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Supercritical Fluid Chromatography Applied to the Characterization of a Siloxane-Based Gas Chromatographic Stationary Phase

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Abstract

Supercritical fluid chromatography using *n*-pentane as a mobile phase and Porasil C as a column packing was applied to the characterization of Dow-Corning 710 fluid, a commonly used gas chromatographic stationary phase. Under the experimental conditions, decomposition of the polymer was observed on columns of alumina, and derivatized Porasil packings were found to be unstable. Linear pressure programming variables were studied at 206 and 216°C by normalizing the total analysis time on a fixed length of column. A series of homologous polymer components was used to demonstrate the effects upon resolution of density-isotherm nonlinearity associated with the mobile phase. The results showed that optimal temperature conditions existed for the use of linear pressure programming, with the choice of temperature conditions dependent upon the molecular weight range. Operational guidelines are suggested. Mixed solvent behavior was investigated for this separation. The effect of changing the polarity of the mobile phase by adding 0 to 20% v/v isopropanol to *n*-pentane was studied under isothermal and isobaric conditions. The alcohol was shown to change adsorption characteristics and alter critical constants. The effect upon the critical constants appeared to conform to Kay's approximation. The results suggest that mixed solvents can be used to speed up separations for mixtures having components of widely different adsorption energies. The pseudocritical concept using Kay's approximation was tested for its qualitative ability to estimate state effects when solvents are mixed. The effect of temperature upon migration behavior was compared for equimolar amounts of

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isopropanol and methanol, each in *n*-pentane. Kay's approximation appeared to be useful for qualitative predictions regarding changes in critical pressure. However, an attempt to predict density isotherm behavior for 20% isopropanol in *n*-pentane relative to pure *n*-pentane suggested that Kay's approximation may not be as useful for predicting critical temperature effects.

INTRODUCTION

When first introduced, supercritical fluid chromatography (SFC) showed that many "nonvolatile" species became mobile through solution in the dense gas phase (*1–7*). Jentoft and Gouw (*8*, *9*) applied SFC to the separation of polystyrene oligomers. They demonstrated that by linearly programming pressure they could achieve higher resolution and a faster separation than could be achieved by steric exclusion chromatography. The molecular weight distribution calculated from their work was found to agree with that obtained by other methods (*10*).

Recently, the strides in gel permeation chromatography have been much faster than in SFC. New smaller packings with closely controlled pore sizes may change the above conclusions (*11*). However, the potential of SFC as an ancillary technique to liquid chromatography for the analysis of medium to high molecular weight compounds has been demonstrated.

The purpose of this study was threefold. The first objective was to explore means of improving separations in SFC by providing operational guidelines for the use of linear pressure programming techniques. The second objective was to explore the feasibility of using this technique as a means of characterizing or preparing pure components from siloxane-based gas chromatographic stationary phases. The final objective was to study mixed solvent behavior and explore its potential for improving separations.

Previously, two observations have been reported which are highly important to linear pressure programming techniques. First, Giddings (*5*, *6*) has shown that solutes remain immobile in the presence of high pressure gases until a definite threshold density has been reached. The pressure producing this density was termed the threshold migration pressure. Second, Meyers and Giddings (*7*) have shown that a plot of reduced threshold density for several *n*-alkanes in the range C_{18} to C_{36} exhibited a linear relationship to carbon number. The former observation relates density, and therefore operating conditions, to the molecular weight of the solute. The latter observation implies that, for a series of homologous compounds, retention regularity can be achieved by linearly programming the mobile-phase density.

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The present study emphasizes that density isotherms are inherently nonlinear in the region of the critical point. A series of homologous polymer components was used to demonstrate the effect of density-isotherm nonlinearity upon chromatographic resolution. The data showed that optimal temperature conditions exist for the use of linear pressure programming. The choice of temperature conditions depends upon the molecular weight range to be chromatographed.

In order to demonstrate the effects of the variables of starting pressure and temperature upon resolution behavior under conditions of linear pressure programming, the technique of time normalization (*12–14*) was used. The total analysis time was maintained constant by simultaneously changing two variables. The variable being studied was changed and simultaneously the programming rate was adjusted. The results suggest that time normalization is an economical method of scouting optimal operating conditions for a particular molecular weight range.

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The effect of changing the polarity of the mobile phase by adding various amounts of alcohol to pure *n*-pentane was studied for this particular separation. Novotny et al. (*15*) and Doran (*16*) have used various amounts of isopropanol in *n*-pentane to shorten elution times for hydrocarbon species. Both authors suggested the use of a polar additive as a means of obtaining separations at lower pressures on either Porasil C or alumina. Jentoft and Gouw (*8, 9*) used 5% methanol in *n*-pentane for the separation of polystyrene oligomers. They gave no reason for the choice of solvent composition, nor did they give details as to the effect of the percentage of alcohol upon the separation. The results of the present investigation show that mixed solvents can speed up the analyses of mixtures having components of widely different adsorption energies. It is shown that the pseudocritical concept and Kay's approximation (*17*) can be used qualitatively to estimate state effects when solvents are mixed. Isobaric and isothermal studies of migration behavior suggest the possibility of designing solvent mixtures to solve particular separation problems.

Dow-Corning 710 silicone fluid was chosen as the solute in this investigation to explore the possibility of using SFC with the eventual goal of preparing some pure single components for use as silicone stationary phases in gas chromatography (GC). These purified phases could then be used to evaluate the effects of oligomeric distribution and the molecular weight of the stationary phase upon retention behavior in GC. Similar studies have been performed with pure hydrocarbons (*18*) and glycols (*19, 20*), but not with silicones, which are very widely used stationary phases. Dow-Corning 710 fluid, a linear polysiloxane polymer of 50%

phenyl composition and average molecular weight 2600 (*21*), is widely used (*22*) and has been suggested as one of a number of preferred liquid phases (*23*). Because of the phenyl content, it is easily detectable in the UV. By using such phases and eliminating the use of redundant GC phases (*18–25*), uncertainties in retention behavior should be smaller when attempting to use data from another laboratory.

EXPERIMENTAL

Reagents

n-Pentane, 99 mole-% minimum (Phillips Petroleum Company, Bartlesville, Oklahoma) was used in all of the mobile phases. Both reagent-grade isopropanol and anhydrous methanol (Mallinckrodt Chemical Works, St. Louis, Missouri) were used with *n*-pentane to produce mixed solvents. Spectrophotometric grade chloroform (Mallinckrodt Chemical Works) was used for gel permeation chromatography.

DC-710 polymer was purchased from Altech Associates, Inc. (Arlington Heights, Illinois).

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Column Packings

Porasil C, 100/150 mesh; *n*-octane bonded to Porasil C, 100/120 mesh; Carbowax 400 bonded to Porasil S, 100/120 mesh; Porapak Q, 80/100 mesh; Woelm Basic Alumina W100 adsorbant grade; and Poragels of less than 37 μm particle sizes and porosities of 60A, 100A, and 200A were purchased from Waters Associates, Framingham, Massachusetts. Dexsil 300 G.C. was purchased from Analabs Inc., North Haven, Connecticut.

Apparatus

Figure 1 shows a block diagram of the experimental apparatus for SFC which was constructed in this laboratory. The apparatus incorporates the same principles described by other workers (*1*, *8*, *26*).

A Model 10-600-2C hydraulic pump (S. C. Hydraulic Engineering Corp., Los Angeles, California) fitted with an air-motor isolator attachment (10-550-33) was used to pump the liquid mobile phase from a reflux condenser, where continuous degassing occurred, into the chromatographic system. The pump works on the principle of hydraulic magnification from the input of 0 to 100 psi of air pressure.

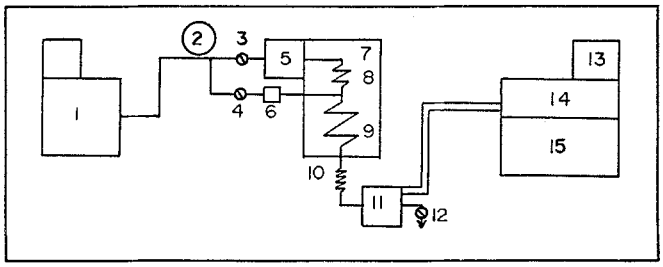

FIG. 1. SFC apparatus. (1) Pumping system—pump, depulsification, pressure programmer. (2) Pressure gauge. (3, 4) Air-actuated valves. (5) Preheater. (6) Injection port. (7) Chromatographic oven. (8) Precolumn. (9) Analytical column. (10) Water-cooled condenser. (11) Ultraviolet detector. (12) Decompression metering valve. (13) Recorder. (14) Digitizer. (15) Teletype punch.

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Pump depulsification was accompolished by insertion of a system of five pressure gauges (#63-3233, Matheson Gas Products, East Rutherford, New Jersey) prior to a fine metering valve (#SS-2MG, Nupro Company, Cleveland, Ohio) which was used to generate a 500 to 700 psi pressure drop at the pump outlet. The metering valve was followed by three 1-m lengths of 1.58 mm o.d. stainless steel tubing which acted as restrictors. Each restrictor was followed by a 0 to 1000 psi gauge (#63-3213, Matheson Gas Products) which provided capacitance. At the outlet of that system, pump pulses averaged ± 2 psi as opposed to ± 150 psi before depulsification.

Pressure programming was accomplished by connecting an 800-step per revolution stepping motor (#HDM-150-800-4), driven by a HDUM-A-K-1 controller unit (USM Corporation, Wakefield, Massachusetts), to an air-line regulator (#3320, Matheson Gas Products) at the air inlet of the pump. A small integrated-circuit timer was constructed using a clock and count-down circuitry. The timer was connected to the external mode of the stepping-motor driver, and it allowed the choice of integral stepping rates from 1 step/sec to 1 step/100 sec. The programmer settings were calibrated by visually observing the Heise gauge, Model #C-54958 (Heise, Newton, Connecticut) shown as item #2 in Fig. 1. Gyrolok fittings were used throughout the chromatographic system (Hoke Inc., Cresskill, New Jersey).

The normal path of flow was from the pumping system, through valve #3, and through a preheater which was maintained about 5°C above column temperature. Supercritical fluid entered the oven, Model 1452-SH

(Becker Delft, Delft, Holland), which contained a 2.7-m precolumn (0.5 mm i.d. by 1.58 mm o.d. stainless steel tubing), and the analytical column before exiting the oven and being condensed to the liquid state upon passing through a water-cooled condenser composed of 1.2 m of 0.5 mm i.d. by 1.58 mm o.d. stainless steel tubing.

Column temperatures were measured by means of a calibrated thermistor (GA71P18, Fenwal Electronics, Inc., Framingham, Massachusetts) suspended in the center of the chromatographic oven.

Sample introduction was accomplished by syringe injection (#4050, Unimetrics Corp., Anaheim, California) into a high-pressure injection port, #6 (#420144, Precision Sampling Corporation, Baton Rouge, Louisiana). Upon inserting the syringe, an air solenoid (V540A 1100, Skinner Electric Valve Co., New Britain, Connecticut) was actuated. This had the simultaneous effect of stopping flow through the preheater by closing the packless valve #3 (air to close, spring open) and initiating flow through the sample bypass by opening valve #4 (air to open, spring close) (Hoke, Inc., Cresskill, New Jersey). At the end of the sampling interval when the sample had been flushed into the column, the solenoid was reversed so as to restore the system to its normal flow configuration. This configuration allowed the injection port to be operated at room temperature.

A high-pressure UV cell was constructed of 316 stainless steel with a light path of 1.5 cm by 1.0 mm i.d. Sapphire windows (0.75 in o.d. by 3/16 in. thick, Edmund Scientific Co., Barrington, New Jersey) were sealed by means of stainless steel "O"-rings which had a 0.001-in. coating of Teflon (#04-2-12-00437-PO-Tl, Vac-Hyd Processing Corp., Indianapolis, Indiana). The seals should allow operation at supercritical conditions of column temperature and pressure (*27*), but that mode of operation was not employed in this work. Instead, the cell was operated at room temperature. The cell compartment was cooled with running tap water to minimize temperature drift. The cell did not leak under 3000 psi of nitrogen pressure. Complete details will be furnished upon request.

Detection was accomplished at 265 nm employing a Beckman DU monochromator and hydrogen lamp source (Beckman Instrments, Inc., Fullerton, California). The beam width from the monochromator had been condensed by changing the exit lens.

The analytical column was maintained under pressure by the insertion of a fine metering valve (#16556, Hoke, Inc., Cresskill, New Jersey), item #12 in Fig. 1, at the end of the chromatographic system. This valve served to set the initial flow rate. In this configuration the detector was maintained under pressure.

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The output current from a photomultiplier (# 1P-28, RCA Corp.) was fed directly into a high-speed picoammeter (Model 417, Keithley Instruments, Inc., Cleveland, Ohio). The picoammeter output was fed into the log inverter amplifier of an Infotronics CRS-30D Digitizer which has been described previously (*28*). Chromatograms were output on a strip chart recorder (LabGraph S, Esterline Angus Instrument Co., Inc., Indianapolis, Indiana).

An Aerograph Model 660 gas chromatograph equipped with a flame ionization detector was used with helium as a carrier gas for the polymer analysis. A 0.35-m by 3.17 mm o.d. by 2 mm i.d. stainless steel column was used. Hamilton (Reno, Nevada) syringes were used for injection. A Keithley Model 417 picoammeter (Keithley Instruments, Inc., Cleveland, Ohio) was used to measure the flame current.

For gel permeation chromatography, three stainless steel columns, 1.2 m by 9.5 mm o.d. by 7.7 mm i.d. containing Poragel of 60A, 100A, and 200A, were connected in series. A Milton Roy Controlled Volume Mini Pump (Model 196-31, Philadelphia, Pennsylvania) was used to pump chloroform through the chromatographic system. The injector and method of injection were the same as described for the supercritical fluid chromatograph. A Laboratory Data Control Corporation (Riviera Beach, Florida) Model 1103 Refractometer having a 6-μl cell volume was used for detection.

Samples for mass spectrometry were run on the direct insertion probe inlet of a Consolidated Electrodynamics Corporation 21-110B double focusing mass spectrometer (Pasadena, California).

Differential thermal analysis was performed in air using a Deltatherm III (Technical Equipment Corporation, Denver, Colorado) differential thermal analysis unit.

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Procedures

For SFC, all porasil columns, both derivatized and nonderivatized, were prepared by adding incremental amounts of the packing as received from the manufacturer into 1 m lengths of 4.5 mm i.d. stainless steel tubing followed by vertical tapping and gentle rapping on the sides of the tube. Columns were coiled after being packed. Nonderivatized Porasil C columns were heated overnight at 230 to 250°C with nitrogen flowing so as to remove adsorbed water.

Alumina of the desired mesh sizes was sonically sieved, starting with the bulk material in this laboratory. Alumina columns were given the same conditioning treatment as nonderivatized Porasil columns.

n-Pentane was used as received without further purification. Mixed solvents were prepared volumetrically, and all compositions refer to volume/volume percent. Upon changing to another solvent, the chromatographic system was thoroughly flushed with the new solvent composition prior to the start of any experiments. Then the pressure at the head of the column and the valve at the exit were adjusted until the desired initial pressure and starting flow rate were achieved.

Samples were introduced as described earlier. The bypass into which the sample was introduced was flushed for a period of 2.5 min before reversing the solenoid and resuming the normal flow path. The sample size in all chromatograms was 10 μl of neat polymer—approximately 10 mg. Benzene (0.04% v/v) was added to the neat polymer to serve as a non-retained species for the calculation of capacity ratios.

The start of the pressure program was manually synchronized with the injection. A single programming rate was used during the course of the entire analysis, and no isobaric periods were introduced.

In time-normalized experiments the total analysis time was maintained constant by simultaneously changing two variables. The variable being studied was changed and simultaneously the programming rate was adjusted.

Gel permeation columns were packed according to a published procedure (*29*). Gels were swelled in acetone and degassed by boiling the mixture. The cooled mixture was decanted to remove fines. A balanced density slurry of toluene mixed with chloroform was used in place of the acetone/tetrachloroethylene mixture described in the literature (*29*). The three-column system generated 6800 plates for benzene under the experimental conditions described here.

The flow rate was was set at 0.35 ml/min. Reported volumes are products of flow rate and retention time.

In testing for decomposition that may have occurred under supercritical conditions, eluents from entire chromatograms were collected from experiments at 900 psi in which a mixture of 10% v/v isopropyl alcohol in *n*-pentane was used. The solvent was allowed to evaporate under a heat lamp. Ten-microliter samples of the neat residue were injected into the gel chromatographic system at room temperature. Each sample was bracketed between two samples of original polymer which had not been subjected to the conditions of the supercritical fluid experiment.

The gas chromatographic column was packed by introducing small amounts of 2% Dexsil-300 coated on to 80/100 mesh AW-DMCS Chrombsorb W while continuously tapping the column with a metal rod.

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Glass wool plugs and Swagelok fittings (Indiana Valve and Fitting, Inc., Indianapolis, Indiana) were used at both ends. The column was conditioned for 4 hr at 400°C with helium flowing.

For analysis the column was first disconnected from the detector. At room temperature the flow rate at the column exit was set to 50 ml/min. The column was then reconnected to the detector. The detector temperature was raised to 400°C and the oven temperature to 125°C. The injection port was raised to 250°C for the injection. Two microliters of a 20% v/v solution of DC-710 in cyclohexane were injected. Temperature programming was immediately started at a rate of 4°C/min. The injection-port temperature was raised to 400°C immediately after the start of the temperature program.

Fractions collected for mass spectral analysis were evaporated to dryness, scrubbed with chloroform, and transferred to a boiling-point capillary for direct probe introduction. Masses were counted directly from oscillograph traces.

Differential thermal analyses were performed in air at a heating rate of 2.5°C/min. The initial temperature was 22°C, and a run was usually ended at 300°C. A sample size of 50 mg was used.

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Calculations

All measurements of retention times were made from the strip charts of the recorders. Calculations were performed on a Digital Equipment Corporation PdP-11/20 computer (Maynard, Massachusetts), by means of programs written in BASIC.

Capacity ratio, k, was calculated using the retention time of benzene as that of a nonretained species according to

$$k = \frac{t_R - t_o}{t_o}$$

where t_R = retention time of the species of interest and t_o = retention time for benzene. Capacity ratios were reproducible to 5% in isobaric experiments.

Resolution, R, was calculated by

$$R = \frac{2d}{w_1 + w_2}$$

where d = distance between two peak maxima, w_1 = extrapolated width at

the baseline of component 1, and w_2 = extrapolated width at the baseline of component 2.

The experimental system produced a nonlinear baseline during the course of a pressure program due to temperature effects. The baseline used in the calculations is shown in the appropriate figures. Calculated resolutions were reproducible to ± 0.05 resolution unit on the same column over periods of days.

The column selectivity is defined as

$$\alpha = k_2/k_1$$

where k_2 = calculated capacity ratio for the longer retained species and k_1 = calculated capacity ratio for the less retained species.

Elution pressure is defined as the experimental pressure at the peak maximum and was calculated as the product of the programming rate and the experimental retention time plus the value of the starting pressure. Retention times were reproducible to 1% in programmed pressure experiments.

Approximate critical constants for mixed solvents as mobile phases were calculated using Kay's method (*17*):

$$T_{C_1M} = Y_A T_{C_1A} + Y_B T_{C_1B}$$

$$P_{C_1M} = Y_A P_{C_1A} + Y_B P_{C_1B}$$

where T_{C_1M} and P_{C_1M} are the calculated critical temperature and critical pressure, respectively, for the mixed solvents; Y_A and Y_B are the respective mole fractions of each of the pure solvents; T_{C_1A} and T_{C_1B} are the critical temperatures of the pure components; and P_{C_1A} and P_{C_1B} are the critical pressures of the pure components.

The values of the critical temperatures and pressures (*17*) for *n*-pentane, isopropanol, and methanol are, respectively, 196.6°C, 33.3 atm; 235.3°C, 47.0 atm; and 240°C, 78.5 atm. The following critical values were calculated for mixed solvents: 10% isopropanol in *n*-pentane, 202.1°C, 35.2 atm; 20% isopropanol in *n*-pentane, 207.6°C, 37.1 atm; and 5.2% methanol in *n*-pentane, 202.8°C, 39.8 atm.

The reported column temperatures are accurate to within 0.5°C.

RESULTS

Preliminary Studies

n-Pentane was chosen as the mobile phase for two reasons. First, it is an excellent room temperature solvent for low molecular weight silicones.

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Second, because it is a liquid at room temperature, fraction collection is simplified.

n-Pentane has been reported to elute most high molecular weight stationary phases (*16*) and, for that reason, solid adsorbants and chemically bonded phases were evaluated. The methods of evaluation for these different types of solid adsorbants are presented in this section.

Porasil C was found to be the most satisfactory adsorbant, providing adequate selectivity and no sample decomposition. Figure 2 shows the general effect of increasing the pressure programming rate when using the same starting pressures and initial flow rates. Pump depulsification had not been perfected in this preliminary study, so there was some peak distortion and loss of resolution at the higher molecular-weight ends of the chromatograms. Nevertheless, it can be seen that resolution and analysis time decreased as the pressure programming rate increased.

Once the preliminary separation had been accomplished, experiments involving mass spectrometry, high-temperature gas chromatography, and gel permeation chromatography were carried out in order to identify the species being chromatographed and to test for the presence of sample decomposition under the experimental conditions.

Fractions were collected from a number of supercritical fluid chromatograms according to the numbers shown in Fig. 2. The results of subjecting these fractions to mass spectral analysis are shown in Table 1.

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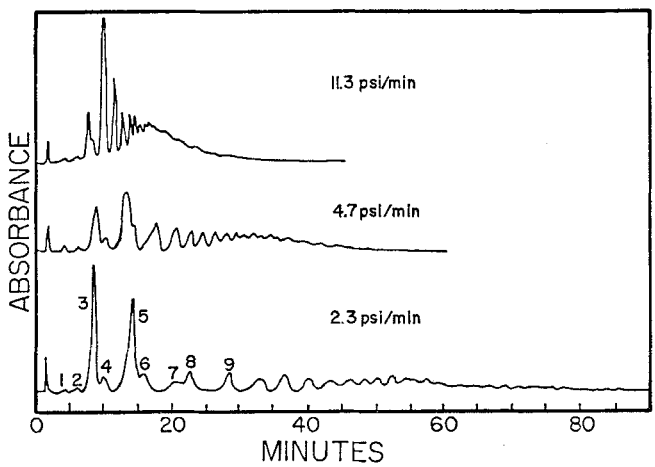

FIG. 2. Effect of pressure programming rate using a fixed column length. Column: 1 m, 100/150 mesh Porasil C. Temperature: 206 °C. Starting pressure: 500 psi. Sample: 10 μl DC–710.

TABLE 1

Mass Spectral Data

SFC fraction no.	Mass	Probable species
2	570	MD_3M
3	544	D_4
4	706	MD_4M
5	680	D_5
6	[a]	[a]
7	816	D_6
8	978	MD_6M
9	1114	MD_7M

[a]Analysis not performed.

The symbols used in Table 1 correspond to the following structural units:

$$M = \text{monofunctional} = CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}{-}O_{0.5}{-}$$

$$D = \text{difunctional} = \overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{-Si-}}}}O-$$

The subscript indicates the number of difunctional units present.

The results listed in Table 1 show the presence of cyclic as well as linear polymer components. The cyclics apparently represent residual starting material from the synthesis of this particular batch of polymer (*30*) and, consequently, the relative amounts and presence of each component would be expected to vary from batch to batch of DC-710. Note that Table 1 suggests the separation is proceeding in the order of phenyl substitution and not directly in the order of molecular weight. Cyclic species of degree of polymerization $n + 1$ eluted after linear components of higher molecular weight but degree of polymerization n.

Figure 3 shows a gas chromatogram recorded employing Dexsil 300 as the stationary phase and DC-710 fluid as the sample. The upper temperature limit in this work was set by the capabilities of our oven. The numbers at various locations in the chromatogram in Fig. 3 are fraction numbers

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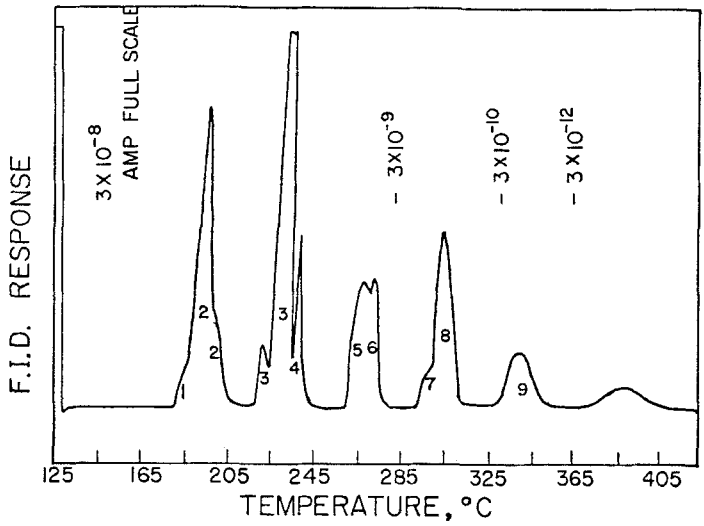

FIG. 3. High temperature gas chromatogram of polymer components.

and show the results of performing GC on the fractions collected for mass spectral analysis. All peaks found in the gas chromatogram on samples of the original silicone oil were present in the supercritical fluid fractions, indicating that the integrity of the low molecular-weight fraction had been retained under the experimental conditions of the supercritical fluid experiment.

Finally, the absence of significant decomposition was demonstrated using gel permeation chromatography. The entire eluent from each of a number of chromatograms from the supercritical fluid experiments using Porasil C was combined and, after evaporation of the solvent, was subjected to gel permeation chromatography. Figure 4 shows a comparison of the reconstituted polymer and the pure polymer which had not been exposed to supercritical conditions. There is no evidence for decomposition. Note, also, that the degree of separation obtained under conditions of classical gel permeation chromatography was much less than that obtained in the supercritical fluid experiment.

As previously noted, the order of elution of polymer components from a Porasil C column seemed to proceed according to the number of benzene rings. The extent to which the nature of the adsorbant surface contributed to this behavior was investigated by switching from Porasil C to a derivatized packing consisting of *n*-octane chemically bonded to a Porasil C

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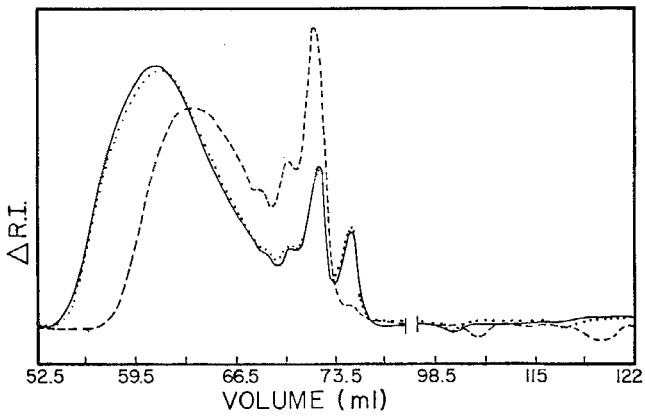

FIG. 4. Gel permeation chromatography of reconstituted polymer samples. (· ·) Porasil C, (– –) basic alumina, and (——) pure DC–710 standard.

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surface. Figure 5 compares the capacity ratios at 206°C for the $n = 4$ cyclic species as a function of pressure on the derivatized and nonderivatized Porasil C. The α values for the $n = 4$ linear/cyclic pair (MD_4M/D_4) are compared in the top portion of this figure. Derivatizing the surface of Porasil C by replacing hydroxyl functions with *n*-octane (*31*) had the effect at lower pressures of increasing the capacity ratios but decreasing the selectivity between linear and cyclic isomers. At higher pressures, capacity ratios for the derivatized and nonderivatized surfaces began to coincide, indicating that the solvent power of the mobile phase had leveled the effect of the stationary support. The above observations show that deactivating the Porasil C surface was deleterious to this separation.

There was another disadvantage of the derivatized surface. The *n*-octyl-bonded Porasil C packing slowly decomposed during the course of its use. This conclusion was reached on the basis that after a few hours of continuous use, k values were found to be lower at lower pressures, and α values agreed with those found on the nonderivatized Porasil C surface. In one earlier case, no decomposition was cited (*8*, *9*), whereas in another paper (*16*) the packing was reported to have decomposed under temperature conditions similar to those reported here.

In separate experiments, differential thermal analyses performed on portions of unused packing indicated that decomposition of the organic layer began at 184°C in the presence of air, in agreement with temperature limits prescribed by the manufacturer.

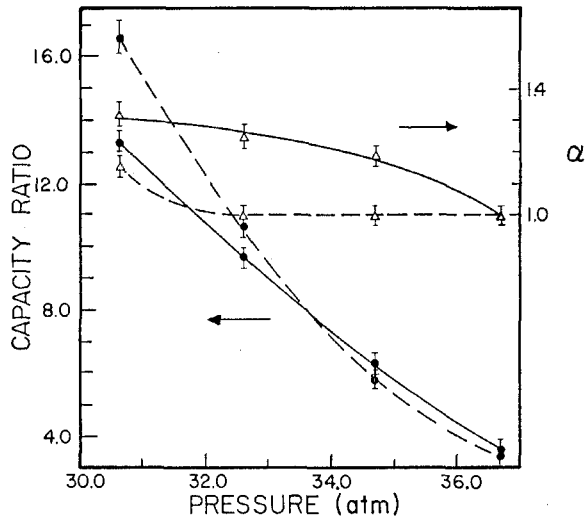

FIG. 5. Comparison of capacity ratios and selectivities on derivatized and nonderivatized Porasil C. (——) 100/150 mesh Porasil C, (– –) 100/120 mesh *n*-octyl bonded Porasil C, (●) D_4, and (△) α for MD_4M/D_4 pair.

A second derivatized Porasil packing was also evaluated. Carbowax 400 bonded to Porasil S was found to decompose very rapidly compared to *n*-octane bonded to Porasil C under the same experimental conditions.

Basic alumina was tested as a stationary adsorbant because of its frequency of use in previous publications (*3*, *8*, *15*, *16*). We hoped that base-catalyzed decomposition (*30*) of polysiloxane might be slow enough to permit its use. Initial experimental reproducibility was good when using a 1-m column with 10% isopropanol in *n*-pentane. (The alcohol was necessary in order to obtain reasonably short retention times.) However, on going to longer columns there were large discrepancies between chromatograms for different column lengths. When fractions were collected from a 1-m column and then subjected to microdistillation on a direct-insertion probe in the mass spectrometer inlet, the mass spectra indicated the presence of hydroxylated and isopropylated end groups in addition to linear polymer components. Hence alumina was sufficiently basic to catalyze the reaction between isopropyl alcohol and siloxane under the experimental conditions. A gel permeation chromatogram, shown in Fig. 4, clearly confirmed that the nature of the sample had been altered.

The third type of column packing evaluated was Porapak Q, a micro-

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porous cross-linked styrene/divinylbenzene copolymer bead (*32*). Using *n*-pentane under the same experimental conditions reported for Porasil C, polymer components exhibited extremely long retention times. Lowering the temperature of operation speeded up elution, but it appeared that the selectivity of this support for the polymer components was much poorer than that obtained using Porasil.

Isobaric and Isothermal Migration Behavior Using *n*-Pentane

The gas phase interactions, which are responsible for the enhanced migration in SFC, are known to be sensitive functions of both temperature and pressure (*1–3*, *15*). We chose to examine the migration behavior of some selected polymer components above their threshold migration pressures. By examining the effects of temperature and pressure on each adsorption equilibrium and on the resolution of selected pairs of components, we obtained information which was useful for understanding the resolution behavior obtained under programming conditions.

The effect of temperature is illustrated in Fig. 6. Log k values were plotted at various temperatures for the $n = 4$ linear and cyclic polymer components and the $n = 5$ cyclic species. α values are plotted in the lower half of this figure. Note that both log k and α decreased with decreasing

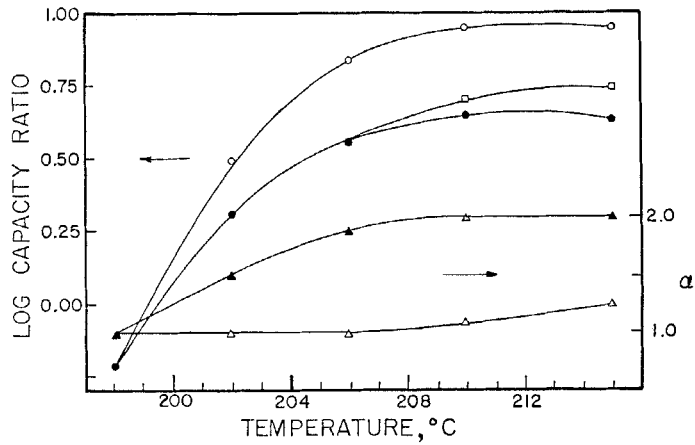

FIG. 6. Logarithm of the capacity ratio and column selectivity values on Porasil C at 540 psi as a function of temperature using *n*-pentane. Capacity ratios: (●) D_4, (□) MD_8M, and (○) D_5. α values: (△) MD_4M/D_4 and (▲) D_5/D_4.

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temperature. The decrease of log k with decreasing temperature indicates that the density of the mobile phase had increased rapidly and was approaching that of the liquid state at lower temperatures. All resolution was lost at 198°C. Notice also the effect of increased solvent power on the more difficult separation. The resolution between the $n=4$ linear/cyclic pair became zero at 206°C, whereas resolution was still finite for the two cyclic isomers.

The effect of pressure is shown in Fig. 7 where log k is plotted at various pressures and temperatures. The α value for the $n=4$ and 5 cyclic species is shown in the lower part of this figure. Note that both log k and α decreased as the applied pressure increased. Figure 6 shows that in a pressure-programmed separation, higher temperature operation will improve resolution by providing a larger capacity ratio for species that are above their threshold migration densities. However, if too fast a programming rate is used, species will elute at higher pressures, a factor which will counterbalance the effect of a higher temperature on resolution by lowering both k and α. A programming rate which causes a species to elute at minimum pressure under isothermal conditions will provide a larger α

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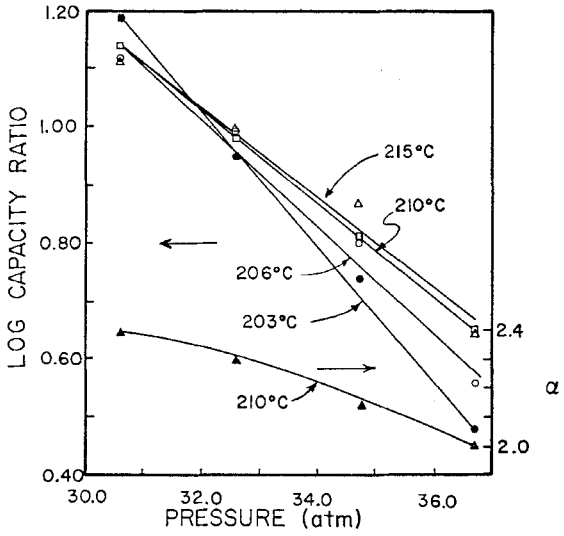

FIG. 7. Logarithm of the capacity ratio and column selectivity as a function of pressure using n-pentane. Capacity ratios are for solute D_4 at temperatures of (●) 203°C, (○) 206°C, (□) 210°C, and (△) 215°C. α values: (▲) D_5/D_4 at 210°C.

and k, which in turn will improve resolution at the expense of an increased analysis time.

Normalization of Total Analysis Time Using *n*-Pentane

This section demonstrates the effects of temperature and starting pressure upon resolution behavior under the conditions of linear pressure programming. Before the results are discussed, further background about the experimental details will be helpful. The 1-m column length was chosen arbitrarily. It seemed adequate to resolve rather well many components over the entire molecular weight range of the sample. The mesh size was not optimized, but it was similar to that reported by other workers (*8*, *15*, *33*) so as to produce a reasonable pressure drop. Large pressure drops have been shown to increase HETP (*15*, *34*, *35*) and to degrade resolution. The temperature range, 206 to 216°C, was chosen because previous polymer separations involving similar molecular weight ranges have been performed within this temperature range (*8*).

The first variable studied was the isothermal operating temperature. Temperature has two effects in SFC. For species above their threshold migration pressure, raising the temperature can increase resolution at the expense of increasing the analysis time. Temperature also affects the manner in which solvent density varies with pressure.

The effect upon resolution behavior of nonlinearity in the density isotherm for the mobile phase is demonstrated here. In order to differentiate between the two effects of temperature, the total analysis time was normalized to within 10% as shown in Fig. 8. The results indicated that programming the pressure linearly was not equivalent to programming the density linearly. An overall gain in resolution was achieved in the same total analysis time by a modest increase in temperature from 206 to 216°C. Figure 9 compares the run at 216°C with the one at 206°C, both at the starting pressure of 500 psi. Calculated resolution versus consecutive peak pairs is plotted for the first 20 peaks. The presence of both cyclic and linear components gives these plots an irregular profile up to consecutive peak pair 8. Note that resolution between the linear and cyclic molecules at consecutive peak pairs 3, 5, and 7 increased at the low molecular-weight end. Likewise, resolution at the high molecular-weight end from consecutive peak pairs 8 through 20 also improved.

The second variable studied was starting pressure. The results showed that the effect of changing the starting pressure at a fixed temperature

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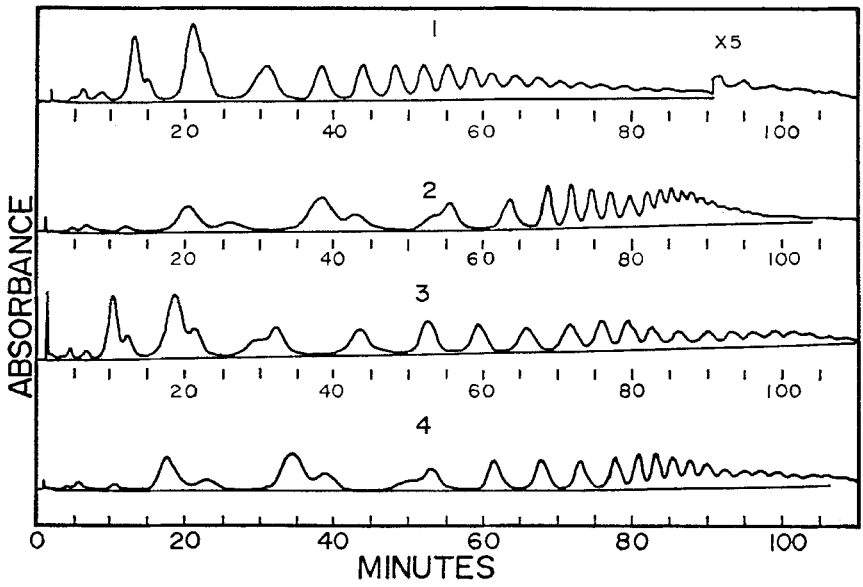

FIG. 8. Time-normalized chromatograms on Porasil C using *n*-pentane. Temperature, starting pressure, programming rate, respectively: (1) 206°C, 500 psi, 1.8 psi/min; (2) 206°C, 400 psi, 2.7 psi/min; (3) 216°C, 500 psi, 2.5 psi/min; and (4) 216°C, 400 psi, 3.5 psi/min. Initial flow rate: 1.9 ml/min.

differs with the molecular weight range. This observation is consistent with Giddings' concept of threshold migration pressures (*5*, *6*). Figure 8 also shows two chromatograms, 2 and 4, recorded at a starting pressure of 400 psi and 206 and 216°C, respectively. Only species which were already near or above their threshold pressures at the starting pressure of 500 psi were affected by lowering the starting pressure to 400 psi. Isobaric experiments performed at 216°C, which have not been presented in this paper, indicated that the first eight species in this polymer were above their threshold pressures at 500 psi as indicated by their ability to elute within 80 min. (This criterion, although arbitrary, provides a useful qualitative guideline.) The effect of lowering the starting pressure at 216°C is also shown in Fig. 9. Note that the resolution between the linear and cyclic species was greatly improved at the low molecular-weight end of the chromatogram. However, resolution at the high molecular-weight end was poorer, reflecting the faster programming rate.

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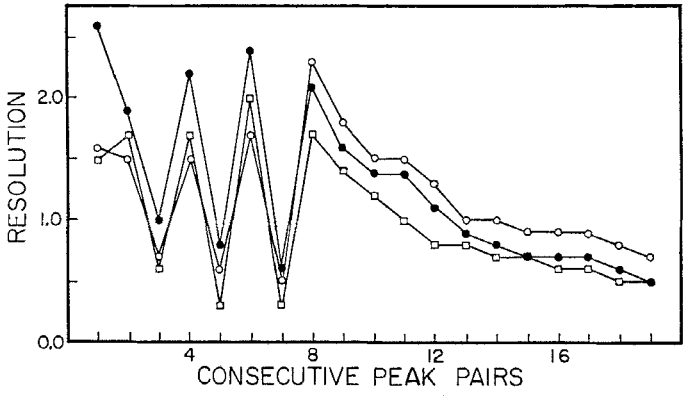

FIG. 9. Calculated resolution values for consecutive peak pairs from the chromatograms shown in Fig. 8. Symbols refer to chromatograms (□) 1, (○) 3, and (●) 4.

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Mixed Solvents

Mixed solvents are expected to have critical properties which differ from those of either pure solvent alone. The term pseudosolvent (*17*) has been used to refer to a solvent mixture that is assumed to behave as a pure fluid. The present study tests the pseudocritical approach and the use of Kay's approximation (*17*) to estimate qualitatively state effects when solvents are mixed.

The first part of this investigation studied the general effect of the percentage of isopropanol upon the migration behavior of selected polymer components under isobaric and isothermal conditions. Two effects were observed. The first involved the ability of the polar additive to act as a displacing agent at low concentrations of alcohol. The second involved an alteration of the gas phase interactions with the solutes. In Fig. 10, k and α values are plotted at different percentages of alcohol for the $n = 4$ linear/cyclic pair. The α values in parentheses at the right of this figure refer to the $n = 4/5$ cyclic pair. Note how the k values increased for the linear/cyclic pair over the range of 0 to 2% alcohol. The cyclic species had a smaller k than the linear component because of its lower adsorption energy. A sharp increase in α (linear/cyclic) occurred because the cyclic species had been displaced by the alcohol relative to the linear component. The percentage increase in α between the cyclic/cyclic components was much smaller than that observed for the linear/cyclic pair. Note also that the behavior of k appeared to conform to Kay's linear approximation over the range 2 to 20% alcohol.

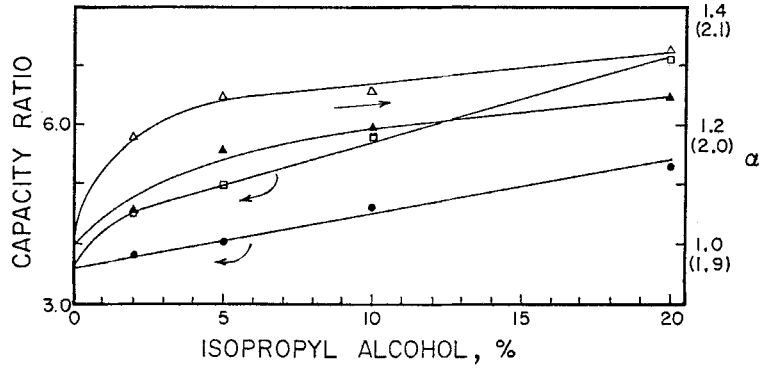

FIG. 10. Capacity ratio and column selectivity values on Porasil C at 206°C and 540 psi as a function of the percentage of isopropyl alcohol added to *n*-pentane. Capacity ratios: (●) D_4 and (□) MD_4M. α values: (△) MDM_4/D_4 and (▲) D_5/D_4. α values in parentheses refer to ▲.

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In the second part of this investigation the objective was to ascertain whether or not the migration behavior of the solutes demonstrated the same regularity as was observed in Figs. 6 and 7 for pure *n*-pentane. For that reason we examined the migration behavior of the same polymer components using a fixed solvent composition of 10% isopropanol in *n*-pentane. The results shown in Figs. 11 and 12 indicated that the mixed solvent behaved like a pure solvent. In Fig. 11, note that the behavior of log k and α followed the same general trends illustrated in Fig. 6. However, the maximum values of log k and α occurred at lower temperatures. For example, the maximum value of α (linear/cyclic) was attained at 215°C in Fig. 6, whereas the same α and log k values for the same solutes were attained at 203°C using 10% isopropanol. Finally, in Fig. 12, the slopes of the log k plots are different from those observed for pure *n*-pentane in Fig. 7. This behavior was probably the combined result of a change in the nature of the dense gas phase interactions, the interaction of the alcohol with the surface, and an altered density isotherm relative to pure pentane.

In the third part of this investigation the effect of temperature under isobaric conditions was studied using an equimolar amount of methanol instead of isopropanol. The comparison in Fig. 11 shows that migration behavior depended upon the nature of the alcohol. Recall that the calculated critical constants for 10% isopropanol in *n*-pentane and 5.2% methanol in *n*-pentane as given in the earlier section on calculations are approximately 202 and 203°C, respectively, for the critical temperatures, and 35 and 40 atm, respectively, for the critical pressures. Increasing the

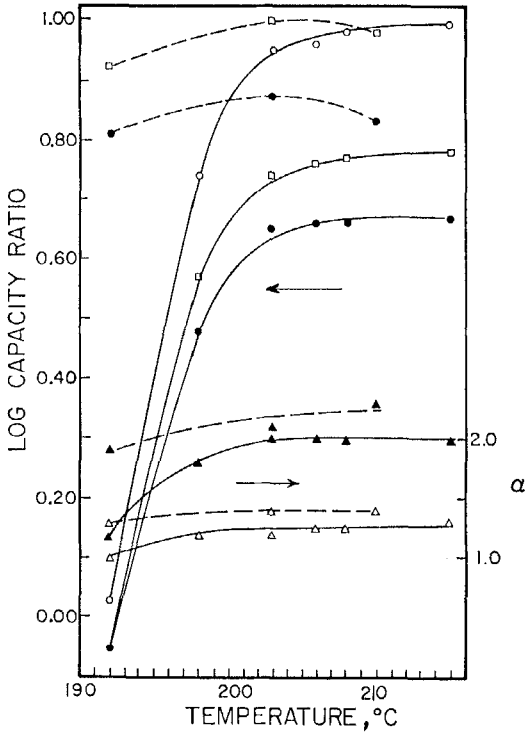

FIG. 11. Logarithm of the capacity ratio and column selectivity values on Porasil C at 540 psi as a function of temperature using 10% isopropanol and 5.2% methanol in *n*-pentane. Eluents: (——) 10% isopropanol and (– –) 5.2% methanol. Capacity ratios: (●) D_4, (□) MD_4M, and (○) D_5. α values: (△) MD_4M/D_4 and (▲) D_5/D_4.

critical pressure would be expected to decrease the solubility of the solutes. Note that both log k and α increased relative to pure *n*-pentane or to 10% isopropanol in *n*-pentane.

The final part of this investigation studied the net effect of the alcohol on the entire separation. Mobile phases consisting of pure *n*-pentane and 20% isopropanol in *n*-pentane were compared under the conditions of time normalization at 216°C. The total analysis time was normalized to 110 min and the starting pressure was 500 psi. Previously, under isobaric and isothermal conditions, the addition of alcohol improved the separation between linear and cyclic molecules. The same result was found under linear pressure programmed conditions. Figure 13 is a plot of resolution

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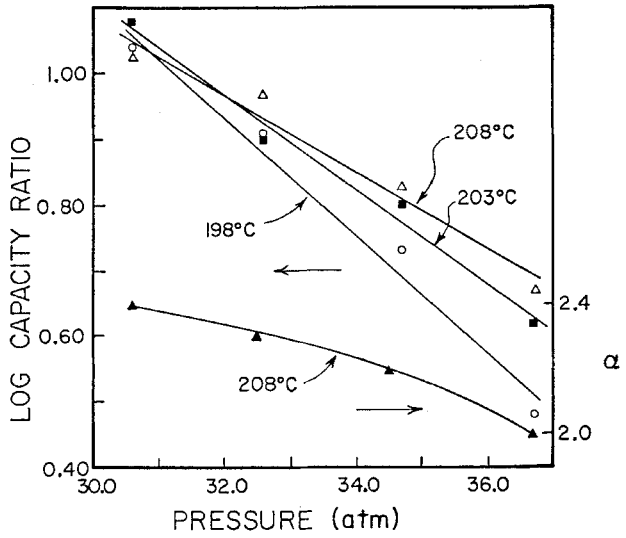

FIG. 12. Logarithm of the capacity ratio and column selectivity values on Porasil C as a function of pressure using 10% isopropanol in *n*-pentane. Capacity ratios are for solute D_4 at temperatures of (○) 198°C, (■) 203°C, and (△) 208°C. α values: (▲) D_5/D_4 at 208°C.

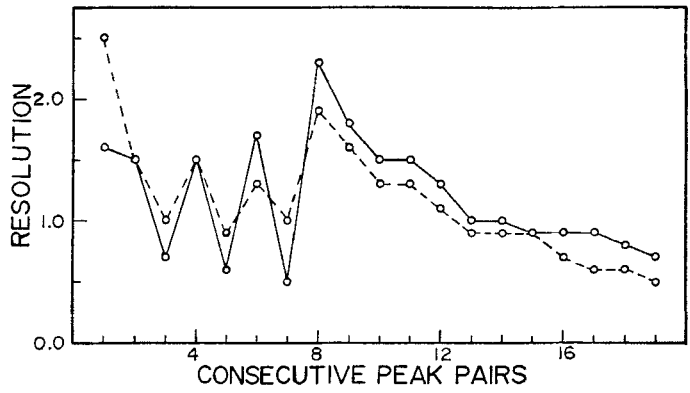

FIG. 13. Comparison of calculated resolution values for consecutive peak pairs for time-normalized separations employing pure *n*-pentane and 20% isopropanol in *n*-pentane as mobile phases: (——) *n*-pentane, 216°C, 500 psi, 2.5 psi/min and (– –) 20% isopropanol in *n*-pentane, 216°C, 500 psi, 3.0 psi/min. Initial flow rate: 1.9 ml/min.

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versus consecutive peak pairs for both separations. The resolution between linear and cyclic molecules at consecutive peak pairs 3, 5, and 7 was better with the mixed solvent. In fact, a comparison with Fig. 9 shows that the resolution was better than that obtained with pure *n*-pentane when the starting pressure was lowered 100 psi.

At the high molecular-weight end, from consecutive peak pairs 8 through 20, the resolution was poorer with the mixed solvent. Based upon the results found previously for *n*-pentane, the poorer resolution for the mixed solvent could have been the result of operation closer to the critical temperature. The approximate critical constants for 20% isopropanol in *n*-pentane as given in the calculations section are 207.6°C and 37.1 atm as opposed to 196.6°C and 33.3 atm for pure *n*-pentane. Hence operation at 216°C with the mixed solvent would be expected to closely parallel operation at 206°C with pure *n*-pentane.

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DISCUSSION

The present study can be used to demonstrate the need to choose judiciously a region of the density isotherm for the mobile phase which varies in a nearly linear manner with pressure. Figure 14 illustrates the variation of the density of supercritical *n*-pentane at 204.4 and 221.1°C as a

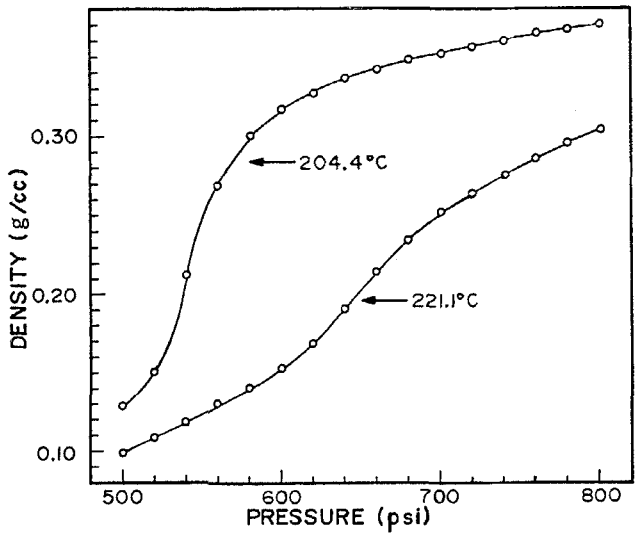

FIG. 14. Density as a function of pressure for pure *n*-pentane. From Ref. *36*.

function of pressure (*36*). These curves show the nonlinearity of the density isotherms for supercritical *n*-pentane over temperature and pressure ranges similar to those employed in this work. The density isotherms for the mobile phase determine the limits of linearity for retention behavior. They can be correlated to the retention exhibited in selected chromatograms by expressing the retention behavior for components in terms of pressure. Figure 15 is a plot of the pressure at the eluted peak maximum versus consecutive peak number for selected chromatograms. It is evident that the curves from chromatograms originating at the starting pressure of 500 psi are sigmoidally shaped as are the density isotherms in Fig. 14.

Three general observations, which suggest guidelines for operational parameters in pressure programming, can be made by comparing Figs. 14 and 15. First, increasing the column temperature for a particular separa-

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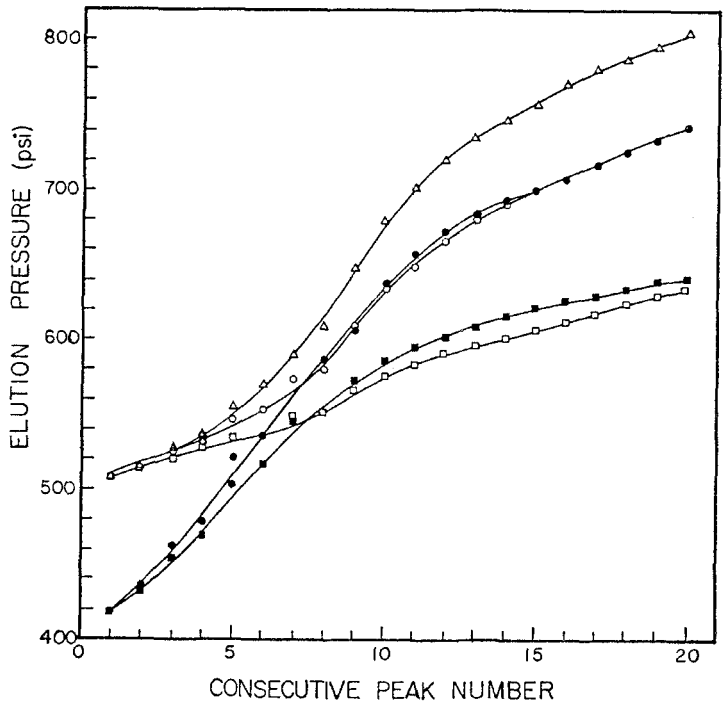

FIG. 15. Comparison of elution pressure values of consecutive peaks for separations on Porasil C: (□) 1, (■) 2, (○) 3, and (●) 4 in Fig. 8; (△) mobile phase 20% isopropanol in *n*-pentane from Fig. 13. (Corresponding chromatogram is not shown.)

tion in the vicinity of the critical temperature requires the use of higher pressures. Figure 14 shows that a small increase in temperature can significantly raise the pressure required to produce a particular density value. In Fig. 15 it is seen that peak number 20 eluted at 640 psi at 206°C and at 740 psi at 216°C. Second, at temperatures less than 10°C above the critical temperature the density isotherm will be steeper than at higher temperatures. From Fig. 15 it is evident that at 206°C a region between peaks 8 and 12 existed where the fixed programming rate was too fast, resulting in faster elution of the higher molecular-weight components. This region, close to the critical temperature, is better suited for the use of long columns or slow programming rates. In this region, nonlinear pressure programming would probably be a better means of optimizing resolution for a wide molecular weight range because of the nonlinear nature of the density isotherm. Third, at temperatures greater than 10°C above the critical temperature, the density isotherm becomes less steep and more nearly linear. In Fig. 15 the density increase was less rapid in the region between peaks 8 and 12 for the higher temperature chromatogram. As a result, a more nearly linear elution profile was observed. Temperature operation greater than 10°C above the critical temperature appears to be more suitable for the use of fixed programming rates.

The above discussion suggests that linear pressure programming should be more beneficial when operating at temperatures well above the critical temperature. Higher temperature operation should also be beneficial to mass transfer, as it is in normal gas chromatography (*37–39*). Novotny et al. (*15*) have shown that HETP, the height equivalent to a theoretical plate, measured for chrysene in pentane was more favorable at higher temperatures over volumetric flow rates typical of those employed in the present work. A recent treatment of mass transfer effects in supercritical CO_2 by Bartmann and Schneider (*40*) suggests that the observed effect could be the combined result of an increased capacity ratio and a more favorable diffusion coefficient for the mobile phase at the higher temperature.

High temperature operation, however, also has disadvantages. The mobile phase must be thermally stable at extended temperatures above the critical temperature. The probability of solute decomposition is increased at high operating temperatures. Finally, the thermal stability of column packing materials must also be considered.

The present study suggests that mixed solvents can be used to improve separations involving compounds of widely different adsorption energies.

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For the separation of individual pairs of geometric isomers in this polymer, the addition of alcohol had the effect of reducing the analysis time required. A comparison of the data at 206°C in Figs. 5 and 10 shows that the same maximum value of α (linear/cyclic) was obtained at 540 psi with 20% isopropanol and at 450 psi with pure *n*-pentane. However, at 450 psi the value of k for the $n=4$ cyclic species was 16.6, which is more than three times as large as that observed for 20% isopropanol at 540 psi.

The above behavior is attributed to a moderator effect arising because of the ability of the alcohol to compete effectively for adsorption sites on the silica surface. As shown in Fig. 10, the largest change in α (linear/cyclic) occurred over the range 0 to 2% isopropanol where minimal alteration of the critical constants for the mobile phase would be expected. Otherwise, state effects cannot be distinguished from any physical-chemical solubility effects on the migration behavior. Unfortunately, the experimental design of the present work did not normalize for state effects by correcting mobile phases to the same reduced states of temperature and pressure relative to their critical points.

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Because of the potential for improving separations by using mixed solvents, we attempted to apply the operational guidelines suggested for pure pentane to the mixed solvent system. At present, no verified means of calculating accurate critical constants for mixed fluids exists when considering molecules of vastly different polarities such as an alcohol and a hydrocarbon (*17*). Recall, however, that the predictions based upon Kay's approximation correlated reasonably well with the experimental behavior. Nevertheless, it must be understood that this approach neglects many factors. Chemical effects associated with the adsorbant surface, "chemical" solubility effects in the mobile phase, and the phase behavior of mixed solvents in the vicinity of the critical point were not considered.

Particular caution should be exercised when attempting to correlate calculated increases in critical temperature and density-isotherm behavior. Recall that under conditions of time normalization, it was shown for pure *n*-pentane that operation at 20°C above the critical temperature was more favorable for this separation than operation at lower temperatures. At 216°C the calculated increase in the critical temperature for 20% ispropanol in *n*-pentane relative to pure *n*-pentane would have been expected to provide a density isotherm resembling that for pure *n*-pentane at 206°C. However, the elution profile shown in Fig. 15 for the mixed solvent more closely resembles the profile for pure *n*-pentane at 216°C than at 206°C.

Acknowledgments

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