

CHROMSYMP. 2226

Review

Sorption isotherms in supercritical fluid chromatography

CLEMENT R. YONKER* and RICHARD D. SMITH

Chemical Methods and Separations Group, Chemical Sciences Department, Pacific Northwest Laboratory^a, Richland, WA 99352 (USA)

ABSTRACT

The continued and growing interest in supercritical fluid chromatography (SFC) has given rise to a need for a better understanding of the solute retention mechanism. One facet of research has aimed at a theoretical description of solute retention using equation of state models based on statistical mechanics and thermodynamic descriptions of the P , V , T relationship for a fluid. A second approach has involved studies of the physico-chemical interaction of the supercritical fluid with the solute molecule and the stationary phase. Solute retention in SFC has been demonstrated to be a dynamic process of intermolecular interactions between the solute and the fluid mobile phase and between the solute and the bonded polymeric stationary phase. This qualitative statement is supported by spectroscopic studies of solvent cluster formation about a solute molecule in a supercritical fluid, partial molar volume studies and isotherm measurements of the fluid in different stationary phases under various conditions in SFC. Progress made to date in determining the sorption isotherms of mobile phase components in SFC is reviewed.

CONTENTS

1. Introduction	775
2. Methodologies	776
3. Discussion	777
4. Conclusions	784
5. Acknowledgements	784
References	785

1. INTRODUCTION

The understanding of the solute retention mechanism in supercritical fluid chromatography (SFC), as in all chromatographic systems, is dependent on determining the complex interaction between multiple chemical processes. These physico-chemical processes involve the intermolecular interactions of the solute molecule with

^a Operated for the US Department of Energy by Battelle Memorial Institute, under Contract DE-AC06-76RLO 1830.

the mobile and stationary phases. Various methodologies have been used to study the mobile and stationary phases in SFC and many excellent papers have been published in these areas [1-8].

The understanding of the molecular dynamics of the retention process in the stationary phase hinges on the ability to study the interactions between the supercritical fluid and the bonded polymeric phase. The investigation of the sorption isotherms of the supercritical fluid mobile phase components in the stationary phase and their effect on solute retention will lead to a more complete understanding of the retention process in SFC.

There are numerous methodologies for the determination of adsorption isotherms in chromatographic systems. Conder and Young [9] presented an excellent discussion of these techniques for gas chromatography, but these methodologies are of equal importance for both liquid and supercritical fluid chromatography. Supercritical fluids present an interesting challenge because of the compressible nature of the solvent and the higher working pressures, but most methodologies are readily amenable to SFC.

The purpose of this paper is to review the progress in determining the sorption isotherms of mobile phase components in SFC and to discuss their relevance to the understanding of retention in SFC. This area is still in its infancy, but already some interesting results have been obtained.

2. METHODOLOGIES

In initial studies, Sie *et al.* [10] 25 years ago measured the solubility of near-critical and supercritical carbon dioxide in squalane and glycerol using a gas volumetric and titration method. These methodologies are better suited for bulk adsorption studies and do not lend themselves readily to *in situ* investigations on a chromatographic column.

In more recent work, Springston *et al.* [11] developed a chromatographic technique to measure the swelling of bonded polymeric films used in modern capillary columns in a supercritical fluid. It is based on the change in elution time of a non-retained marker as the film thickness in the capillary varies. This hydrodynamic method of determining stationary phase swelling was used to investigate thick-film coatings in capillary SFC. The advantage of this technique lies in its ability for *in situ* measurements of stationary phase swelling in capillary SFC. Disadvantages of this method arise from practical constraints on film and column preparation and their resulting impact on the precision of such measurements.

Lochmüller and Mink [12,13] measured the adsorption isotherm of ethyl acetate, methanol and 1-hexanol on silica from supercritical carbon dioxide using the peak maxima method. In this chromatographic technique, the capacity factors of the peak maxima were determined for various solute concentrations injected into the column. The analysis of the chromatographic retention data can be used to obtain the sorption isotherm of the solute molecule [14]. The integration of the first-derivative plot in this technique could prove difficult in multi-component systems.

Janssen *et al.* [15] studied the adsorption isotherms of different supercritical fluid modifiers on octadecyl-modified silica using the breakthrough method. This technique involves the determination of the breakthrough profile of the solvent mod-

ifier from the chromatographic column. The stationary phase coverage of the modifier can then be easily determined as a function of pressure, temperature and fluid modifier concentration [16]. The ease of studying multiple simultaneous isotherms is questionable with this technique.

Selim and Strubinger [17,18], Yonker and Smith [19,20] and Parcher and co-workers [3,21–23] used tracer pulse chromatography to study the adsorption isotherms in SFC. The advantage of this technique is that multi-sorbate isotherms can be readily determined. The basic requirement for a solute is a detectable difference between itself and the background solvent. This is readily accomplished through the use of either mass isotopes or radioisotopes. There are several excellent discussions of tracer pulse chromatography in the literature, as applied to high-pressure gas chromatography, that describe the technique and theory [24–27].

3. DISCUSSION

The adsorption of high-pressure gases on solid surfaces under both near-critical and supercritical conditions has been studied since the early 1930s [28–31]. The work of Coolidge and Fornwalt [28] investigated the adsorption of carbon dioxide, nitrous oxide and silicon tetrafluoride on charcoal under various temperature and pressure conditions. Their results using a gravimetric technique based on the quartz spring balance showed S-shaped adsorption isotherms for carbon dioxide on charcoal. A successful fitting of the carbon dioxide adsorption data using the Polanyi treatment of multi-layer adsorption was completed.

The next high-pressure gas adsorption study was reported by Jones *et al.* [32], who investigated the adsorption of carbon dioxide and nitrogen on porous plugs of lamp black. Again a gravimetric technique was used. At 32°C, they reported a sharp maximum in the carbon dioxide adsorption data as the pressure increased. The pressure of this adsorption maximum was reported at 74 atm. Above this pressure the adsorption isotherm was seen to rapidly decrease.

When measuring adsorption isotherms, one either determines the absolute adsorption or the differential adsorption. Differential or Gibbs adsorption is defined as the excess solute present in a volume on the surface, beyond that which would be present owing to the normal density of the solute at that temperature and pressure. If measured at sufficiently high pressures, Gibbs adsorption isotherms always show a maximum. The simple explanation of this phenomenon is that as the background pressure increases, the density of the bulk solvent approaches that of the adsorbed solvent. This can continue until the bulk and adsorbed densities are equal; according to definition, at this point the adsorbed amount becomes zero. Therefore, high-pressure Gibbs adsorption isotherms must exhibit a maximum by definition, as reported by Jones *et al.* [32]. Menon's review [33,34] of high-pressure adsorption data further clarifies this point and demonstrates the difference between absolute and differential isotherm measurements for different systems.

Kobayashi and co-workers [35,36] described the high-pressure adsorption of methane and propane on silica gel (Porasil A) and the use of a chromatographic technique (tracer pulse chromatography) for the experimental study of these systems. The Gibbs adsorption isotherm obtained for methane on Porasil A first increased as a function of density and then decreased with continued increases in solvent density.

Values for the absolute adsorbed amount of methane and the density of the sorbate were determined from the Gibbs isotherms. This investigation was the first work employing tracer pulse chromatography on a chromatographic stationary phase.

Findenegg and co-workers [37,38] later studied the physical adsorption of krypton and propane on graphitized carbon black. The differential molar enthalpy of adsorption was derived from the temperature dependence of the Henry's law constant. Gibbs adsorption isotherms for supercritical fluids at the critical temperature were seen to pass through an adsorption maximum between $0.5\rho_c$ and the critical density, ρ_c .

The initial studies of high-pressure gas adsorption on solid surfaces demonstrated the important result of a maximum being reached in the Gibbs isotherm as a function of pressure. This adsorption maximum appeared to occur between a reduced density of 0.5 and 1.0. The use of tracer pulse chromatography for the determination of Gibbs adsorption isotherms demonstrated the applicability of this technique to SFC. In SFC, the chromatographic surface consists of a bonded polymer (capillary SFC) or a bonded hydrocarbon chain (packed-column SFC). The chromatographic stationary phase adds complexity to the sorption mechanism and increases the intermolecular dynamics between the fluid solvent and the stationary phase.

The initial work of Sie *et al.* [10] investigated the solubility of the supercritical fluid in a typical bulk stationary phase. This study demonstrated that supercritical carbon dioxide was soluble in a coated liquid stationary phase. The swelling of a bonded polymeric stationary phase in capillary SFC was demonstrated by Springston *et al.* [11] for SE-30 using supercritical butane and carbon dioxide. Butane expanded SE-30 to nearly three times its initial thickness, whereas the swelling observed with carbon dioxide was much less. These interactions between the fluid mobile phase and the stationary phase could alter the chromatographic retention mechanism for SFC.

Lochmüller and Mink [12,13] studied the adsorption isotherms of ethyl acetate, methanol and 1-hexanol on silica from supercritical carbon dioxide with the peak maxima method. Their results of fitting the adsorption isotherms to the Langmuir equation suggest monolayer adsorption for the fluid modifier. Modifier surface coverage was determined as a function of temperature at constant density and was seen to decrease with increasing temperature. The retention of substituted and unsubstituted aromatic solutes was determined in the presence of methanol modifier (0–1%, w/v) in supercritical carbon dioxide. For methoxynaphthalene and nitronaphthalene, the retention was lower than expected owing to competition between the solute and methanol for the active sites on the silica surface. For chloronaphthalene, the retention increased in the presence of methanol on the silica surface. This behavior was ascribed to either an increase in dispersive interactions with the modified silica surface because of covered active sites or lateral interactions between the solute molecule and the adsorbed methanol. The selectivity for a given solute pair was studied in the methanol-modified fluid, in which one solute molecule competed with methanol for the active sites on the silica surface and the other did not. The selectivity between these two solutes reached a maximum as a function of methanol modifier concentration (*ca.* 0.4%, w/v) and decreased with increasing methanol concentration. The relationship between surface site coverage and methanol modifier concentration controlled the change in selectivity for this system. 1-Hexanol was more effective in covering active sites on the silica surface because of its greater molecular surface area.

The retention data and adsorption data presented by Lochmüller and Mink [13] demonstrate that for certain solutes competitive solute-modifier active site adsorption occurs with silica in packed-column SFC.

The work of Janssen *et al.* [15] was similar to that of Lochmüller and Mink, except they studied an octadecyl-modified silica stationary phase. Various polar modifiers in supercritical carbon dioxide were investigated using the breakthrough method to determine the modifier surface coverage. The adsorption isotherms were fitted to a Langmuir-type adsorption equation and solute retention was based on a dual retention mechanism. Overall solute retention was considered to be a combination of selective interactions with the silanol surface sites and the chemically bonded surface. Retentions of various solutes were monitored as a function of modifier concentration, and their results were similar to those reported by Lochmüller and Mink [13]. The maximum amount of modifier sorbed on the surface was clearly correlated with molecular size and structure. Solute retention correlated with the amount of polar modifier adsorbed on the surface, leading to the conclusion that the modifier serves to deactivate residual silica surface sites in the chemically modified stationary phase. The interaction of the polar modifiers with the surface silanols was found to be important in altering the extent of the individual contributions to the dual retention mechanism.

Mass isotope tracer pulse chromatography (MITPC) has recently been applied to the investigation of the dynamic stationary phase sorption process for bound polymeric systems in SFC. Selim and Strubinger [17] first reported the use of MITPC for the study of sorption isotherms of supercritical *n*-pentane on SE-30 and SE-54 stationary phases in SFC. They reported a high solubility of *n*-pentane near its critical temperature in both the SE-54 and SE-30 stationary phases, which decreased with increasing pressure. A minimum in the adsorption isotherm was reported at a pressure of 650–700 p.s.i. for both stationary phase studies. At higher temperatures (250–300°C), the total amount of *n*-pentane sorbed into the stationary phases was appreciably lower than that measured at 220°C, and pressure had a minimal effect on the sorption behavior. The effect of film thickness of the stationary phase on sorption behavior was investigated at these higher temperatures. Enhanced sorption or solubility of the fluid in the thicker stationary phase was a general phenomenon seen under constant conditions.

Strubinger and Selim [18] also studied the isotherms of *n*-pentane in an SE-54 stationary phase using a mobile phase that contained various amounts of methanol as a polar modifier in supercritical *n*-pentane. The trends obtained were similar to those in their previous study using pure *n*-pentane as the supercritical fluid. The amount of sorbed *n*-pentane in the stationary phase decreased with increasing pressure and temperature. The presence of the polar modifier, methanol, had a slight effect on the amount of *n*-pentane sorbed into the stationary phase, the postulated reason for this effect being the direct interaction between methanol and any residual active sites on the capillary surface. The coverage of these sites by methanol changed the surface activity, making the surface less polar, which increased the amount of *n*-pentane sorbed into the stationary phase. They also proposed a thermal relaxation process as the possible mechanism through which the amount of *n*-pentane taken up by the stationary phase decreases with increasing temperature and pressure.

Yonker and Smith [20] studied the Gibbs adsorption isotherms of carbon diox-

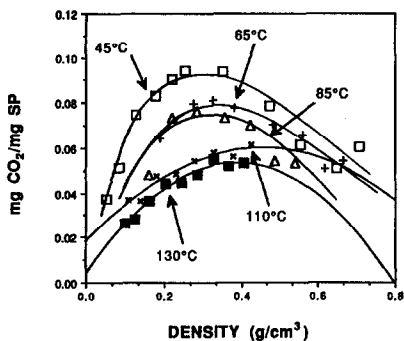


Fig. 1. Plot of mg adsorbate (CO_2) per mg of stationary phase (SP) versus bulk fluid density for temperatures of (\square) 45, (+) 65, (\triangle) 85, (\times) 110 and (\blacksquare) 130°C.

ide as a function of density on a bonded SE-54 stationary phase in capillary SFC. The results of these investigations are shown in Fig. 1. The Gibbs isotherms exhibit a maximum with density over a range of $0.5\rho_c < \rho < 1.0\rho_c$, where ρ_c , the critical density for carbon dioxide, is 0.468. This supports the findings of Findenegg and co-workers [37] in their studies of the adsorption of krypton on graphitized carbon black. As density (pressure) continues to increase the measured differential adsorption isotherms for carbon dioxide decrease. This effect arises as the density of the bulk solvent approaches the density of the adsorbed carbon dioxide. As the two densities approach one another, the differential adsorption isotherm for carbon dioxide on the surface approaches zero [32–34]. As the temperature increases, the excess amount of carbon dioxide sorbed in the stationary phase decreases. This result was comparable to that seen for *n*-pentane on SE-54 as reported by Selim and Strubinger [17,18]. The enthalpy of sorption of carbon dioxide in the polymeric stationary phase was determined to be *ca.* -4 kcal/mol (at a density of 0.23 g/ml) and -2.0 kcal/mol (at a density of 0.38 g/ml). The isosteric heats of adsorption (determined at constant volume) for propane, butane and acetone on graphitized carbon black were -5.6 , -7.7 and -7.5 kcal/mol, respectively [39]. The isosteric heats of adsorption on graphite for propane and butane are -6.26 and -8.10 kcal/mol, respectively [40]. Findenegg and co-workers [37] reported an isosteric enthalpy for krypton on graphitized carbon black of -2.95 kcal/mol, whereas Ross *et al.* [40] reported a value of -3.20 kcal/mol. The enthalpy values reported by Yonker and Smith [20] compare favorably with the isosteric enthalpies in the literature for high-pressure adsorbate isotherms on solid surfaces.

Further work by Yonker and Smith [19] involved the study of the Gibbs adsorption isotherms of the polar fluid modifier 2-propanol in SE-54 as a function of temperature, density and modifier mole fraction. The general trend in the Gibbs isotherm data can be seen in Fig. 2. At each temperature studied, the amount of 2-propanol adsorbed into the stationary phase decreased with increasing density and converged to a limiting value. The temperature effect shown in fig. 2 is pronounced at the lower densities. The increase in temperature could contribute enough thermal energy to the system to begin to overcome the attractive interactions between 2-propanol and the stationary phase, thus contributing to the decrease in the amount of

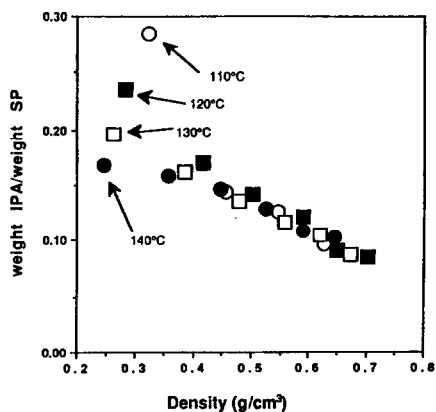


Fig. 2. Plot of weight of 2-propanol (IPA) per weight of stationary phase (SP) versus bulk fluid density for a constant mole fraction of 0.0258 2-propanol in CO_2 at (○) 110, (■) 120, (□) 130 and (●) 140°C.

2-propanol absorbed into the stationary phase as temperature increases. The 2-propanol was determined to be partitioning into the stationary phase based on the calculation of 2-propanol monolayer surface coverage relative to the amount of 2-propanol absorbed in the stationary phase, which was at least two orders of magnitude greater than that needed for monolayer coverage. In this study the authors demonstrated that the weight percentage of 2-propanol in the stationary phase was greater at lower bulk densities and decreased as the bulk density increased. A proposed explanation for this observation is the increase in solvent strength of the supercritical fluid as density increases. Similar results were observed in spectroscopic investigations of the local composition of the binary modifier in the cybotactic region of the probe molecule as a function of density for supercritical fluids [41]. The local composition of the binary modifier was found to be substantially enriched at lower pressures. The local composition of the modifier decreased and approached the bulk composition as density increased, reflecting the increasing solvent strength of the bulk fluid as density increased. At constant temperature, an increase in mole fraction of the polar modifier 2-propanol in the bulk fluid resulted in an increase in the amount of 2-propanol sorbed into the stationary phase. These results are shown in Fig. 3. The trend shown in Fig. 3 again demonstrates the effect of bulk solvent strength. At constant modifier mole fraction for lower bulk fluid densities, the polymeric stationary phase is a better solvent for 2-propanol than the supercritical fluid. As the bulk fluid density increases and its solvent strength increases, the amount of 2-propanol sorbed into the stationary phase concomitantly decreases.

Yonker and Smith [19] determined the enthalpy of sorption for 2-propanol into the polymeric stationary phase for densities of 0.35 and 0.40 g/cm^3 . The heats of sorption for these densities at increasing mole fractions of 2-propanol in the bulk fluid (0.04–0.07) ranged from -3.5 to -4.7 kcal/mol and -2.8 to -3.8 kcal/mol, respectively. Again, these values are comparable to those reported by Ross *et al.* [40]. The heat of vaporization of 2-propanol is -9.5 kcal/mol at its boiling point of 82.2°C [42]. If 2-propanol were adsorbing in multi-layers on the stationary phase surface, then one might expect the heat of adsorption to approach the heat of vaporization. The

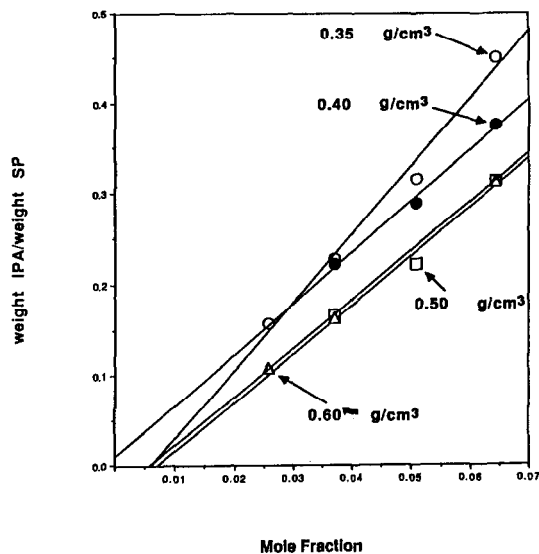


Fig. 3. Plot of weight of 2-propanol (IPA) per weight of stationary phase (SP) versus mole fraction of 2-propanol in the binary supercritical fluid at 140°C for bulk fluid densities of (○) 0.35, (●) 0.40, (□) 0.50 and (△) 0.60 g/cm³.

measured experimental enthalpies reflect the intermolecular interaction between 2-propanol and the bound polymeric stationary phase. As the amount of 2-propanol sorbed into the stationary phase increases, the enthalpy of sorption for 2-propanol approaches the limiting value, the heat of vaporization.

Parcher and co-workers [3,21,22] studied the Gibbs adsorption isotherms of carbon dioxide on typical adsorbent materials used in packed-column SFC. These materials included silica and octadecyl-, cyano- and diol-modified silica. Their work demonstrated no major difference between the Gibbs adsorption isotherms for these four adsorbent materials. Multi-layer adsorption of carbon-dioxide above the critical pressure was observed independent of surface preparation. In packed-column SFC, the effect of the pressure drop down the length of the column must be taken into consideration. Parcher and Strubinger meticulously avoided any pressure drop in their columns during isotherm determination. The general trends seen in these isotherms were similar to those found in capillary SFC. At temperatures and pressures above the critical point, these workers reported that the amount of carbon dioxide sorbed decreased with increasing pressure at constant temperature and decreased with increasing temperature at constant density. Maxima in the Gibbs isotherms were seen near the critical pressure and temperature. The shape of the isotherm is due to the contribution of several interrelated factors, the high density of the adsorbate, temperatures close to the critical temperature and only the excess amount of carbon dioxide sorbed can be determined experimentally. A near-critical isotherm at 30°C showed the expected behavior at the vapor pressure for carbon dioxide (71.8 atm). A discontinuity was observed in the adsorption isotherm. Below this pressure, typical gas-solid adsorption behavior was noted; above this pressure, normal liquid-solid adsorption was encountered. Parcher and Strubinger attempted to calculate the abso-

lute adsorption isotherms based on the parameters of the specific surface area of the adsorbent and the thickness of the adsorbed layer. The accuracy of their results is limited by the assumed values of these parameters. These investigators also determined the effect of carbon dioxide adsorption in the stationary phase on the retention of benzene. At pressures below the critical pressure for carbon dioxide, benzene was highly retained on the surface at the temperatures investigated. As the pressure increased, the solute retention showed the expected exponential decrease with increasing density. At fixed pressure, the retention of benzene increased with temperature, which was postulated to occur as a result of the decreased sorption of carbon dioxide on the surface and the decreased density of the carbon dioxide mobile phase as temperature increases.

Parcher and co-workers [22,23] further studied the adsorption isotherms for supercritical carbon dioxide on an SE-30 bonded capillary column and the adsorption isotherms of a binary supercritical fluid composed of methanol in carbon dioxide on silica and octadecyl-bonded silica. They measured the specific volume of carbon dioxide in the polysiloxane bonded phase and showed that it increased with the concentration of carbon dioxide in the polymer. Further, the maxima determined in the adsorption isotherms as a function of density for supercritical carbon dioxide supported the earlier findings of Findenegg and co-workers [37] that the maxima occurred in the range $0.5\rho_c < \rho < \rho_c$. A comparison of carbon dioxide sorption between silica and octadecyl-modified silica showed that the bare silica adsorbed more carbon dioxide than the modified surface, the difference being the decrease in surface area on surface modification. A qualitative relationship between P_R^{\max}/ρ^{\max} (the reduced pressure at maximum adsorption/density at the adsorption maximum) *versus* reduced temperature was seen to be a common straight line for all systems studied. They also developed a similar qualitative relationship between the reduced maximum adsorption *versus* reduced temperature. This qualitative relationship is similar to the quantity discussed earlier by Menon [33], in which $P_{\max} = P_c T_r^2$ is constant for all high-pressure adsorption studies (where P_{\max} is the pressure of maximum adsorption and P_c and T_r are critical pressure and reduced temperature of the adsorbate, respectively).

The work of Parcher and co-workers [23] on the adsorption of binary supercritical fluid mobile phases on silica and octadecyl-modified silica represents an initial attempt to define the roles of temperature, pressure and composition on the retention mechanism in packed-column SFC. At the three temperatures investigated, the adsorption of carbon dioxide with methanol present was enhanced relative to the adsorption of pure carbon dioxide, and the adsorption maxima were shifted to higher densities. Therefore, in this system the adsorption process was interpreted to be a cooperative process. The amount of methanol adsorbed at 50°C increased with decreasing pressure as one approached the critical point. The composition of methanol in the stationary phase was much greater than that present in the bulk binary fluid. This result is similar to that reported earlier by Yonker and Smith [19] with an SE-54 stationary phase in capillary SFC. The amount of methanol adsorbed on the bare silica surface was greater than that on the modified surface owing to the greater number of polar adsorption sites.

The retention of two solutes were monitored during the adsorption isotherm studies and the general chromatographic trend in retention for supercritical fluids was

observed with increasing fluid density of the solutes. However, the addition of methanol to the mobile phase increased the retention of benzene at a fixed density on the octadecyl-bonded phase. The increased solvent strength of the mobile phase with methanol addition should decrease solute retention. Parcher and co-workers postulated that the increased retention was due to the following: (1) the adsorbed methanol increases the stationary phase volume while decreasing the mobile phase volume, which results in a net increase in the phase ratio for the separation; assuming a constant distribution coefficient, then solute retention will increase; (2) the distribution coefficients for the solutes may be greater in methanol than in either octadecane or liquid carbon dioxide; and (3) the increase in volume of the stationary phase with methanol leads directly to an increase in the distribution coefficient, if the solute molecule partitions directly into the sorbed phase.

4. CONCLUSIONS

The understanding of the retention mechanism in supercritical fluids is dependent on continuing efforts to investigate the dynamics of stationary phase solvation through the determination of the adsorption and absorption isotherms in both packed-column and capillary SFC. The physico-chemical interaction between the solute and the sorbed fluid in the stationary phase, as shown with MITPC studies and other techniques, directly impacts on retention in SFC. High-pressure adsorption processes have been studied for near-critical and supercritical fluids on both solid and polymeric surfaces. The classical methodologies are surpassed by the speed and flexibility of tracer pulse chromatographic techniques under such conditions. The ability to study simultaneously multiple adsorbates in one experiment is a distinct advantage of mass isotope tracer pulse chromatography. The determination of the exact extent of interaction between the fluid and the silica surface or the polymeric stationary phase still remains to be elucidated, but initial studies on sorption isotherms are beginning to address these questions. The understanding of the solute-sorbed fluid interactions and the extent of these interactions with fluid modifier concentration and bulk fluid density are necessary to obtain a greater insight into the retention mechanism in SFC. The studies reviewed here have attempted to understand the physico-chemical interactions involved during solute retention in SFC. The determination of adsorption isotherms in supercritical chromatography will contribute to the goal of understanding the retention mechanism in both SFC and LC. Further efforts are required to increase the ability to derive both qualitative and quantitative contributions of the intermolecular interactions in the solvated stationary phase and their effect on solute retention in SFC.

5. ACKNOWLEDGEMENTS

Work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract DE-AC06-76RLO 1830, and the US Army Research Office under Contract DAAL03-87-K-0042. The content of this paper does not necessarily reflect the position or the policy of the government, and no official endorsement should be inferred.

REFERENCES

- 1 D. E. Martire, *J. Chromatogr.*, 461 (1989) 165.
- 2 C. R. Yonker and R. D. Smith, *J. Phys. Chem.*, 92 (1988) 1664.
- 3 J. R. Strubinger and J. F. Parcher, *Anal. Chem.*, 61 (1989) 951.
- 4 E. P. Schmitz and E. Klesper, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 519.
- 5 K. D. Bartle, A. A. Clifford, J. P. Kithinji and G. F. Shilstone, *J. Chem. Soc., Faraday Trans. 1*, 84 (1988) 4487.
- 6 P. J. Schoenmakers, L. G. M. Uunk and P. K. DeBokx, *J. Chromatogr.*, 459 (1988) 201.
- 7 T. A. Berger, *J. Chromatogr.*, 478 (1989) 311.
- 8 T. L. Chester, L. J. Burkes, T. E. Delaney, D. P. Innis, G. D. Owens and J. D. Pinkston, *ACS Symp. Ser.*, 366 (1988) 144.
- 9 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York, 1979, Ch. 9.
- 10 S. T. Sie, W. Van Beersum and G. W. Rijnders, *Sep. Sci.*, 1 (1966) 459.
- 11 S. R. Springston, P. David, J. Steger and M. Novotny, *Anal. Chem.*, 58 (1986) 997.
- 12 C. H. Lochmüller and L. P. Mink, *J. Chromatogr.*, 409 (1987) 55.
- 13 C. H. Lochmüller and L. P. Mink, *J. Chromatogr.*, 471 (1989) 357.
- 14 A. W. J. deJong, J. C. Kraak, H. Poppe and F. Nooitgedacht, *J. Chromatogr.*, 193 (1980) 181.
- 15 J. G. M. Janssen, P. J. Schoenmakers and C. A. Cramers, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 12 (1989) 645.
- 16 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 58 (1971) 137.
- 17 M. I. Selim and J. R. Strubinger, *Fresenius' Z. Anal. Chem.*, 330 (1988) 246.
- 18 J. R. Strubinger and M. I. Selim, *J. Chromatogr. Sci.*, 26 (1988) 579.
- 19 C. R. Yonker and R. D. Smith, *Anal. Chem.*, 61 (1989) 1348.
- 20 C. R. Yonker and R. D. Smith, *J. Chromatogr.*, 505 (1990) 139.
- 21 J. F. Parcher and J. R. Strubinger, *J. Chromatogr.*, 479 (1989) 521.
- 22 J. R. Strubinger, H. Song and J. F. Parcher, *Anal. Chem.*, 63 (1991) 98.
- 23 J. R. Strubinger, H. Song and J. F. Parcher, *Anal. Chem.*, 63 (1991) 104.
- 24 D. L. Peterson and F. Helfferich, *J. Phys. Chem.*, 69 (1965) 1283.
- 25 F. Helfferich, *J. Chem. Educ.*, 41 (1964) 410.
- 26 D. L. Peterson, F. Helfferich and R. J. Carr, *AIChE J.*, 12 (1966) 903.
- 27 J. F. Parcher, *J. Chromatogr.*, 251 (1982) 281.
- 28 A. S. Coolidge and H. J. Fornwalt, *J. Am. Chem. Soc.*, 56 (1934) 561.
- 29 H. E. Morris and O. Maass, *Can. J. Res.*, 9 (1933) 240.
- 30 J. Edwards and O. Maass, *Can. J. Res.*, 12 (1935) 357.
- 31 J. Edwards and O. Maass, *Can. J. Res.*, B13 (1935) 133.
- 32 W. M. Jones, P. J. Isaac and D. Phillips, *Trans. Faraday Soc.*, 53 (1959) 1953.
- 33 P. G. Menon, *J. Phys. Chem.*, 72 (1968) 2695.
- 34 P. G. Menon, *Chem. Rev.*, 68 (1968) 277.
- 35 J. J. Haydel and R. Kobayoshi, *Ind. Eng. Chem., Fundam.*, 6 (1967) 546.
- 36 Y. Hou and R. Kobayoshi, *J. Chem. Phys.*, 54 (1971) 281.
- 37 S. Blümel, F. Köster and G. H. Findenegg, *J. Chem. Soc., Faraday Trans. 2*, 78 (1982) 1753.
- 38 G. H. Findenegg and R. Loring, *J. Chem. Phys.*, 91 (1984) 3270.
- 39 J. F. Parcher, P. J. Lin and D. M. Johnson, *Anal. Chem.*, 58 (1986) 2207.
- 40 S. Ross, J. K. Saelens and J. P. Olivier, *J. Phys. Chem.*, 66 (1962) 696.
- 41 C. R. Yonker and R. D. Smith, *J. Phys. Chem.*, 92 (1988) 2374.
- 42 R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 3rd ed., 1977, Appendix A.