EFFECTS OF TEMPERATURE AND DENSITY ON RETENTION IN CAPILLARY SUPERCRITICAL-FLUID CHROMATOGRAPHY

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SUMMARY

Retention of fluoranthene using carbon dioxide and a methyl silicone capillary column was measured at multiple, constant densities while changing temperature. Log k' vs. $1/T$ plots (at constant density) yielded straight lines with different slopes. Each slope gave a value for the total enthalpy of interaction between solute, mobile, and stationary phase, at each density. Gas chromatographic measurements using the same column and low pressure carbon dioxide gave a value for the interaction of the solute and the stationary phase. The difference between the total enthalpy and the solute–stationary phase enthalpy gave an approximate value for the solute–mobile phase enthalpy of interaction. Solubility problems emerged as temperature was decreased while density was held constant.

INTRODUCTION

Supercritical-fluid chromatography (SFC) is a bridge between gas chromatography (GC) and liquid chromatography (LC). In GC, solute volatility and solute–stationary phase interactions determine retention. Increasing temperature tends to increase volatility and decrease retention. In LC, solute volatility is unimportant. Instead, the mobile phase acts as a solvent and the competition between solute–stationary phase interactions and solute–mobile phase interactions determines retention. In SFC both volatility and solvation of the solute by the mobile phase are important.

In SFC, a number of authors have observed maxima in solute partition coefficients, k', vs. temperature (while keeping pressure constant) on both packed and capillary columns[1–7]. Leyendecker et al.[7] explained this behavior as the counteraction of two effects. At temperatures above the maxima, solute volatility dominates over solvation effects. At temperatures below the maxima, decreasing temperature produces increasing density and, consequently, increasing solvation of the solute by the mobile phase. Solvation dominates over volatility in this temperature region.

The change from volatility dominated retention phenomena to solvation dominated retention phenomena could be construed as a change from one type of pure performance to the other. Maxima in constant pressure plots of k' or log k' vs.

temperature are frequently referred to as indicating a change in retention mechanism[6,8]. However, Klesper's explanation of these maxima, as the counteraction of two effects, suggests that two mechanisms are always operating and it is the sum of the two that is observed. This subtle difference in interpretation is often overlooked.

Giddings' concept of threshold density[9] has also been widely misunderstood. He clearly states that threshold density is only a convenient means of comparing the relative solubility of solutes and is dependent on the type and sensitivity of the detector used. The concentration of solute in the mobile phase can increase from virtually nil at atmospheric pressures to measurable levels in some manner related to density. However, if the detector used is not very sensitive this steady increase in concentration is not observed. Plots of detector output vs. density would yield a horizontal line (equal to detector background noise) until some "threshold density" is reached. Above this density, both detector signal and solute concentration increase in proportion to the mobile phase density. Unfortunately, the shape of such curves has been widely interpreted as indicating the sudden onset of solvation effects at this characteristic "threshold" density of each solute. Instead, differences between threshold densities merely indicate the relative solvation power of the mobile phase for various solutes.

From the literature, one is often left with the erroneous impression that the complex retention behavior typical in SFC is caused by some unusual or unique aspect of supercritical gases in comparison to subcritical gases or liquids. It is often assumed that solvation of solutes by gases only occurs above the critical temperature of the gas. As early as 1972, Doran[10] demonstrated that organic vapors like pentane, used as a chromatographic carrier gas, produced nearly identical chromatograms when used above or below the critical temperature of the gas. In another study paralleling that of Doran, Lauer et al.[11] used carbon dioxide as both a liquid and a supercritical gas to elute a number of solutes from packed columns. Again, no sudden changes in retention behavior were observed upon crossing the critical temperature of the mobile phase. The experimental results of both Doran and Lauer et al. indicate that dense gases and liquified gases tend to solvate solutes both above and below the critical point. There is no sudden onset of solvation when the critical point of the mobile phase is exceeded.

If there is no sudden onset of solvation above or even near the critical temperature, the next question must be at what density does solvation commence? Carbon dioxide has been used as a carrier gas in GC at pressures from near ambient to 50 atm (refs. 12–14). Retention of many solutes on several types of packed columns was shown to decrease with increasing pressure. While decreasing retention with increasing pressure is a general phenomenon with all carrier gases, retention decreased much faster when carbon dioxide was used compared to retention when nitrogen was used as the carrier gas. One possible explanation of this behavior is that carbon dioxide gas is a solvent for the solute. In addition, it is a better solvent than nitrogen, and its solvent strength increases with increasing pressure. Supporting this conclusion is a rather extensive, but often overlooked, body of literature describing solvation by gases as both chromatographic mobile phases and as regular solvents. Besides carbon dioxide[12–15], these gases include: steam[16–21]; organic dopants in steam, such as formic acid[22–24], and vapors of organic compounds[25–29]. Although much of this literature attributes retention shifts caused by these gases to the dynamic modification of the stationary phase[30–32] by the gases, adsorption or dissolution of the non-inert carrier[33,34] on or into the stationary phase does not appear to be substantial enough to

completely explain observed changes in solute retention. Some gases, used as the GC mobile phase, appear to exhibit solvation effects (solute–mobile phase interactions similar to those in LC) even at low densities, in addition to the normal solute–stationary phase effects typical in GC.

The purpose of this work is to verify the relationship between GC and SFC and attempt to measure both the enthalpy of interaction between the mobile phase and the solute and the enthalpy of interaction between the stationary phase and the solute as a function of density. It is also intended to demonstrate that chromatographic results obtained at constant density but different temperatures and pressures can be very different.

THEORETICAL

A number of papers have appeared which attempt to describe the thermo-dynamics of the retention process operating in capillary SFC. Yonker et al.[35] attempted to relate changes in the solvent heat capacity (constant pressure, C_p) vs. temperature to changes in solute retention (at constant pressure) vs. temperature. Unfortunately, the solutes chosen (as in most studies[1–5,7,35] showing maxima in constant pressure plots of k' vs. T) are quite volatile near the critical temperature of the solvents used. Since capillary SFC is only useful when solvation effects are significant, examples using solutes and temperatures where volatility provides the dominant separation phenomenon do not provide a realistic test of the theory. It was of some interest, therefore, to determine what effect the use of higher boiling solutes might have on the temperature of the maximum in plots of k' vs. temperature.

Chester and Innis[36] attempted to relate SFC retention to GC retention. They noted that, in GC, the slope of van't Hoff plots of $\ln k'$ vs. $1/T$ equals the enthalpy of interaction between the solute and the stationary phase, ΔH_{s-sp}, divided by the universal gas constant, R. Similar plots of $\ln k'$ vs. $1/T$ (at constant pressure) in SFC yield a straight line at high temperatures, the slope of which they assumed also yielded a value for $\Delta H_{s-sp}/R$. Small deviations from straight line performance were assumed to indicate stationary phase "swelling". At low temperatures, the curves of $\ln k'$ vs. $1/T$ roll over and change the sign of their slope. This corresponds to a change from volatility controlled to solvation controlled retention. The difference between the extrapolated straight line performance from high temperature and the specific values of retention at each low temperature was attributed to equal the enthalpy of interaction between the solute and mobile phase, ΔH_{s-mp}. This description can be summarized as

$$\ln k' = \frac{-\Delta H_{s-sp}}{RT} - \ln \beta + \frac{(\Delta H_{s-mp})_d}{RT}$$

where the subscript d indicates density dependence.

Chester and Innis proceeded to plot log k' vs. density at a small number of constant temperatures and stated that the slope of such curves yields values for ΔH_{s-mp}. However, the plots are only linear over a narrow range of densities and only a small number of temperatures covering only a narrow range of temperatures was used. No GC results for ΔH_{s-sp} were presented. While it is felt that this approach is

essentially correct, the narrow range of temperatures and densities employed, the low molecular weight of the solutes studied, and the lack of a comparison to GC results on the same column make it difficult to determine the accuracy of the theory or to provide quantitative measures of ΔH_{s-sp} or ΔH_{s-mp}.

Chester and Innis included a term to account for changes in the column phase ratio, β, caused by stationary phase "swelling". The choice of the term "swelling" is very common[3,5] and implies a strictly mechanical change in the stationary phase volume. It might be preferable to use a less descriptive name, such as stationary phase–mobile phase interactions, since either a mechanical change in the stationary phase volume and/or a change in the "polarity" of the phase could be caused by the dissolution of the mobile phase in the stationary phase[30-32].

Lauer et al.[11] interpreted the slope of ln k' vs. $1/T$ plots as being equal to the enthalpy of the overall interaction between the solute, stationary phase, and mobile phase. Yonker and Smith[8] extended this description by including the entropy of transfer in their equations. They then observed the retention of a number of lower boiling solutes over the widest range of densities studied to date. However, they do not attempt to relate SFC retention to GC retention and they use terminology for the enthalpy of transfer which produces a different value for a standard state (their ΔH_T°) at each density.

It was felt that part of the theories of both Chester and Innis[36] and Yonker and Smith[8] could be combined to produce a somewhat more complete model of retention, relating GC and SFC results and providing a fairly easy means of testing its validity.

The conventional approach to describing the thermodynamics of chromatographic retention begins with relating Gibbs free energy, ΔG°, to the solute distribution coefficient, K_D = concentration in stationary phase/concentration in the mobile phase:

$$\Delta G^{\circ} = -RT \ln K_D = \Delta H^{\circ} - T\Delta S^{\circ}$$

Since the distribution coefficient is also the product of the partition ratio, k', and the phase ratio, β

$$K_D = k'\beta$$

retention can be related to enthalpy:

$$\ln k' = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} - \ln \beta$$

Since β is nominally a constant, plots of ln k' vs. $1/T$ should have a slope of ΔH°. However, retention can be described as the sum of two competing phenomena. The interaction of the solute with the stationary phase is routinely measured in GC using Van't Hoff plots. If it is assumed that the stationary phase does not change much with the introduction of a supercritical carrier gas, solute–stationary phase (s–sp) interactions should be the same in GC or SFC. It is also well known that in capillary SFC, the natural logarithm of the partition ratio (ln k') decreases linearly with increasing density.

columns were purchased from J&W Scientific. Columns were 10 m × 50 μm I.D., with a methyl silicone stationary phase. Polycyclic aromatic hydrocarbons were purchased in a kit from Chemical Services, and were generally better than 99% pure. Long-chain fatty acids were purchased in a kit from Supelco. Most samples were prepared using carbon disulfide as the solvent to minimize detector response. All solvents were reagent grade or better.

A restrictor, serving as a split vent for split injections, was installed in the side arm of the "tee" and consisted of either a piece of 5, 10 or 25 μm I.D. tubing (linear restrictor) or an "integral" (steep taper) restrictor. Integral restrictors were preferred, but we required a large range of split restrictor flow-rates to cover the range of pressures and densities investigated. Integral restrictors were not readily available with the full range of flow-rate vs. pressure required. Integral (steep taper) restrictors, used as the split vent to control split ratio, were mounted in the base of the second flame ionization detector. This detector was only used as a heated zone to control the temperature of, and mass flow-rate through, the split vent independent of the oven temperature. Restrictors used at the end of the column were also integral or linear types with the former preferred, since the latter tends to cause spiking in the detector output (unless excessive temperatures are used or the solutes are very volatile).

Procedure

It was assumed that partition ratios, k', did not change significantly with mobile phase linear velocity, over the range of linear velocities employed. Since changes in efficiency were not of primary interest in this work, the reduced velocity of the mobile phase through the column was permitted to change slightly with pressure and density to minimize the number of restrictors required. Column linear velocity, estimated by solvent peak transit times, was controlled to between 2 and 5 cm/s (approximately 10 times optimum) for high density work (above ≈ 0.25 g/cm³), and was allowed to rise somewhat as density dropped or temperature rose (more GC-like conditions with higher optimum linear velocity, μ_{opt}). Chromatograms were collected at constant pressure and temperature. Partition ratios were estimated from: the solvent (t_0) and the solute (t_R) retention times reported by the integrator, and the standard equation: $k' = (t_R - t_0)/t_0$. All experimental measurements were taken in triplicate and averaged. The data was more precise than the circles in the figures indicate.

Solutes were dissolved in carbon disulfide to allow retention data at very low values of k' to be collected. Since carbon disulfide hardly responds in the detector, the signal from the solute can be observed in the tail of large excesses of solvent. The solute, therefore, may elute during a time when significant amounts of solvent are still emerging from the column (even though the detector output may not make this obvious). This raises some uncertainty as to whether the solute, emerging with the carbondisulfide solvent, experiences a modifier effect, which could distort the data. Solvatochromic shift measurements indicated that carbon disulfide is only moderately stronger[38], as a solvent, than carbon dioxide. Binary mixtures of similar solvents tend to have solvent strengths between the two pure solvents.

The gas chromatograph was a new unit taken from the production line and the oven temperature was checked with a platinum resistance standard. Accuracy was better than 1°C and precision better than 0.01°C.

The density of carbon dioxide at different temperatures and pressures was

Because of this linear dependency, any density can serve as a standard state to which the results at other densities can be referred. Meyer[37] developed the concept of molar concentrations in each phase as the proper standard state at which to define free energy. Adjustment of physical parameters to achieve molar concentrations in each phase seems unwieldy and difficult to confirm. Instead, the distribution coefficient at density = 1 g/cm^3 could be used as a standard state, although this "convenience" further requires the naming of some temperature as a standard. Using the convention of a density of 1 g/cm^3 as the standard state, the measured enthalpy from the slope of ln k' vs. $1/T$ plots (at constant density) can then be related to standard enthalpies of interaction between the solute and the stationary phase and the solute and mobile phase, since

$$\varDelta H_{meas} = \varDelta H^{\circ}_{s-sp} - \text{density} \cdot (\varDelta H^{\circ}_{s-mp})$$

where $\varDelta H^{\circ}_{s-sp}$ is obtained from ln k' vs. $1/T$ plots in GC and $\varDelta H_{meas}$ is obtained from similar plots obtained in SFC at various fixed densities.

The difference between $\varDelta H_{meas}$ and $\varDelta H^{\circ}_{s-sp}$ provides a measure of $\varDelta H^{\circ}_{s-mp}$ since a plot of $\varDelta H_{meas}$ vs. density will have a slope of $\varDelta H^{\circ}_{s-mp}$ and an intercept of $\varDelta H^{\circ}_{s-sp}$. Deviations from straight line behavior between $\varDelta H_{meas}$ and $1/T$ indicate the magnitude of changes in β and in stationary phase–mobile phase interactions with density.

Stationary phase–mobile phase interactions appear to be small compared with solute–mobile phase interactions. If stationary phase–mobile phase interactions are small: $\varDelta H_{s-mp} + \varDelta H_{sp-mp} \approx \varDelta H_{s-mp}$.

EXPERIMENTAL

Instrumentation and chemicals

A Suprex Model 200A supercritical-fluid chromatograph pump module was used to pump carbon dioxide. In a few cases a Varian Model 4100 syringe pump, modified to provide constant pressure, was used instead of the Suprex unit. For pressures above 60 atm, the mobile phase was SFC grade carbon dioxide supplied in aluminum cylinders with dip tubes purchased from Scott Specialty Gases. For pressures below 60 atm, small aluminum cylinders of the same grade CO_2 with a dip tube were used but the cylinders were inverted to draw gas from the headspace above the liquid CO_2 in the tank. For pressures below 60 atm, pressure was controlled by a high pressure, two-stage, forward pressure regulator. A Hewlett-Packard Model 5890 gas chromatograph with two standard flame ionization detectors was used as the chromatographic oven. One flame ionization detector was used as the system detector and its output was monitored using a recording integrator. A Valco Model 2WI4W.06 micro injection valve was mounted on top of the gas chromatograph. A 0.8 mm outside diameter stainless steel tube was connected between the valve outlet and a "tee" located inside the GC oven. The chromatographic column was inserted through the tee and the stainless steel tube until it butted against the valve body, and was then withdrawn a fraction of a millimeter.

Empty 25 and 50 μm I.D. tubing, used for retention gaps and transfer lines, was purchased from Polymicro Devices. Linear restrictors of 5 and 10 μm I.D. were made from tubing purchased from Scientific Glass Engineering. Integral restrictors and

calculated using the equation of state of Bender[39] and Reynolds[40], which was checked against values from the Gas Encyclopedia[41].

RESULTS AND DISCUSSION

Location of maxima in k' vs. T plots at constant pressure

The theory of Yonker *et al.*[35] was tested by selecting solutes which could not be eluted in GC at temperatures near the critical temperature of the mobile phase. The retention behaviour of polycyclic aromatic hydrocarbons was measured at constant pressure and varying temperature and the results are shown in Fig. 1. Among the facts that are immediately obvious from the figure, is the location of the maxima around 115–130°C even at pressures well below 200 atm. The theory of Yonker *et al.*[35] suggested that the maxima ought to occur between 40 and 80°C, at the same temperatures as the maxima in carbon dioxide heat capacity, c_p, *vs.* temperature curves. Since the maxima in solute retention occur at temperatures up to 50°C higher than maxima in heat capacity, it appears that, while the theory may describe the general shape observed, it is certainly not very accurate. Long chain fatty acids (C_{20}–C_{24}) were also studied and gave similar results.

Constant density lines in k' vs. T plots at constant pressure

A more detailed set of k' *vs.* temperature measurements was collected, using fluoranthene as the solute over a range of fixed pressures from 90 to 140 atm and the results are presented in Fig. 2a. Again, maxima occur at temperatures above 100°C and the temperatures at which the maxima occurs increase with increased pressure. Since pressure is only a control variable, it is more informative to examine the retention phenomena in Fig. 2a as a function of density. Constant density lines can be drawn through the data represented in Fig. 2a as shown in Fig. 2b, where the light dashed lines represent constant pressure and the heavier lines approximate constant density conditions. The numbers next to the heavy lines indicate density values in g/cm^3. Note that, at densities above 0.20 g/cm^3, the constant density lines show a major change in slope, *i.e.*, maxima between 60 and 80°C. This is the same temperature region where the heat capacity of carbon dioxide, C_p, exhibits maxima. However, in Fig. 2a, the temperature of the maxima decreases with increasing pressure, whereas the maxima in
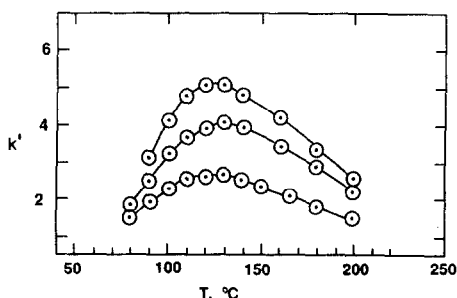

Fig. 1. Retention of selected polycyclic aromatic hydrocarbons *vs.* temperature at listed fixed pressures. Column: 10 m × 50 μm I.D., methyl silicone. Mobile phase: carbon dioxide. Upper curve: perylene at 155 atm, middle curve: benzo[e]pyrene at 160 atm. Lower curve: chrysene at 155 atm.
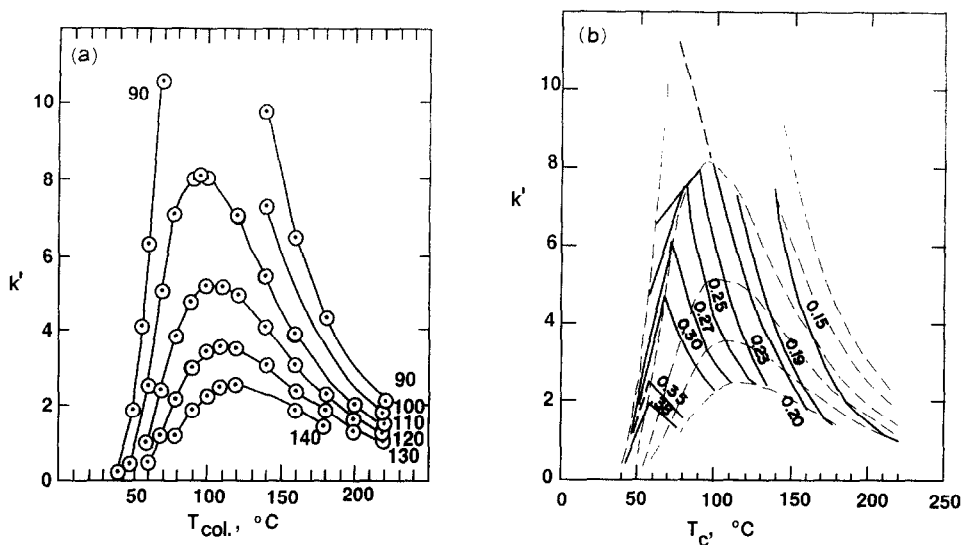
Fig. 2. (a) Retention of fluoranthene vs. temperature. Numbers next to curves indicate fixed pressures in atm. Same column and fluid as in Fig. 1. (b) Same data as in (a) but heavy lines indicate constant density. Numbers above heavy lines indicate density in g/cm^3.

heat capacity increase with increasing pressure. Lauer et al.[11] and Chester and Innis[36] found no change in slope of plots of ln k' vs. $1/T$ collected at constant density. However, the conditions required to cross the maxima in Fig. 2b are difficult to access experimentally. Chester and Innis used capillary columns and temperatures and pressures to the right of the density maxima in Fig. 2b. Lauer et al.[11] used packed columns and reported difficulty in obtaining chromatograms with a fluid density below 0.7 g/cm^3 due to severe tailing. The linear portion of their constant density plots covers the range of 22–55°C and, therefore, the pressure/temperature region to the left of the density maxima Fig. 2b. The constant density lines in Fig. 2b are only approximate. The solute studied was different from those in either of the previous studies[11,35]. Therefore, no attempt was made to directly compare the previous and present results.

Change in enthalpy vs. density from slopes of ln k' vs. $1/T$ at constant density

The retention of fluoranthene was restudied under carefully controlled constant density conditions and the results plotted as ln k' vs. $1/T$, at each of a number of constant densities. Plots of ln k' vs. $1/T$ at eight different densities were plotted and are shown in Fig. 3. Gas chromatograms at four different temperatures were also collected and the results were also plotted as ln k' vs. $1/T$ in Fig. 3. The GC results provide a quantitative measurement of the solute–stationary phase interaction, assuming the slope of the curve is $-\Delta H_{s-sp}/R$. In contrast to the confusing nature of Fig. 2a and b, Fig. 3, yields straight lines with no change in slope over the temperature range from 60 to 280°C, the pressure range from a few atmospheres to 400 atm, or for densities from 0.005 to 0.45 g/cm^3.

If the enthalpy values from the GC chromatograms are assumed to represent the
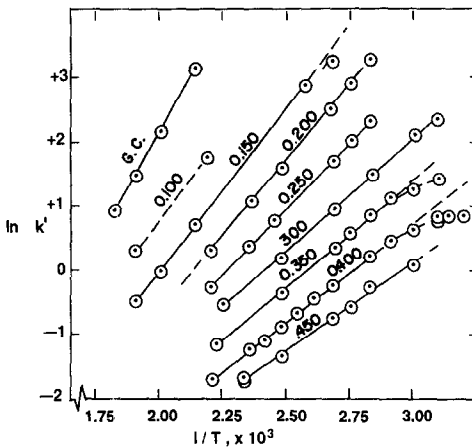
Fig. 3. Retention of fluoranthene *vs.* temperature at different constant densities. Numbers above curves are densities in g/cm³. Note GC data on top left. Same column and fluid as in Fig. 1.

energy of interaction between the solute and the stationary phase, independent of mobile phase effects, then the difference between this value and the energy values at other densities must represent mobile phase effects. These mobile phase effects measure density-dependent interactions between the mobile phase and the solute and interactions between the two phases. The data seem to fit the relationships

$$\ln k'_{SFC} = \ln k'_{GC} + \rho(\Delta H^\circ_{s-mp}/RT + \Delta H^\circ_{mp-sp}/RT)$$

or

$$\ln k'_{SFC} = -\Delta H^\circ_{s-sp}/RT + \rho(\Delta H^\circ_{s-mp} + \Delta H^\circ_{mp-sp})/RT$$
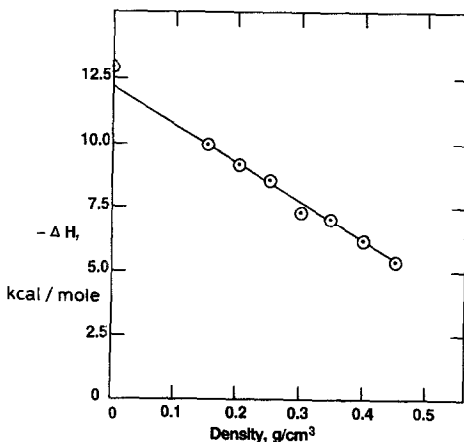
where ρ is density.

Fig. 4. Enthalpy of interaction between fluoranthene, carbon dioxide and methyl silicone stationary phase from slopes of lines in Fig. 3.

TABLE I

VALUES FOR $\Delta H_{s\text{-}mp}$ OBTAINED AT DIFFERENT DENSITIES

$\Delta H_{s\text{-}sp} = 12.98$ kcal/mol.

Density (g/cm^3)	ΔH_{tot} (kcal/mol)	$\Delta H_{s\text{-}mp}$ (kcal/mol)
~0.005	12.98	—
0.15	10.00	19.9
0.20	9.30	18.4
0.25	8.65	17.3
0.30	7.42	18.5
0.35	7.13	16.7
0.40	6.22	16.9
0.45	5.65	16.29

The slopes of the lines in Fig. 3 yield calculated values of energy which are plotted vs. density in Fig. 4. The energy values obtained from the eight curves in Fig. 3 form a nearly straight line in Fig. 4 with a zero density intercept very nearly equal to the $\Delta H^{\circ}_{s\text{-}sp}$ value obtained from the GC data (also presented in Fig. 3). The difference between the zero density intercept of the SFC data and the GC data is probably due to stationary phase–mobile phase interactions which are not directly proportional to density. If the energy values, obtained from the slopes of the curves at each density, are each subtracted from the GC value, and the results are divided by the appropriate density, a value for $\Delta H^{\circ}_{s\text{-}mp}$ should be obtained (assuming $\Delta H^{\circ}_{mp\text{-}sp}$ is small). Values for $\Delta H^{\circ}_{s\text{-}mp}$ obtained in this way are presented in Table I and average approximately 16.5 kcal/mol at high densities.

Comparisons of solvent strength from solvatochromic shift measurements and chromatographic retention

The energy of interaction between solvatochromic dyes and supercritical mobile phases can be measured, independent of stationary phase effects. Such dyes show a shift in the wavelength of their absorption spectra proportional to the solvent
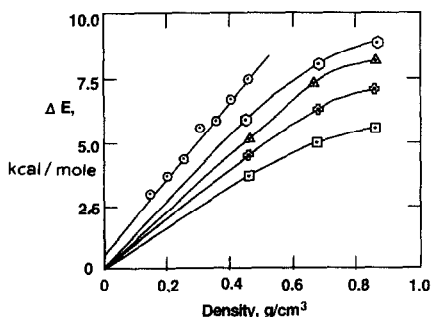

Fig. 5. Comparison of published solvatochromic dye measurements to present measurement of apparent energy of mobile phase–solute interaction. See text for details. ○, Fluoranthene; □, 4-nitrophenol; +, 4-nitroanisole; △, N,N-diethyl-4-nitroaniline; ○, 4-nitroaniline.

strength of the solvent in which they are dissolved. The results of such measurements can be compared to the enthalpy values obtained chromatographically. Many of the dyes used by Kamlet et al.[42] (to develop their π^* scale of solvent polarity) are soluble in carbon dioxide. Sigman et al.[43] measured the absorbance maxima of ten of these dyes in both supercritical carbon dioxide at various densities and in the CO_2 vapor phase, i.e., no solvent. Energy values were calculated using Sigman et al.'s published wavelengths of the absorption maxima by dividing the constant, 28 592, by the wavelength of maximum absorption (in nanometers) to yield an energy in kcal/mol (ref. 44). The difference in energy between the vapor phase measurements and the SFC measurements at each density were calculated and are presented in Fig. 5.

The enthalpy values at each density, presented in Fig. 4, were subtracted from the enthalpy value obtained from the GC chromatograms. The resulting differences in enthalpy were also plotted vs. density in Fig. 5. Although the solutes are different, both the dyes and the chromatographic retention measurements indicate approximately the same level of mobile phase–solute interactions.

Plots of ln k′ vs. density

The energies of interaction, calculated from solvatochromic shifts, tend to roll-off in Fig. 5 at high densities. In the limited range of densities studied in Fig. 5, the chromatographic results appear to produce a straight line with no appreciable roll-off. The unified chromatography theory of Martire and Boehm[45] predicts a roll-off (see Fig. 1, ref. 45) but at higher densities than covered in the experiments summarized by Fig. 3–5. They also predict minima in ln k′ vs. density plots and crossing of such curves obtained at different temperatures. This contradicts the linear relationship between ln k′ and density reported by Chester and Innes[35], but the data from the latter group was only collected over a narrow density range. Yonker and Smith[46] reported that plots of ln k′ vs. density for a number of solutes separated on capillaries were non-linear but did not exhibit minima.

The data in Fig. 3 could be replotted as ln k′ vs. density but does not cover a wide enough density range to fully test the model. Additional data were collected to increase the range of densities studied. With the assumption that carbon disulfide did not significantly distort retention through a modifier effect, partition ratios, k′, of fluoranthene were measured at densities up to 0.74 g/cm³; the results are shown in Fig. 6. No minima were observed and the curves collected at different temperatures did not cross, over the density range studied. However, very small values of k′ were obtained at high densities. In an attempt to study higher densities with more reasonable values of k′, long chain fatty acids with greater retention than fluoranthene were also evaluated. Plots of ln k′ vs. density were similar to those in Fig. 6 but offset to slightly higher retention for any given temperature and density. No minima were observed in ln k′ vs. density for tetracosanoic acid at densities up to 0.905 g/cm³ but ln k′ decreased to less than − 3.

In a similar study on other solutes, Yonker and Smith[46] also report ln k′ values as low as − 3. Such small values for retention suggest a potential problem with all such measurements. Dobbs et al.[47] report that even small amounts of non-polar modifiers added to carbon dioxide, grossly increase the solubility of many solutes compared to their solubility in pure carbon dioxide. They specifically report that the solubility of phenanthrene doubles when the mole percent of octane in carbon dioxide doubles
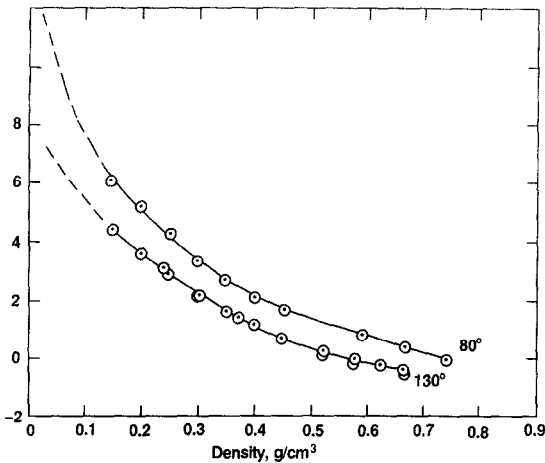
Fig. 6. Retention of fluoranthene plotted against density at higher densities than available from Fig. 3. No minima or crossing observed in range of densities studied. Carbon dioxide mobile phase, methyl silicone 10 m × 50 μm column. Numbers next to curves are temperatures.

from 3.5 to 7%. While that is not the specific system studied here it is similar. Carbon disulfide is much more "polar" than octane and is likely to have a larger modifier effect on polar solutes like the acids. With very small values of k', the solutes must experience a significant modifier effects during a substantial fraction of their residence time in the column. This suggests that the unified chromatography theory of Martire and Boehm[45] may not yet have been properly tested and may not be testable using the approach taken.
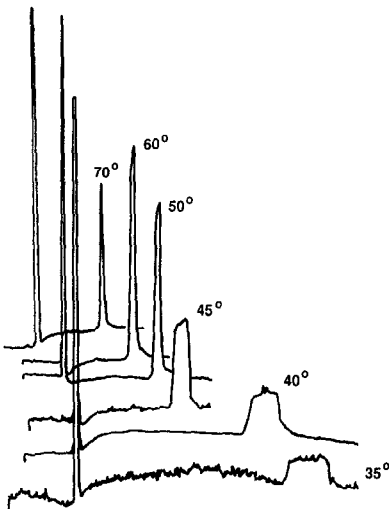

Fig. 7. Chromatograms of fluoranthene collected at a constant density of 0.400 g/cm³ but different temperatures. Numbers next to curves indicate temperature. Same column and mobile phase as previous figures.

Other results

In Fig. 3, some constant density lines became non-linear below 60°C. The constant density line for a density of 0.40 g/cm^3 in Fig. 3 is a good example. Superficially, the roll-off in ln k' below a temperature of 60°C appears to agree with the change in slope of the approximate constant density lines in Fig. 2b. However, the chromatograms presented in Fig. 7, are representative of those used to obtain the last five data points on the right end of the 0.4 g/cm^3 curve in Fig. 3. Since all the chromatograms were collected at the same density, the dramatic decrease in amplitude should logically be due to a decrease in volatility caused by the rather modest decrease in temperature of 35°C. Therefore, the solvation energy produced by substantial densities is not necessarily adequate to offset decreases in volatility caused by small decreases in temperature.

CONCLUSIONS

Solvation of solutes by some carrier gases begins at very low densities, corresponding to pressures and densities encountered in normal GC. This solvation increases steadily and linearly with increasing gas density. There are no unusual properties or capabilities of supercritical gases that suddenly or dramatically appear near or above the critical temperature.

Retention in capillary SFC can be thermodynamically and practically related to retention in GC. The energy of interaction between solutes and stationary phases can be obtained from GC retention data. SFC retention data allows calculation of the solute–mobile phase interactions, provided the GC data is available. Measured values of solute–mobile phase enthalpies were much larger than solute–stationary phase enthalpies, suggesting that carbon dioxide is a very good solvent for the solutes examined and that solvation effects should greatly enhance solute mobility. For fluoranthene in carbon dioxide, and a methyl silicone column, ΔH_{s-mp} is 16–17 kcal/mol; whereas, ΔH_{s-sp} is more like 13 kcal/mol. This difference in energy suggests that the range of solutes that can be eluted by SFC ought to be much larger than the range of GC.

Pressure and temperature are not equivalent means of changing column density. The former primarily changes solvation and tends to slightly increase partial pressure of the solute in the carrier. The latter changes both the partial pressure (or volatility) of the solute and solvation of the solute by the carrier. The technique of inverse temperature programming to increase column density while decreasing column linear velocity is gaining widespread acceptance. While this technique has some very desirable attributes, the above analysis suggests that inverse temperature programming will produce substantially different results than pressure programming producing the same density *vs.* time profile.

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