of stationary phase solvation lapsed until the report of Springston *et al.*[2] in 1986. These authors reported the swelling of non-extractable polymer film stationary phases in supercritical fluids. The determination of the adsorption isotherms of ethyl acetate modifier in supercritical CO_2 on silica was studied by Lochmüller and Mink[3] in 1987. These workers reported stationary phase saturation coverage of the silica surface at approximately 1% (g/ml) ethyl acetate in CO_2.

Studies of supercritical fluid mobile phase component adsorption isotherms using tracer pulse chromatography-mass spectrometry (TPC-MS) have been reported by Strubinger and Parcher[4], Selim and Strubinger[5,6], and Yonker and Smith’. Strubinger and Parcher[4] have studied the surface excess adsorption isotherms of supercritical carbon dioxide on packed columns with octadecyl silica stationary phases. Selim and Strubinger[5,6] have studied the absorption isotherms of supercritical pentane and methanol-modified supercritical pentane using bonded polymeric stationary phases in capillary supercritical fluid chromatography (SFC). Yonker and Smith’ studied the surface excess adsorption isotherms of 2-propanol from supercritical 2-propanol–CO_2 binary solutions using a bonded polymeric stationary phase in capillary SFC as a function of density, temperature and modifier mole fraction.

The study of stationary phase swelling or solvation and the isotherm determination of mobile phase components could lead to a greater insight into the physicochemical processes governing the retention mechanism in SFC. The effects of small amounts of modifiers in supercritical mobile phases and their effects on solute retention have been well documented[8-11] Whether these modifiers interact with the stationary phase covering active sites, modify the bound polymeric stationary phase, or simply alter the mobile phase solvating power remains to be elucidated. Spectroscopic studies of pure and binary supercritical fluid mobile phases have demonstrated many interesting results concerning possible intermolecular interactions in the fluid phase[12–14]. The study of stationary phase solvation is more complex and dependent on the direct determination of the adsorption isotherms of the mobile phase components into the bound polymer.

The purpose of this paper is to present results obtained using TPC-MS to determine the surface excess adsorption isotherms of supercritical CO_2 in capillary SFC. The results for pure CO_2 are contrasted with similar studies using a 2-propanol–CO_2 binary solvent system with the same stationary phase under similar experimental conditions.

EXPERIMENTAL

SFC-MS system

The SFC-MS system has been described in detail in earlier work[15]. The effluent from the capillary column was introduced into a splitter directing the flow to either the MS ion source or into a second restrictor which controlled the flow-rate through the capillary column. Through appropriate adjustment of both restrictors one could accurately control the flow-rate through the column, while keeping the pressure in the MS ion source region sufficiently low for electron impact ionization. This splitter interface for the MS system is an ideal compromise allowing maximum experimental flexibility when using gases (e.g., argon and CO_2) as solute probe molecules.

Materials and column

SFC-grade CO_2 was obtained from Scott Specialty Gases (Plumsteadville, PA, U.S.A.). Oxygen-labeled carbon dioxide ($C^{18}O_2$, mol.wt. 48.0) was obtained from Cambridge Isotope Labs. (Woburn, MA, U.S.A.) and was mixed in a gas mixture of non-labeled CO_2 and argon. The argon was used to determine the void volume of the capillary ‘column. Therefore, from a 0.2-μl injection of this gas mixture one could simultaneously determine the retention time of an unretained component t_0 (argon) and the retention time t_R ($C^{18}O_2$) at the system pressure and temperature.

The capillary column, 7.5 m x 100 μm I.D., was prepared in our laboratory. The column was coated by using a pentane solution of the SE-54 stationary phase and was cross-linked twice with azo-tert.-butane (Alfa, Danvers, MA, U.S.A.), which prevents extraction of the bound polymer by supercritical CO_2. The stationary phase had a calculated film thickness of approximately 1.0 μm.

Distribution isotherms

The TPC-MS technique used in this study is based upon the detection of an isotopically labeled solvent molecule ($C^{18}O_2$) as it elutes from the capillary column. The surface excess isotherm (the excess amount of sorbate present on the surface beyond that corresponding to the bulk density of the gas phase above the surface) can be determined from a simple chromatographic experiment that measures the retention time of the tracer pulse. The assumptions made when applying the TPC-MS technique to isotherms studies are: (i) there is fast equilibration between the mobile and stationary phase; (ii) there are no isotope effects; (iii) the pressure drop across the column should be low, and (iv) the accurate determination of the time of an unretained component. This technique, using a tracer pulse to study adsorption isotherms, was first described by Helfferich and co-workers[16,17].As the amount of carbon dioxide sorbed into the stationary phase increases, so does the retention time of the isotopically labeled $C^{18}O_2$. The isotherm data for $C^{18}O_2$ in the bound SE-54 polymeric stationary phase were determined at 45, 65, 85, 110 and 130°C and for pressures ranging from 65 to 220 atm. The amount of adsorbate in the stationary phase (N_i^{sp}) for the TPC-MS technique is related to

$$N_i^{sp} = V_n Y_i P/ZRT \qquad (1)$$

where V_n is the net retention volume, Y_i is the mole fraction of the solvent molecule under study (in this case $Y_i = 1$), P is the system pressure, Z is the compressibility of the fluid (determined through an appropriate equation of state), R is the gas constant and T is the system temperature[7,18]. From the net retention time of the labeled CO_2 and argon, the net retention volume for the isotope can be calculated:

$$V_n = [(t_R - t_0)/t_0]\,\pi R^2 L \qquad (2)$$

where R is the column radius and L is the column length. The term $\pi R^2 L$ is the geometric volume of the capillary column. The use of column radius instead of free radius ($R - d_f$) contributes less than a 4% difference to the volume determination and negates the need to determine the film thickness (d_f) variation as conditions changed. Therefore, using eqn. 1, knowing the pressure, temperature, and calculating the compressibility of supercritical CO_2, one can calculate the number of moles of CO_2 sorbed into the bonded polymeric stationary phase. Estimated precision (relative standard deviations, R.S.D.) on the retention time for the gases and the calculation of the number of moles of CO_2 sorbed are 2.0 and 18%, respectively. Dividing the number of moles of CO_2 absorbed into the stationary phase by the weight in milligrams of the polymer cross-linked in the capillary column, one can compare results between different column types and different stationary phase film thicknesses.

RESULTS AND DISCUSSION

The study of sorption at high pressures is an important area leading to a greater insight into the physicochemical processes and intermolecular interactions between molecules and surfaces. There have been few studies to date involving dense gases above their critical conditions on simple adsorbent surfaces[19–22]. The extension of this

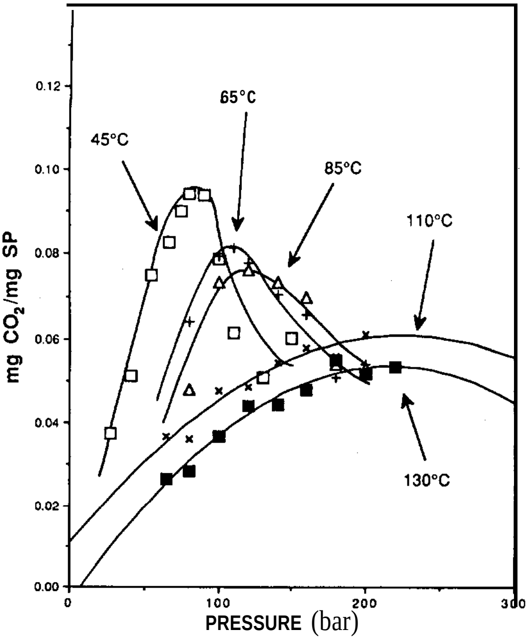

Fig. 1. Plot of mg CO_2/mg stationary phase (SP) versus pressure of supercritical CO_2 for temperatures of (□) 45, (+) 65, (A) 85, (x) 110 and(W) 130°C.

area of research to chromatographically interesting phases and surfaces presents an important opportunity. TPC-MS allows one to study the role of fluid pressure, temperature and modifier mole fraction on the physicochemical processes relevant to stationary phase solvation in SFC.

The data for the sorption isotherms for CO_2 on the SE-54 stationary phase are presented in Fig. 1. For the temperatures of 45, 65 and 85°C, maxima in the isotherms are seen at different experimental pressures. At 110 and 130°C the maxima in the isotherms are just being reached or lie at slightly higher pressures, due to the lower density of CO_2 at these temperatures. Similar behavior for "surface excess" adsorption isotherms has been reported by Findenegg and co-workers[19,20] and Hori and Kobayashi[21].This behavior can qualitatively be thought of as the density difference between the bulk fluid phase and the absorbed phase (surface excess). This differential value will reach a maximum with increasing pressure of the supercritical fluid. Upon increasing the pressure, one gradually approaches the limit in which the density of the bulk fluid equals that of the absorbed phase, at which point the surface excess becomes zero. Therefore, the behavior of the isotherms in Fig, 1 follows qualitative expectations. The swelling factor (defined as the relative expansion of the stationary phase volume[2]) of SE-54 using supercritical CO_2 at 45°C is cu. 0.4, which is comparable to the values reported by Springston *et al.*[2] using supercritical butane and SE-54. As a function of temperature, the amount sorbed is seen to decrease with increasing temperature. The increased thermal energy added to the system most likely accounts for this behavior. Similar results as a function of pressure (density) were reported previously' for the CO,-2-propanol binary supercritical fluid system on SE-54. In this case, the absorption isotherms for 2-propanol also decreased with increasing pressure of the binary supercritical fluid as shown in Fig. 2. The data in Fig. 2 were all obtained at 110°C; it is interesting to note that the absorbed amount of 2-propanol in the stationary phase is approximately 3 to 4 times greater than the amount of CO_2 at similar densities. Carbon dioxide appears to be partitioning into the bonded polymeric stationary phase, similar to that seen for the 2-propanol. The data in Fig. 2 do not take into account any possible synergistic effects due to 2-propanol and CO_2 solvation of the stationary phase, which could lead to a greater amount of CO_2 for the binary fluid system as compared to that seen for pure CO_2. However, the conclusions drawn from Fig. 2 suggest that 2-propanol interacts more effectively with the SE-54 polymeric stationary phase than CO_2. With a single-fluid system, such as CO_2, a larger pressure range can be investigated as compared to a binary fluid, where the pressure region for a two-phase system must be avoided when performing these experiments.

A more effective means of presentation of the data in Fig. 1 is to plot the amount absorbed against fluid density and reduced density. The replot of these data is shown in Fig. 3. Blümel et *al.*[19] have reported that the isotherms at supercritical temperatures usually pass through a maximum for a density (p) between 0.5 $\rho_c < \rho < 1$ .O ρ_c (where ρ_c is the critical density). The surface excess isotherms for CO_2 also reach their maximum value in this range as shown in Fig. 3.

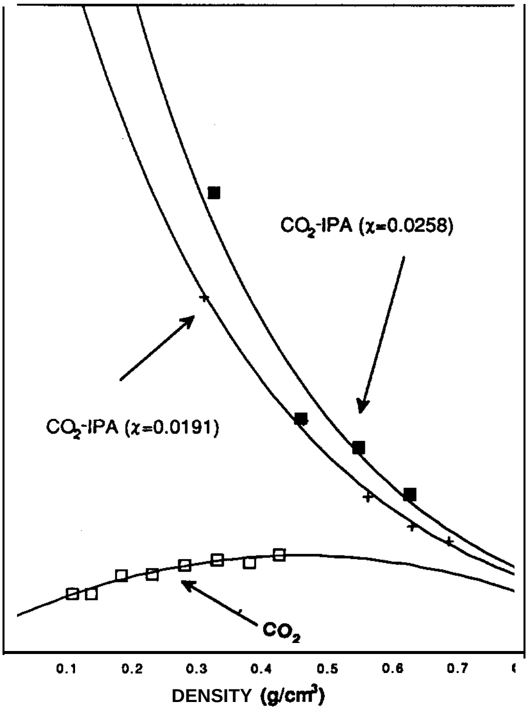

Fig. 2. Plot of mg absorbate/mg stationary phase (SP) versus density at 110°C for pure CO_2 (□) and for CO_2–2-propanol (IPA) in the binary supercritical fluid systems for CO_2–2-propanol at (+) 0.0191 mole fraction and (■) 0.0258 mole fraction.

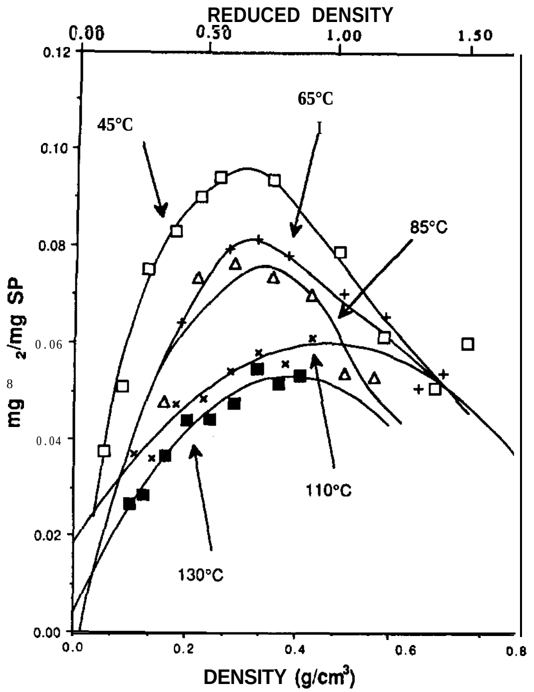

Fig. 3. Plot of mg CO_2/mg stationary phase (SP) *versus* density and reduced density for the temperatures of (□) 45, (+) 65, (A) 85. (x) 110 and (■) 130°C.

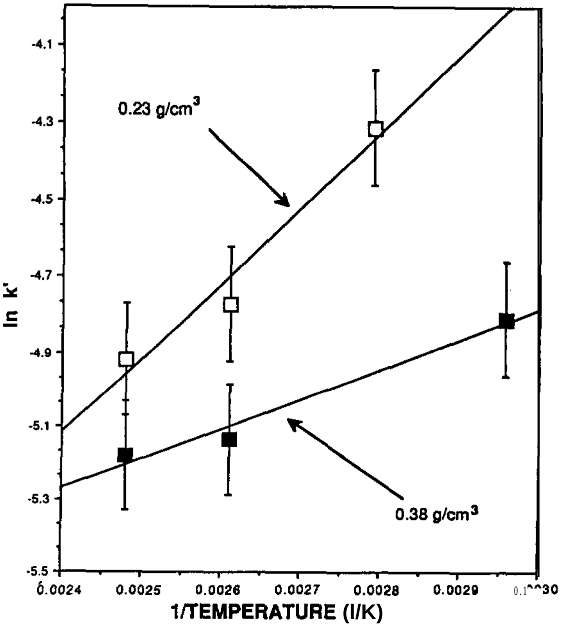

Fig. 4. Plot of ln *k'* for $C^{18}O_2$ *versus* reciprocal temperature at a constant density of (□) 0.23 g/ml and (■) 0.38 g/ml for supercritical CO_2.

The enthalpy for CO_2 sorption in the polymeric stationary phase can be obtained from the TPC-MS experiment. The retention factor, k', for the $C^{18}O_2$ molecule can be obtained experimentally. The retention time difference for $C^{18}O_2$ is very small in this system compared to argon, therefore, k' values will be quite small and prone to an experimental error of *ca.* 10 to 20% R.S.D. One can still obtain an approximate value for the sorption enthalpy for CO_2 at constant mobile phase density and compare it to isosteric enthalpies (determined at constant volume) reported in the literature. Van ‘t Hoff plots for the natural logarithm of the retention factor for $C^{18}O_2$ *versus* reciprocal temperature are shown in Fig. 4. The heats of sorption for CO_2 determined from this technique are approximately -4 kcal/mol (density of 0.23 g/ml) and approximately -2 kcal/mol (density of 0.38 g/ml). The isosteric heats of adsorption for propane, n-butane and acetone on graphitized carbon black were – 5.6, -7.7 and – 7.5 kcal/mol, respectively[23]. The isosteric enthalpy of krypton on graphitized carbon black reported by Blümel *et al.*[19] was -2.95 kcal/mol, whereas Ross *et al.*[24] obtained a value of -3.20 kcal/mol. Comparing the enthalpy of CO_2 sorption with enthalpies values reported for retention in SFC and gas chromatography provides an interesting contrast. Yonker and Smith[25] have reported enthalpies of transfer of heptadecane in SE-54 with supercritical CO_2 of – 8.6 kcal/mol (density of 0.30 g/ml), -6.5 kcal/mol (density of 0.40 g/ml), and -3.9 kcal/mol (density of 0.50 g/ml). Lauer *et al.*[26] have reported average enthalpy values of -6.0 kcal/mol (density of 0.80 g/ml) with supercritical CO_2 using a PRP-1 packed column. Meyer *et al.*[27] and Martire *et al.*[28,29] have reported enthalpies of transfer for the n-alkanes of hexane, heptane and octane of -6.8 to -9.1 kcal/mol using n-tetrocosane as the stationary phase with gas chromatography (temperature range was 76–88°C). The values obtained for the enthalpy of CO_2 sorption from k' determinations at the two densities follow the trend reported by Yonker and Smith for the enthalpies of transfer as a function of density in supercritical CO_2, but the absolute values of the enthalpy of sorption is less than the enthalpy of transfer in both SFC and gas chromatography. In fact, the enthalpy of sorption values obtained do not vary greatly from the isosteric enthalpies reported for krypton on graphitized carbon black. This could point to a possible conclusion that in this case CO_2 is behaving in a manner similar to krypton adsorption on carbon black. The sorbed CO_2 is not interacting with the polymer; it is forming solvent multilayers on the polymer surface. Further improvements of k determinations for the sorbed species is desirable to obtain more accurate enthalpy determinations which will aid in data interpretation.

CONCLUSIONS

Implications of these studies for understanding the retention process for SFC are significant. The TPC-MS technique can be used to determine sorption isotherms under supercritical fluid conditions. This presents the opportunity to study the intermolecular interactions between a molecule and the surface directly and investigate their effects on retention in SFC. The sorption isotherm for CO_2 showed maxima in the reduced density region of 0.5 to 1.0, which is consistent with studies reported in the literature for other systems[19]. As pressure (density) increased the amount of CO_2 sorbed decreased. The excess amount of CO_2 associated with the polymeric stationary phase was determined to be less than that seen for 2-propanol using the binary supercritical fluid of 2-propanol–CO_2. The amount of CO_2 associated with the stationary phase decreased as a function of temperature over the temperature range used in this study. Sorption enthalpies for CO_2 were determined from the measured retention factors for the isotopically labeled CO_2. These values were shown to compare favorably with isosteric heats of adsorption for krypton reported in the literature[19,24].

Further studies need to be undertaken involving the role of fluid modifiers and solvation of the bound polymeric stationary phase, to define any synergistic effects between the modifier and dense gas relating to an enhanced sorption isotherm. The distinction between solvent multilayers on the polymer surface or the intercalation of the solvent into the bound polymer, and their roles in determining solute retention in SFC, needs to be better understood. The TPC-MS technique presents an important opportunity for studying these questions and other solvation models rapidly and accurately. Our aim is to extend these methods to high-temperature systems of much more highly solvating polar fluids.

ACKNOWLEDGEMENT

The authors acknowledge the support of the U.S. Army Research Office, Contract DAAL03-87-K-0042.

The content of the information contained in this report does not necessarily reflect the position or the policy of the Government, and no official endorsement should be inferred.

REFERENCES

1 S. T. Sie, W. van Beersum and G. W. A. Rijnders, *Sep. Sci.,* 1 (1966) 459.
2 S. R. Springston, P. David, J. Steger and M. Novotny, *Anal. Chem.*, 58 (1986) 997.
3 C. H. Lochmüller and L. P. Mink, *J. Chromatogr.,* 409 (1987) 55.
4 J. R. Strubinger and J. F. Parcher, *Anal. Chem.,* 61 (1989) 951.
5 M. I. Selim and J. R. Strubinger, *Fresenius' Z. Anal. Chem.*. 330 (1988) 246.
6 J. R. Strubinger and M. I. Selim, *J. Chromatogr. Sci.,* 26 (1988) 579.
7 C. R. Yonker and R. D. Smith, *Anal. Chem.*, 61 (1989) 1348.
8 J. M. Levy and W. M. Ritchey, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 503.
9 A. L. Blilie and T. Greibrokk, *Anal. Chem.*, 57 (1985) 2239.
10 Y. Hirata and F. Nakata, *J. Chromatogr.*, 295 (1984) 315.
11 Y. Hirata, *J. Chromatogr.*, 315 (1984) 31.
12 C. R. Yonker, S. L. Frye, D. R. Kalkwarf and R. D. Smith, *J. Phys. Chem.*, 90 (1986) 3022.
13 C. R. Yonker and R. D. Smith. *J. Phys. Chem.*, 92 (1988) 2374.
14 S. Kim and K. P. Johnston, *AIChE J.,* 33 (1987) 1603.
15 R. D. Smith, H. T. Kalinoski and H. R. Udseth, *Mass Spectrom. Rev.,* 6 (1987) 445.
16 D. L. Peterson and F. Helfferich, *J. Phys. Chem.*, 69 (1965) 1283.
17 D. L. Peterson, F. Helfferich and R. J. Carr, *AIChE J.*, 12 (1966) 903.
18 J. F. Parcher, *J. Chromatogr.,* 251 (1982) 281.
19 S. Blümel, F. Köster and G. H. Findenegg, *J. Chem. Soc., Faraday Trans. 2,* 78 (1982) 1753.
20 G. H. Findenegg and R. Löring, *J. Chem. Phys.,* 81 (1984) 3270.
21 Y. Hori and R. Kobayashi, *J. Chem. Phys.*, 54 (1971) 1226.
22 J. J. Haydel and R. Kobayashi, *Ind. Eng. Chem. Fundam.*, 6 (1967) 547.
23 J. F. Parcher, P. J. Lin and D. M. Johnson, *Anal. Chem.,* 58 (1986) 2207.
24 S. Ross, J. K. Saelens and J. P. Olivier, *J. Phys. Chem.,* 66 (1962) 696.
25 C. R. Yonker and R. D. Smith, *J. Chromatogr.,* 351 (1986) 211.
26 H. H. Lauer, D. McManigill and R. D. Board, *Anal. Chem.*, 55 (1983) 1370.
27 E. F. Meyer, K. S. Stec and R. D. Hotz, *J. Phys. Chem.*, 77 (1973) 2140.
28 D. E. Martire, Y. B. Tewari and J. P. Sheridan, *J. Phys. Chem.,* 74 (1970) 2345.
29 D. E. Martire, Y. B. Tewari and J. P. Sheridan, *J. Phys. Chem.,* 74 (1970) 2363.