Gas−Liquid Chromatography with a Volatile "Stationary" Liquid Phase

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A unique type of gas−liquid chromatography is described in which both mobile and "stationary" phases are composed of synthetic mixtures of helium and carbon dioxide. At temperatures below the critical point of the binary mixture and pressures above the vapor pressure of pure liquid carbon dioxide, helium and carbon dioxide can form two immiscible phases over extended composition ranges. A binary vapor phase enriched in helium can act as the mobile phase for chromatographic separations, whereas a CO_2-rich liquid in equilibrium with the vapor phase, but condensed on the column wall, can act as a pseudostationary phase. Several examples of chromatographic separations obtained in "empty" capillary columns with no ordinary stationary liquid phase illustrate the range of conditions that produce such separations. In addition, several experiments are reported that confirm the proposed two-phase hypothesis. The possible consequences of the observed chromatographic phenomenon in the field of supercritical fluid chromatography with helium headspace carbon dioxide are discussed.

The term "chromatography" is commonly used to describe any separation technique that involves the equilibrium distribution of solutes between two immiscible phases ordinarily designated as the mobile and stationary phases.[1] The primary role of the mobile phase is to transport the solute through the column while the stationary phase and any solutes interacting with this phase remain relatively fixed within the column. If one solute resides in the stationary phase longer than another solute, the two solutes will be resolved in time at the detector. This primitive model is useful for simple systems but frequently proves inadequate for complex systems. For example, size exclusion chromatography utilizes the chemically unselective distribution of solutes between moving and stagnant zones of the mobile phase. The stagnant regions are usually located within the small pores of a solid adsorbent or gel. In this case, a portion of the mobile phase actually acts as the stationary phase and resolution of the solutes is accomplished by differential distribution of the solutes between two phases of the same composition.

In addition to mobile phase held stagnant in pores, it is possible for the stationary phase to be composed simply of a portion of a binary mobile phase adsorbed on a solid adsorbent. If the composition and density of the mobile and adsorbed phases differ,

some form of chromatographic resolution may be achieved between solutes that can distribute between the two immiscible phases. One such example is the reported use of liquid nitrogen adsorbed on graphitized carbon black at 77 K to resolve a mixture of permanent gases.[2]

Binary mobile phases are commonly used in both liquid (HPLC) and supercritical fluid chromatography (SFC), and the mobile-phase components are almost always completely miscible in the liquid state. Binary liquids or fluids are most often used to increase the solvent strength of a mobile phase and to lessen the retention of polar solutes. Most binary mobile-phase systems used in chromatography display so-called type I phase behavior in which the critical loci of the mixture vary continuously over the entire composition range.[3] One of the major problems with SFC using CO_2 and polar modifiers, however, is the possibility that two mobile-phase components, which are miscible as liquids, may separate into two immiscible phases in the column under certain conditions. Such phase segregation does not require the participation of an active solid adsorbent. Unfortunately, formation of two phases in a chromatographic column can result in flow instabilities, loss of efficiency, unusual peak shapes, or increased detector noise.[4,5] In fact, Chester[6,7] developed a method for measuring the critical loci of binary mixtures of CO_2 and SFC modifier by observing the point at which chromatographic peaks of the modifier component became flat-topped when injected as a plug into a stream of carbon dioxide. To guard against these undesirable anomalies, experimental conditions that could result in phase segregation are normally avoided in the everyday practice of SFC.[8]

On the other hand, phase separation in the absence of a solid adsorbent has been used to advantage in capillary gas chromatography to facilitate on-column injections of large-volume samples for trace analysis. An uncoated section of column can be employed at the head of the analytical column as a so-called "retention gap".[9–13] If the column temperature is maintained near the boiling

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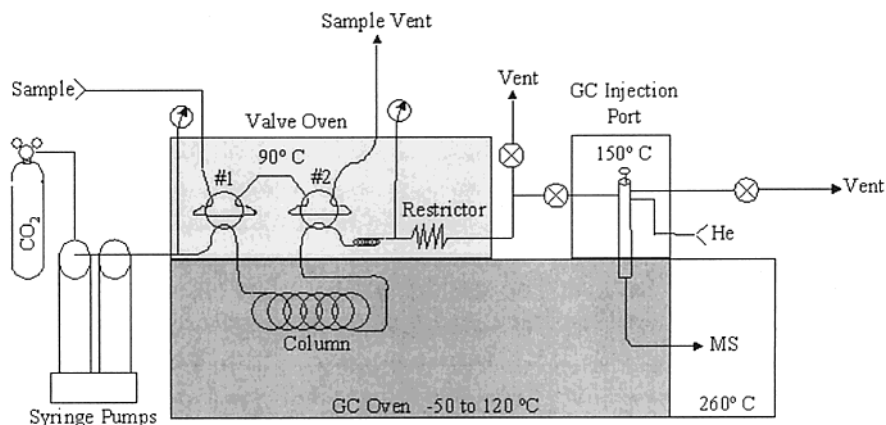**Figure 1.** Schematic diagram of the SFC instrumentation.

point of an injection solvent ($P_{Solvent}^0 \approx 1$ atm), the solvent/carrier gas binary system can segregate into two phases, viz., a carrier-rich vapor phase and an injection solvent-rich liquid phase condensed on the wall of the retention gap segment. The liquid phase can extend over a significant length of the uncoated column forming a "flooded" zone. The injected analytical solutes are distributed throughout the liquid film not necessarily in a uniform manner. If the vapor pressures of the solutes are significantly less than 1 atm, this detrimental dispersion of the analyte solutes "in space"[9] can be ameliorated by reconcentration of the solutes at the downstream end of the flooded zone. This reconcentration is accomplished by removal of the more volatile solvent due to the flushing action of the carrier gas at the upstream end of the flooded zone. In this case, the condensed injection solvent acts as a pseudostationary phase with the solutes dispersed throughout the flooded zone rather than injected as a plug. This is, however, an example of the clever use of dynamic phase separation to accomplish a unique type of capillary column injection for both gas and supercritical fluid chromatography.[6,14]

It is also possible that binary mobile phases may be formed unintentionally in a chromatographic system. The most insidious example of this phenomenon arises from the common use of helium headspace carbon dioxide for SFC. Helium headspace CO_2 tanks are used to improve the delivery of CO_2 from storage tanks to SFC pumps. Several authors, however, have shown that the fluid delivered from such tanks can contain up to 5 mol % dissolved helium.[4,5,15] Even a small amount of helium in the mobile phase can produce such adverse effects as irreproducible peak areas and retention times.[4,16] These problems are usually attributed to the influence of helium on the density, and hence the solvent strength, of the mobile phase.

The phase behavior of mixtures of helium and CO_2 were studied experimentally by Burfield[17] and Mackendrick[18] over a range of temperatures from −60 to +20 °C. These results show that even small amounts of helium in CO_2 can cause the formation
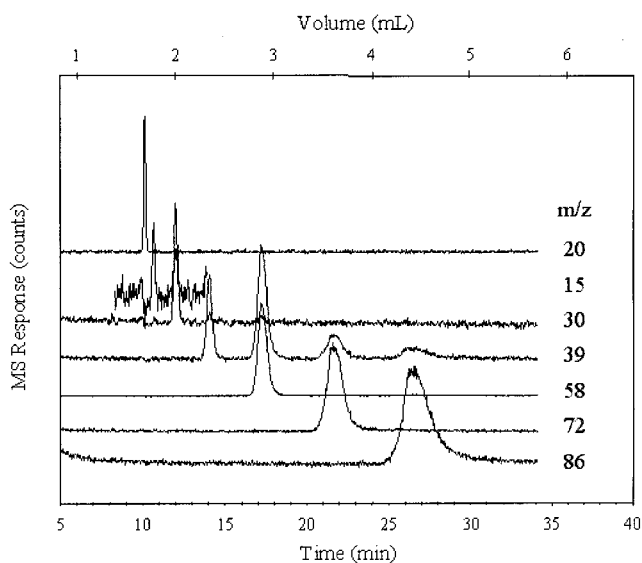

Figure 2. Chromatogram showing the separation of C_1-C_6 n-alkanes and neon in a stainless steel column (500 μm × 25 m). The numbers indicate the monitored mass for each solute: neon ($m/z = 20$), methane (15), ethane (30), propane (39), butane (58), pentane (72), and hexane (86).

of two phases under conditions where pure CO_2 would be a liquid. To date, however, no report of actual phase separation in helium headspace SFC systems has been reported, probably because few SFC applications involve subambient temperatures. Nevertheless, it is at least theoretically possible that analytical separations could be observed in SFC systems with binary mobile phases in which a stationary phase was created dynamically in a empty chromatographic column with no solid adsorbent or nonvolatile stationary liquid phase. Phase segregation could be induced under properly controlled conditions of temperature, pressure, and composition. The main purpose of the present work is to demonstrate that such chromatographic separations can be achieved in columns with no nonvolatile stationary liquid phase and to investigate the conditions under which such separations can occur.

EXPERIMENTAL SECTION

A schematic diagram of the basic instrumentation (HP-5971A GC/MS) is shown in Figure 1. Pure SFC-grade CO_2, SCF-grade CO_2 from a helium headspace tank, and synthetic mixtures of

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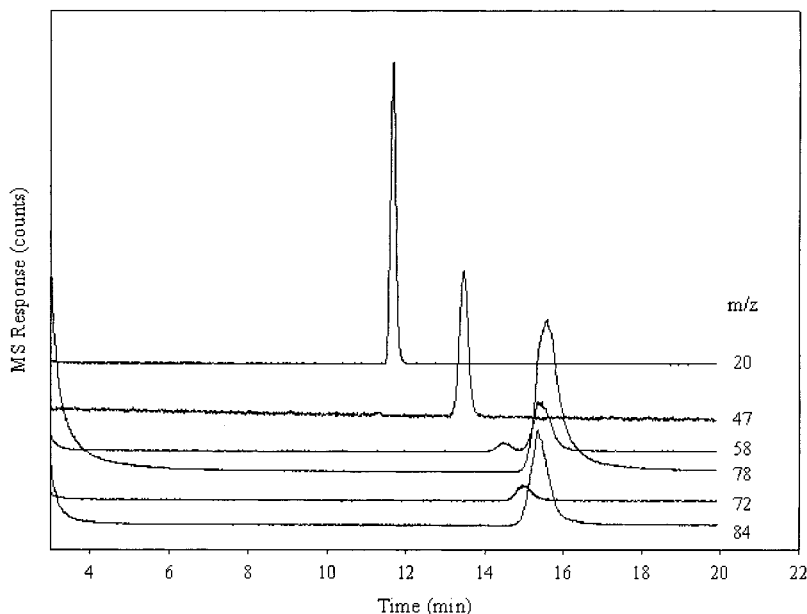(18) Mackendrick, R. F.; Heck, C. K.; Barrick, P. L. *J. Chem. Eng. Data* **1968**, *13*, 352−353.

Figure 3. Chromatogram showing the separation of neon ($m/z = 20$), isotopically labeled CO_2 (47), acetone (58), benzene (78), n-pentane (72), and cyclohexane (84).
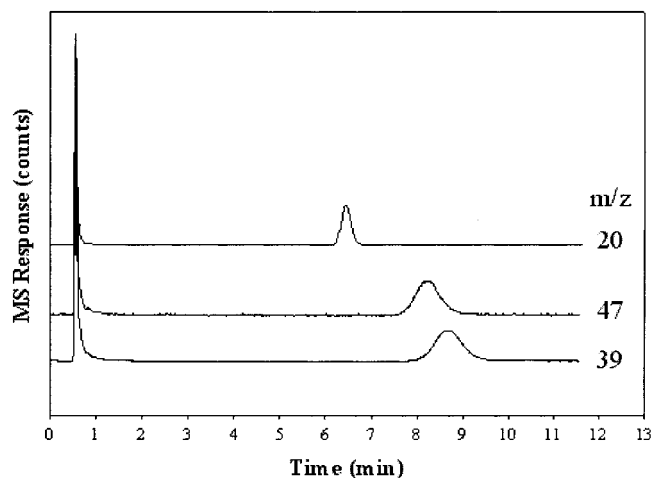

Figure 4. Separation of neon ($m/z = 20$), isotopic carbon dioxide (47), and propane (39) in an fused-silica-lined stainless steel column (762 μm $\times$ 7.6 m). The unresolved peaks at 0.8 min are due to the postcolumn injector.

helium and CO_2 were pumped through chromatographic columns at pressures from 20 to 200 atm and temperatures from -50 to $+200$ °C. The mobile-phase pressure was controlled by two high-pressure (Isco DM-500) syringe pumps with a capacity of 500 mL. The temperature of the column was controlled by the GC oven equipped with a liquid CO_2 cryogenic unit for subambient temperatures.

Gaseous solutes (neon, isotopically labeled CO_2, benzene, acetone, cyclohexane, and normal hydrocarbons from CH_4 to C_6H_{14}) were injected as a pulse by mechanical valves mounted before and after the column. This configuration allowed the assessment of the volume of mobile phase in the column—more accurately, the volume between the two injectors—separate from the extracolumn volume, which was considerable in the GC/MS system. The concentrations of the solutes in the mobile phase were all very low.

The flow rate of the mobile phase through the column was controlled by a fused-silica restrictor (0.05 mm $\times$ 25 cm.) located at the exit of the chromatographic column. The injection valve and restrictor were located in a separate oven whose temperature could be controlled independent of the column temperature. The pressure drop across the chromatographic columns was always less than 1 atm. The detection system was a mass spectrometer which was operated in the selected-ion-monitor mode to allow the detection of the solutes in the natural $^{12}CO_2$ elution gas.

Synthetic mixtures of helium and carbon dioxide were prepared in the syringe pumps. The pump heads were heated to 50 °C to maintain the mixture in a supercritical fluid state to increase the diffusion and mixing of the binary fluids. The compositions of the synthetic mixtures of helium and CO_2 were measured at the outlet of the chromatographic column by means of a second gas chromatograph equipped with a thermal conductivity detector. In this instrument, nitrogen was used as the carrier gas and the analytical column was a packed column containing a carbon adsorbent (Carbosphere) as the stationary phase.

RESULTS AND DISCUSSION

The present investigation was undertaken because several unusual chromatographic separations were observed in capillary columns with no stationary liquid phase when the carbon dioxide mobile phase was obtained from a helium headspace tank. All of the separations occurred at temperatures below the critical temperature of pure CO_2 and at pressures greater than the vapor pressure of pure, liquid CO_2. Figure 2, for example, illustrates such a separation for a series of C_1–C_6 n-alkane solutes observed with an "empty" stainless steel column. The experiment was carried out at conditions, viz. 10 °C and 120 atm, where pure CO_2 would exist as a homogeneous liquid. There are two particularly unique aspects to this chromatogram. First, the separation was accomplished without the requisite nonvolatile stationary phase. Second, the "retention" volumes of the solutes were less than the
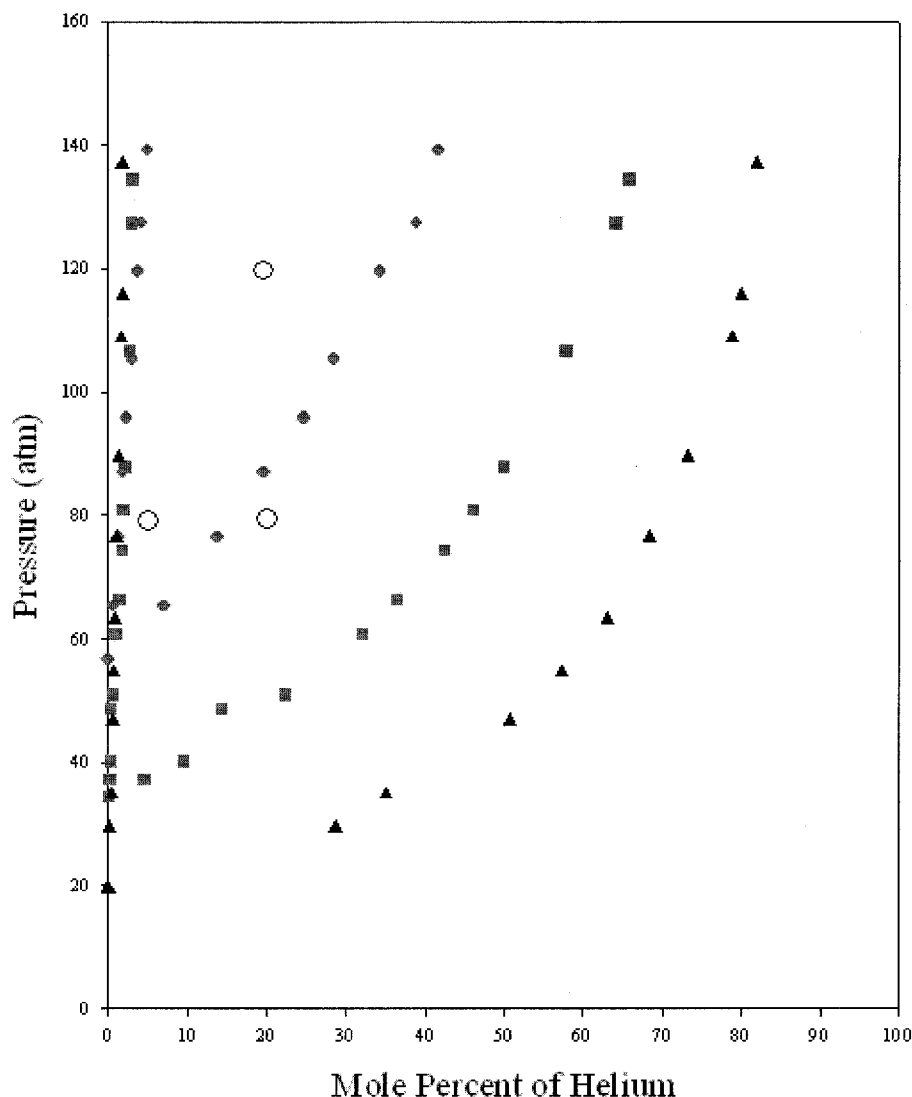
Figure 5. Phase diagram for a binary carbon dioxide–helium system.[17] (▲) −20, (■) 0, and (●) 20 °C; (○) indicate the experimental conditions for the compositions and pressure change experiments.

geometric volume ($\pi r^2 L$ = 4.9 mL) of the chromatographic column. Figure 3 shows a similar separation of Ne, labeled CO_2, acetone, benzene, cyclohexane, and n-pentane in the same column at 15 °C and 80 atm.

The detection system used in these experiments was a mass-specific detector operated in the selected-ion-monitor mode. The m/z values monitored for each solute are shown in the figures. Equivalent chromatograms were observed with a flame ionization detector. The major advantage of the mass-specific detector for this type of investigation is its ability to detect an inert gas, neon, and a labeled isotope of CO_2 in the normal CO_2 carrier gas. This tracer pulse technique could be used to determine the total amount of CO_2 in a chromatographic column. Concurrently, the amount of CO_2 in the mobile phase could be determined from the carrier flow rate and the retention time of a "dead time" marker, i.e., a solute that only exists in the mobile phase. The mathematical expressions are $n_{CO_2}^{Total} = F_M t_R^*$ and $n_{CO_2}^{mobile} = F_M t_0$, where F_M is the molar flow rate of CO_2 mobile phase, t_R^* is the retention time of the CO_2 tracer, and t_0 is the retention time of the dead time marker. Figure 4 shows a separation of neon,

labeled CO_2, and propane obtained in an empty fused-silica-lined, stainless steel capillary column 760 μm × 7.6 m at 26 °C and 80 atm. In this case, the fact that $t_R^* > t_{neon}$ is clear evidence that some CO_2 present in the column is not part of the mobile phase. Because there is no classical stationary phase, the excess CO_2 must exist in the form of liquid droplets either dispersed in the mobile phase or condensed on the walls of the capillary column. The liquid phase would support a lower concentration of neon than the gas phase. These tracer pulse separations were only observed when helium headspace CO_2 was used as the carrier fluid.

The presence of small amounts of dissolved helium in the mobile phase obviously produced some effect that resulted in the unique separations illustrated in Figures 2−4 for columns containing no ordinary stationary liquid or solid phase. Binary mixtures of He and CO_2, such as those obtained from helium headspace CO_2 tanks, have extraordinary phase properties because the two components are immiscible as liquids over a wide range of concentrations. Figure 5, for example, shows the experimental results for the phase equilibrium data (binodal curves) of He−
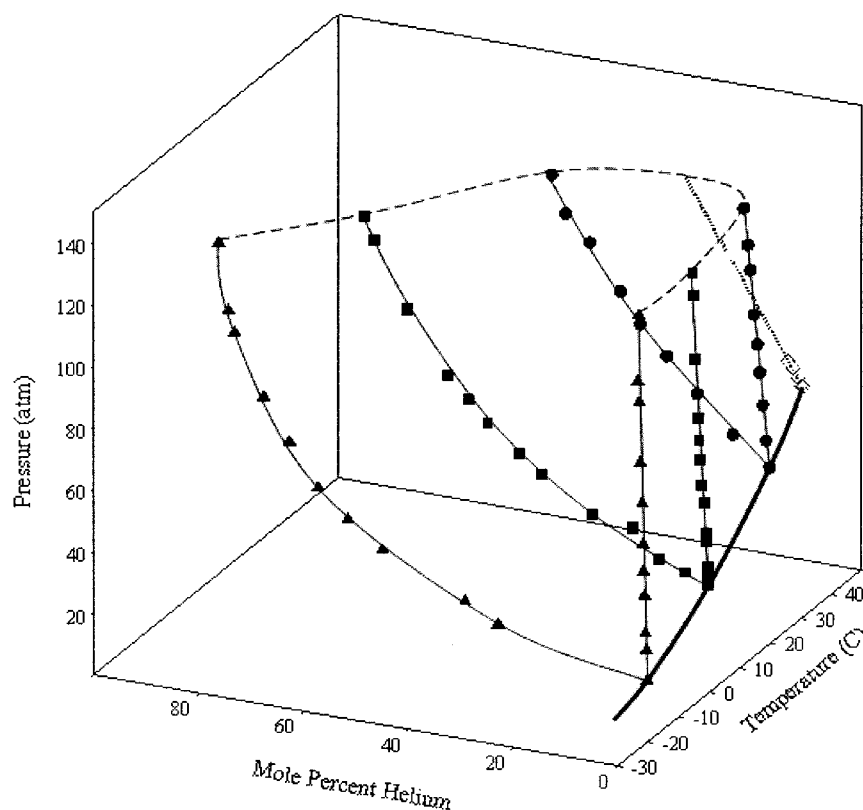
Figure 6. Three-dimensional phase diagram for helium and carbon dioxide.[17,18] (▲) −20, (■) 0, and (●) 20 °C; (◇) critical loci.[18]

CO_2 binary systems from −20 to +20 °C.[17] The mixtures display type III phase behavior rather than the type I observed for most CO_2−modifier SFC systems in which the components are completely miscible as liquids.[3] The mixtures of inert gases and CO_2 are also unique because they can display so-called gas−gas immiscibility of the first kind.[19] Systems of this class have critical temperatures and pressures that *increase* with helium content at low helium concentrations. The particular system He−CO_2 has a critical pressure of ∼8000 atm and critical temperature of ∼80 °C at relatively low concentrations of helium.[16] This means that two phases may coexist in a column at pressures and temperatures well above the critical points of both pure helium and pure CO_2. This unusual phase behavior is illustrated in three dimensions in Figure 6 for pressures within the operating range of most supercritical fluid chromatographs (<200 atm).[17,18] The interior portion of the diagram delineates the physical conditions that result in the development of two phases, i.e., a helium-enriched vapor phase on the left and a CO_2-rich liquid phase on the right. Experimental conditions representing those within the two phase boundaries, i.e., the dew and bubble lines, will result in the formation of both vapor and liquid phases which could act as the mobile and "stationary" phases for chromatographic processes. Thus, relatively small amounts of helium in CO_2 can induce phase segregation at temperatures and pressures where pure CO_2 would be a homogeneous liquid. The separations observed with helium headspace CO_2 could be the result of such phase separation.

It is proposed that the retention mechanism for separations, such as those illustrated in Figures 2−4, is the partitioning of

solutes between vapor and liquid phases both compossed of helium and carbon dioxide. The volume occupied by the liquid phase would account for the elution of some solutes in a volume less than the geometric volume of the column as shown in Figure 2 if these solutes were not very soluble in (retained by) the liquid acting as a stationary phase. This hypothesis was tested in a series of experiments involving the deliberate formation and destruction of single- and two-phase mixtures of helium and CO_2 within the chromatographic column. Chromatographic separations could then be turned on and off by the formation and elimination of the liquid phase. Thus, phase transitions were induced by changes in temperature, pressure, and composition of the mobile phase. The experimental regimes are illustrated by the open circles in Figure 5.

Composition Change Experiments. This set of experiments was carried out at 20 °C and 80 atm in a stainless steel column of 250 μm i.d. × 25 m. The composition of the mobile phase was varied from 0 to 7 and 20 mol % helium in CO_2 by filling each of the two pumps with either pure CO_2 or a 7 or 20% mixture of helium in CO_2. No separation was observed in the empty stainless steel column at any temperature or pressure with pure CO_2. The experiments with 7 and 20% helium were carried out by switching from one syringe pump to the other during the run. The composition of the mobile phase was analyzed concurrently with the auxiliary TCD chromatograph. The results of this experiment are shown in Figure 7. The top chromatogram shows the results of the TCD analysis of the He−CO_2 mobile phase. The helium and CO_2 peaks have opposite polarity because of the nitrogen carrier gas. The dashed lines in the figure show the times at which

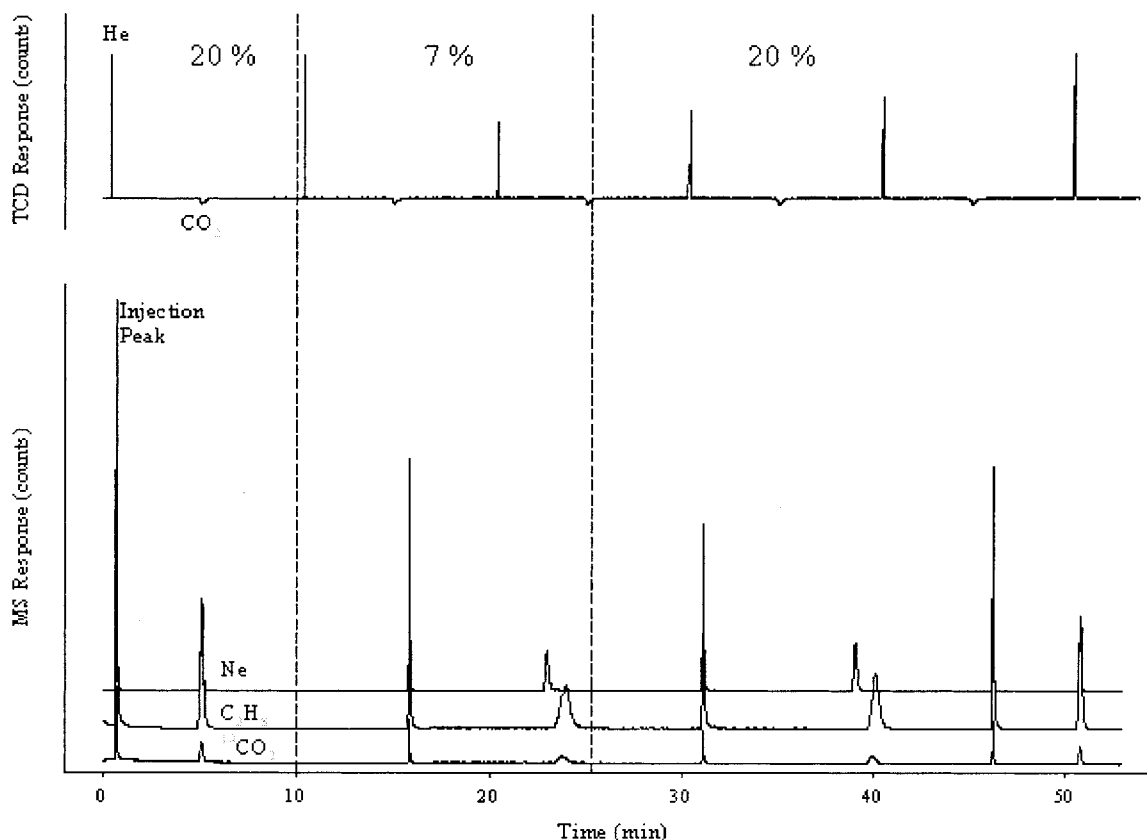(19) Tsiklis, D. S. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 1159−1161.

Figure 7. Chromatogram showing the effect of the composition of the helium−CO_2 mixture on the separation of three test solutes at fixed pressure (80 atm) and temperature (20 °C).

the flow was switched from one pump to the other. The bottom chromatogram illustrates the results of several injections of a mixture of neon, isotopically labeled CO_2, and propane repeated at 15-min intervals. The first peaks from each injection series resulted from the injection of the test mixture at the outlet of the column. The retention time of this set of unresolved peaks indicates the time required for the sample to flow from the column outlet to the mass-specific detector. From the phase diagram (Figure 5), it can be seen that at 20 °C and 80 atm pressure the mobile phase with 20% helium was a homogeneous vapor whereas the mixture with only 7% helium would separate into two phases under the same conditions. If phase segregation was necessary for the chromatographic separation, then the 20% mixture should show no separation of the test mixture, but the 7% mixture should provide the necessary phase distribution needed to support the separations. Although there was some delay between the change in composition at the pumps and the analysis by the GC/TCD at the outlet of the system, the pattern of no separation, separation, and no separation is clear.

Another interesting phenomenon is the change in the retention times of the solutes with the composition of the carrier fluid. The retention times were considerably longer with 7% helium when a separation was observed than with 20% helium. The measured retention times of the solutes were determined by a variety of experimental factors, viz., the volume flow rate and density of the mobile phase, the thickness of the liquid film, and the partition coefficient of the solutes in the liquid film. The volume flow rate in the column was determined by the molar flow rate through

the restrictor and the density of the mobile phase. The restrictor was maintained at a constant pressure and temperature; however, the molar flow rate was influenced by the viscosity of the He−CO_2 carrier. Thus, the molar flow rate for the 7% composition mixture would have been higher than that for the 20% mixture. The volume flow rate through the column, on the other hand, was inversely proportional to the mobile-phase density, which was higher for the 7% mixture than for the 20% mixture at a fixed molar flow rate. Thus, the volume flow rate would have been lower for the 7% mixture if density was the controlling factor. The final two factors that could have influenced the elution times of the solutes were retention in and exclusion from the liquid condensed on the column walls. This effect would depend on the relative solubilities of the various solutes in the condensed liquid phase and the thickness of the liquid film. The latter is important because the holdup volume of the column and thus the retention volume of the solutes would diminish with increasing liquid film thickness.

Temperature Change Experiments. A second way to induce a phase transition in the He−CO_2 systems was to change the temperature at fixed pressure and composition of the mobile phase. The experiments were carried out with the 20 mol % helium in CO_2 mixture at 80 atm. The temperature was changed from 20 °C, where the mobile phase was a homogeneous vapor, to 0 °C, where two phases were formed, and then returned to 20 °C. If the hypothesis was correct, this sequence would effectively turn the separation off, on, and then back off. The results are shown in Figure 8.
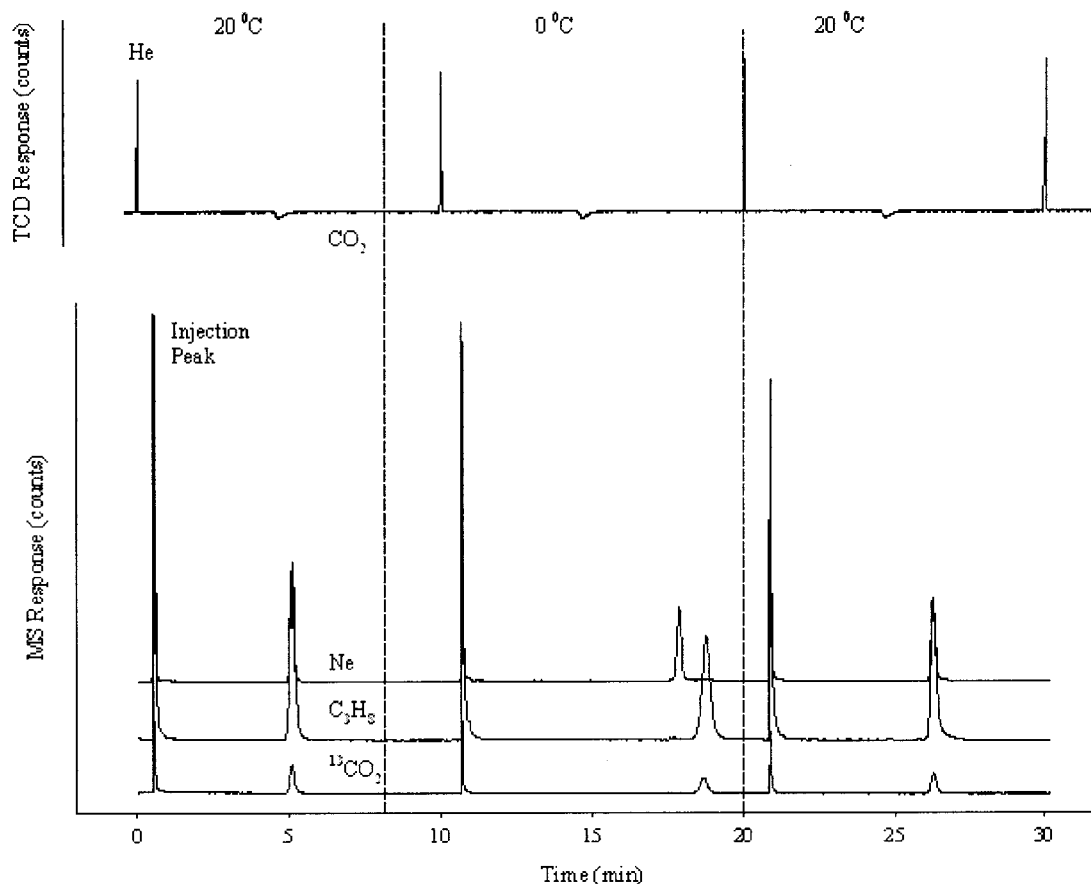
Figure 8. Chromatograms showing the effect of temperature on the separation of three test solutes at fixed pressure (80 atm) and composition (20%).

Pressure Change Experiments. The final way to span the dew line in this system was by varying the pressure at fixed temperature and mobile-phase composition. This set of experiments was performed at 20 °C with the 20 mol % helium in CO_2 mixture. The pressure was changed from 80 to 110 atm and then back to 80 atm. From the phase diagram at 20 °C, it can be seen that the system should have been a homogeneous vapor at 80 atm but segregated into two phases at 110 atm. Again, the results illustrated in Figure 9 confirm the hypothesis.

Phase Ratios. If phase segregation of the He−CO_2 mixtures occurs dynamically within a chromatographic column, the composition of the mixture in the pump and the composition of the mobile phase in the column will differ. At equilibrium, the composition of the mixture in the pumps and the effluent of the column must be the same; however, the composition of the mobile phase within the column may be different because of the dynamic equilibrium phase distribution established within the column at column conditions. For a given inlet composition, the molar phase ratio of liquid and vapor phases in the column after two-phase equilibrium was established can be calculated from the phase diagram using Lever's rule.[20] The volume phase ratio would be determined by the densities of the two phases, which in turn depend on the composition. Accurate calculation of the densities of the liquid and vapor phases can be accomplished from an

applicable equation of state. Roth[21] used the Peng−Robinson EOS[22] to calculate the vapor−liquid equilibrium properties as well as the vapor and liquid densities of helium−CO_2 mixtures. In the reported experiments, however, the precision of the experimental control of pressure and composition is insufficient to report any meaningful phase ratios.

Helium Headspace Carbon Dioxide. Several authors[4,23−25] have pointed out the potential problems that can be encountered when using CO_2 from a delivery tank in which the pressure has been increased above the vapor pressure of liquid CO_2 by the addition of helium gas. Commercial suppliers still offer this type of tank despite the repeated warnings from practicing chromatographers. This investigation highlights many other problems that warrant the discontinuance of the use of helium headspace CO_2. Some of the potential problems are as follows:

(i) Even small amounts of helium in CO_2 can significantly diminish the density of the mobile phase. Because the density of the mobile phase is the primary parameter controlling the retention of solutes in SFC, any uncontrolled variation in the density may have serious consequences, such as irreproducible retention times for chromatographic solutes. It also means that

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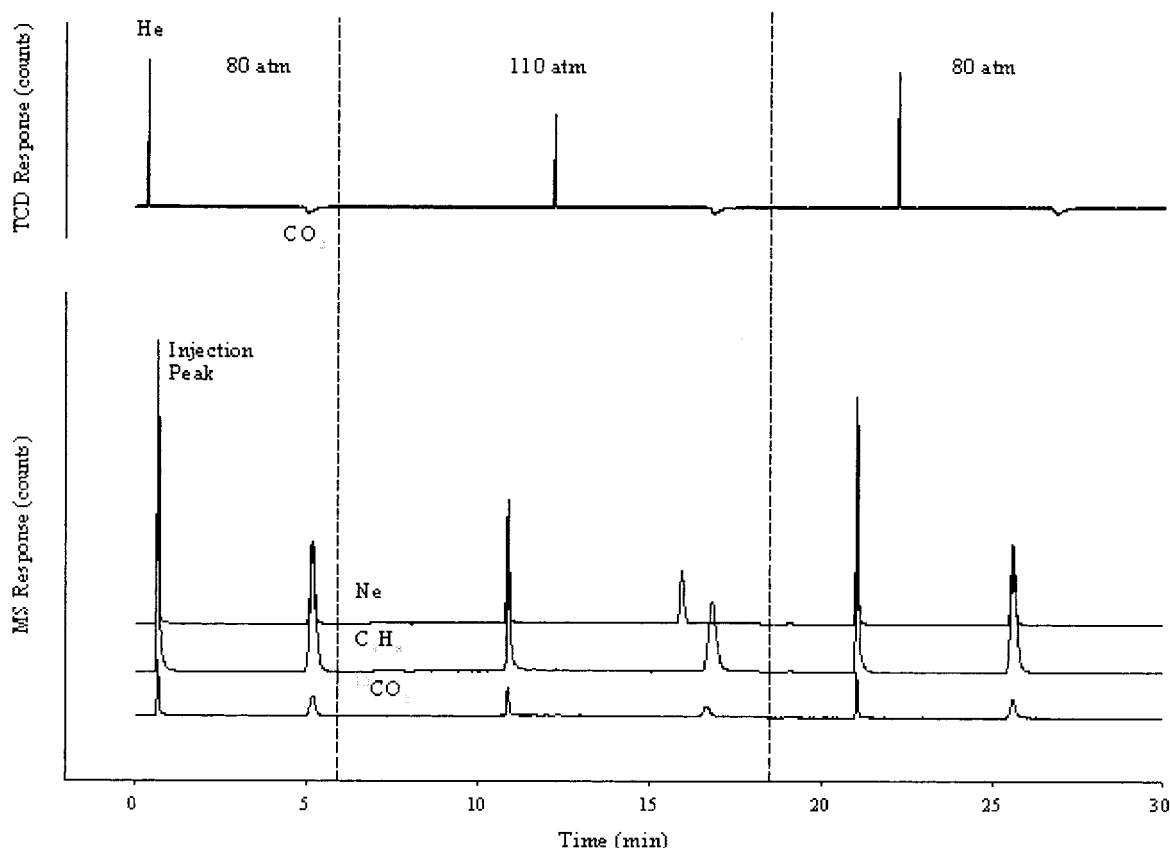
Figure 9. Chromatogram showing the effect of pressure on the separation of three test solutes at fixed temperature (20 °C) and composition (20%).

the density of the mobile phase cannot be calculated accurately from any of the equations of state available for pure CO_2.

(ii) If SFC pump heads are cooled below ambient temperature, as is often done to facilitate loading of the pumps, phase segregation of helium-contaminated CO_2 within the pump can occur. Two phases can be generated over a wide range of helium concentrations and at almost any pressure above the vapor pressure of liquid CO_2 at the pump temperature. This phenomenon would cause erratic delivery of the pump contents.

(iii) Probably the most significant problem with helium headspace CO_2 tanks is the fact that the concentration of helium dissolved in the liquid CO_2 in the tanks depends on environmental factors and the history of the particular tank involved.[16] This problem arises because of the very slow diffusion of helium in the liquid carbon dioxide.

(iv) If phase segregation of a CO_2–helium mixture used as an SFC mobile phase occurred in a column containing a normal stationary liquid phase, the results would be totally unpredictable. The CO_2-rich liquid phase would presumably condense out on and perhaps dissolve in the polymeric stationary liquid phase. Moreover, the mobile-phase composition and density would be significantly altered by the depletion of CO_2. Both of these effects could have disastrous consequences for practical analytical applications.

The disadvantages cited above are most meaningful at experimental column or pump conditions where phase separation of He–CO_2 mixtures can occur, i.e., at subambient temperatures.

CONCLUSIONS

The primary conclusion from this study is that any possible advantages gained by the use of helium headspace carbon dioxide tanks for SFC/SFE applications are more than offset by the uncertainties and uncontrolled effects possibly introduced into the analytical techniques by the presence of uncontrolled contamination of helium in the CO_2 mobile phase.

In addition, the unusual phase properties of mixtures of helium and carbon dioxide illustrated in Figure 5 result in the formation of two-phase systems over a wide range of compositions at pressures greater than 70 atm and temperatures less than 30 °C. If such phase segregation is recognized, it can be used as the basis for chromatographic separations in supposedly empty columns. Because the two immiscible phases are stable over a range of experimental conditions, it is relatively easy to generate such systems in a chromatographic column. If the two phases have different densities and compositions, chromatographic separations can be observed in capillary columns containing no classical (nonvolatile) stationary liquid phase.

Gas liquid chromatography with a dynamically created pseudostationary phase has the following potential advantages compared to normal GLC or GSC:

(1) All of the problems normally associated with classical, nonvolatile stationary liquid phases can be avoided. Empty capillary tubing can be used for columns without the expense or bother of maintaining a stationary liquid phase.

(2) The chromatographic separations can be accomplished at room temperature.

(3) Normal SFC detection systems, such as UV, FID, or MS, can be used with the new type of chromatography. Similarly, any practical SFC injection system can be used.

(4) The solvent strength of the mobile phase can be varied by changing the density similar to SFC. The film thickness of the "stationary" phase can be varied by controlling the ratio of liquid to gas in the column by means of manipulation of temperature, pressure, and composition.

To date, the method has not been investigated with modifiers such as those commonly used for SFC applications or with gases other than carbon dioxide. The exact effect of these added parameters can only be predicted from detailed knowledge of the phase behavior of these complex systems.