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# Influence of mobile phase composition on methylene group selectivity and homologous compound retention in near-critical mobile phases

John A. Blackwell\*, Rodger W. Stringham

*Dupont Merck Pharmaceutical Company, Chemical Process Research and Development, Chambers Works, PRF-1 (S-1), Deepwater, NJ 08023, USA*

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## Abstract

A number of near-critical mobile phases were evaluated with respect to methylene group selectivity and overall eluotropic strength on a polymeric column. Binary mobile phases, consisting of mixtures of carbon dioxide and 1,1,1,2-tetrafluoroethane (HFC-134a), showed strong temperature and compositional dependence on both retention and selectivity. Binary mobile phases, consisting of mixtures of carbon dioxide and conventional modifiers such as alcohols, acetonitrile and tetrahydrofuran, also showed a strong temperature dependence on methylene group selectivity and relative retention. In contrast to the behavior observed using a polymeric column, a bonded silica-based stationary phase displayed significant deviations from the Martin rule, even with high order homologs. Of all the systems evaluated in this study, a binary mixture of carbon dioxide and 2-methoxyethanol proved to be optimal for obtaining a high degree of methylene group selectivity and strong eluotropic strength. Published by Elsevier Science B.V.

*Keywords:* Mobile phase composition; Methylene group selectivity; Eluotropic strength

## 1. Introduction

SFC has proven to be an extremely useful tool for the analysis of petrochemicals and low molecular mass polymers [1–4]. Applications describing the use of open tubular capillary, packed capillary or packed column SFC with a variety of mobile and stationary phases abound. Comparisons to similar separations using GC or high temperature GC show SFC to have a much larger dynamic range due, in part, to the enhanced solvating ability of the mobile phase. HPLC separations overcome this limitation,

but the higher analyte diffusivity in a near-critical or supercritical mobile phase is superior to that in a condensed phase. The result is much higher efficiencies and higher optimum linear velocities.

Despite a great deal of experimentation in this area, little has been done to systematically examine the factors which govern methylene group selectivity in SFC. A number of examples have been cited where the homolog selectivity is improved by a change in the mobile or stationary phase, yet no physicochemical correlations between selectivity and the system have been forwarded [5]. In this study, the correlation between homolog selectivity and mobile phase composition was examined for a series

\*Corresponding author.

of alkyl benzenes and alkyl phenones on a variety of hydrophobic stationary phases. Carbon dioxide mobile phases modified with conventional modifiers were compared at a variety of temperatures to determine the relative effects on methylene group selectivity.

1,1,1,2-Tetrafluoroethane (HFC-134a), an environmentally friendly alternative to chlorine-containing chlorofluorocarbons and hydrochlorofluorocarbons, was also examined both as a pure mobile phase and as a modifier for carbon dioxide. The relatively high eluotropic strength of HFC-134a has been well established, but its effect on methylene group selectivity remains to be determined [6–8]. The relative eluotropic strengths of each of these mobile phases were also compared to determine the optimum mobile phase composition for these analytes.

## 2. Experimental

### 2.1. Chromatographic system

The chromatographic system used in this study was a Gilson SF3 system (Gilson, Inc. Middleton, WI, USA). Carbon dioxide mobile phase was pumped with a Gilson model 308 pump with thermostatted head. Modifiers, including HFC-134a, were pumped with a Gilson model 306 pump. Mixing took place in a Gilson model 811C dynamic mixer with a 1.5 ml mixing chamber. Fixed loop injections (5  $\mu$ l) were made using a Gilson model 231XL sampling injector. Column thermostating

was accomplished using a Gilson model 831 temperature regulator. Detection was accomplished at 210 nm using a Gilson model 117 variable wavelength UV detector with a 7  $\mu$ l high pressure flow cell. Column backpressure was maintained using a Gilson model 821 pressure regulator.

### 2.2. Columns

Jordi-Gel RP-C<sub>18</sub> columns (250 $\times$ 4.6 mm; 5  $\mu$ m particles) were obtained from Alltech Associates (Waukegan, IL, USA). This packing material is a highly porous particulate homopolymer of divinylbenzene. Octadecyl ligands are ligated to the particle surface via arylamine linkages. Zorbax SB-C<sub>18</sub> columns (150 $\times$ 4.6 mm; 5  $\mu$ m particles) were obtained from Mac-Mod (Chadds Ford, PA, USA).

### 2.3. Chromatographic conditions

Alkylphenone and alkylbenzene homologs were chromatographed at 75 and 125°C using HFC-134a/carbon dioxide binary mobile phases. These binary mobile phase components were mixed at approximately 200 bar and 25°C. Flow-rate was 1.0 ml/min with a backpressure of 200 bar. Carbon dioxide and HFC-134a densities were obtained using NIST REFPROP v4.0 [9]. The properties of these mixed mobile phases are given in Table 1.

The homologous compounds were also chromatographed using carbon dioxide modified with 11.7 mol% of various conventional modifiers. Total flow through the system was 1.5 ml/min (liquid flow).

Table 1  
Properties of HFC-134a/carbon dioxide mixed mobile phases [8]

HFC-134a (vol.%)	HFC-134a (mol%)	$T_c$ (°C)	Density at 75°C/200 bar (g/ml)	Density at 125°C/200 bar (g/ml)
100.0	100.0	101.2	1.147	0.985
80.0	70.6	94.9	1.250	1.107
62.2	50.0	81.1	1.179	0.996
60.0	47.7	79.4	1.169	0.979
54.2	41.8	75.0	1.141	0.932
40.0	29.0	64.7	1.065	0.796
20.0	13.1	51.0	0.933	0.576
0.0	0.0	30.9	0.629	0.386

Table 2  
Calculated binary mixture critical parameters for 11.7 mol% modified carbon dioxide

Modifier	$k_{ij}$	Modifier volume fraction	Mixture critical temperature (°C)	Mixture critical pressure (bar)
Methanol	0.190	10.0	64.2	119.8
Ethanol	0.150	14.2	71.5	121.5
<i>n</i> -Propanol	0.130	18.2	83.6	133.0
iso-Propanol	0.080	18.6	76.4	115.0
2-Methoxyethanol	na	19.2	na	na
Trifluoroethanol	na	17.6	na	na
Acetonitrile	−0.015	12.7	79.4	116.4
Tetrahydrofuran	0.010	19.7	85.0	114.0

$k_{ij}$  is the estimated binary interaction parameter.

na: indicates data not available.

Backpressure was maintained at 200 bar. Table 2 gives the calculated critical parameters for most of the mobile phases using the Cheuh–Prausnitz manipulation of the Redlich–Kwong equation of state [10]. Pure component critical parameters and acentric factors were obtained from literature references where available [11]. Binary interaction parameters ( $k_{ij}$ ) were iteratively estimated by comparison to phase boundary data [12,13].

Separations performed on the silica-based stationary phase were performed at a flow-rate of 1.0 ml/min with a backpressure of 200 bar. Methanol was added to the carbon dioxide mobile phase at 5 volume percent (5.88 mol%). All data represent the average of replicate injections.

#### 2.4. Chemicals

Alkylphenones and alkylbenzenes were obtained from Aldrich (Milwaukee, WI, USA) and were reagent grade or better. Methanol, acetonitrile, tetrahydrofuran, *n*-propanol, isopropanol and 2-methoxyethanol were obtained from EM Science (Gibbstown, NJ, USA). 1,1,1-Trifluoroethanol was obtained from PCR (Gainesville, FL, USA). Ethanol was obtained from Quantum Chemical Co (Newark, NJ, USA). SFC grade carbon dioxide (without helium headspace) was obtained from Scott Specialty Gases (Plumsteadville, PA, USA). HFC-134a (SUVA grade) was obtained from Dupont (Deepwater, NJ, USA).

### 3. Results and discussion

The relatively high eluotropic strength of HFC-134a makes it an ideal candidate for the separation of homologous materials, especially those of relatively high molecular mass. Previous studies have shown that the high eluotropic strength of HFC-134a often results in retention factors which are too low to be useful [6]. In order to overcome this problem, yet still take advantage of the ability to elute higher molecular mass compounds, HFC-134a may be combined with carbon dioxide to form a binary mixture of variable eluotropic strength. This approach is a significant departure from the use of conventional modifiers in that the mobile phase composition may be varied from 0 to 100% HFC-134a at 200 bar without producing a two-phase mobile phase, as is often the case with conventional modifiers [14]. The pressure and temperature boundaries of the carbon dioxide/HFC-134a binary system at other conditions may be readily calculated using commercially available software [9]. Previous studies involving binary carbon dioxide/HFC-134a mobile phase have shown these fluids to be compatible under normal operating conditions and produce mobile phases with significantly different character than either fluid alone [6].

Figs. 1 and 2 show the retention factors obtained for homologous alkyl benzenes and alkyl phenones, respectively, when chromatographed at 75 and 125°C

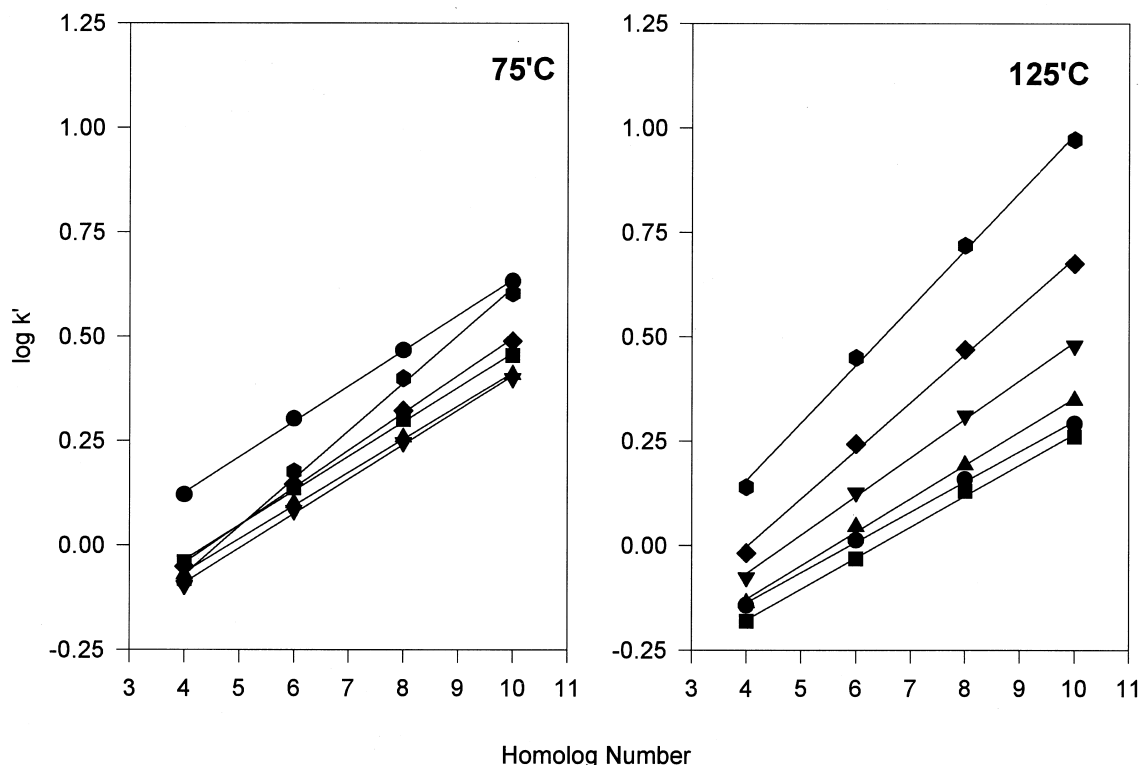


Fig. 1. Retention of homologous alkylbenzenes in carbon dioxide/HFC-134a binary mobile phases. Vol.% of HFC-134a: (●) 0%, (◆) 20%, (▼) 40%, (▲) 60%, (■) 80% and (●) 100%. Flow-rate was 1.0 ml/min at: (left) 75°C and (right) 125°C using a Jordi Gel RP-C<sub>18</sub> column (150×4.6 mm) at 200 bar backpressure.

on a Jordi Gel RP-C<sub>18</sub> polymeric column at 200 bar. In each figure, the homolog number corresponds to the number of carbon atoms present on the non-aromatic portion of the molecule. For example, propiophenone, having three carbon atoms on the alkyl portion of the molecule would be designated as having a homolog number of three. Each of the mobile phase/temperature combinations produces a linear relationship between  $\log k'$  and homolog number with excellent correlation coefficients ( $0.9989 \pm 0.0008$ ).

Deviations in homolog retention linearity due to residual silanol effects observed using silica-based stationary phases [5] are absent when using the polymeric stationary phase. The linearity of these plots is in excellent agreement with the Martin rule [15] which relates the logarithm of the capacity factor with the homolog number for a homologous series using the following equation:

$$\log k' = A + Bn \quad (1)$$

where  $n$  is the homolog number, and  $A$  and  $B$  are constants for a given homologous series and chromatographic system. The coefficient  $B$  is, therefore, a measure of homolog selectivity for a given chromatographic system. In the two series used in this study,  $B$  is a measure of methylene group selectivity, since the methylene group is the repeat unit in these homologous series. While the Martin rule is an empirical relationship, its applicability in a wide range of chromatographic systems is excellent [15].

It is apparent from Figs. 1 and 2 that various mobile phase compositions result in different Martin rule slopes. The relationship between mobile phase composition and Martin rule slope is more readily apparent in Fig. 3. The maximum Martin rule slope is obtained when HFC-134a is absent from the mobile phase. As the volume percentage of HFC-

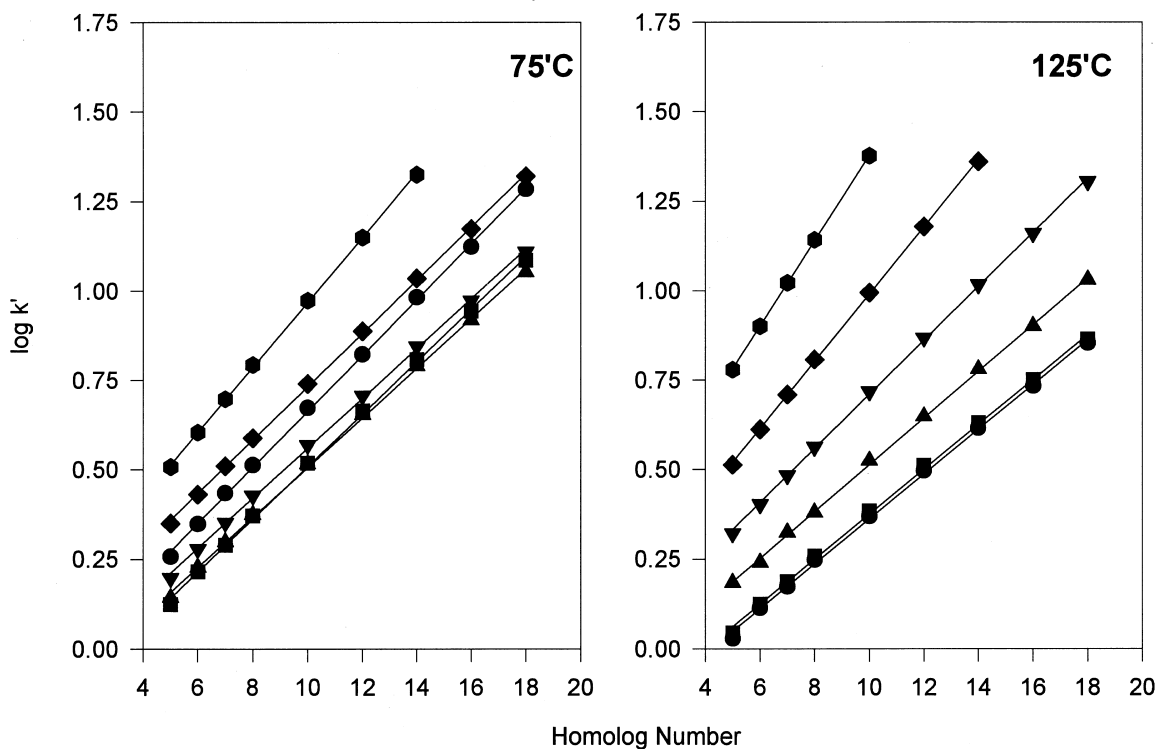


Fig. 2. Retention of homologous alkylphenones in carbon dioxide/HFC-134a binary mobile phases. Vol.% of HFC-134a: (●) 0%, (◆) 20%, (▼) 40%, (▲) 60%, (■) 80% and (●) 100%. Flow-rate was 1.0 ml/min at: (left) 75°C and (right) 125°C using a Jordi Gel RP-C<sub>18</sub> column (150×4.6 mm) at 200 bar backpressure.

134a in the mobile phase increases, the Martin rule slope decreases, but eventually begins to increase at very high HFC-134a concentrations. This behavior is slightly more pronounced at lower temperatures where HFC-134a is a subcritical modifier than at higher temperatures where the system remains supercritical.

Fig. 4 shows the effect of mobile phase composition for a subset of the alkylphenone series at 75°C. Pure carbon dioxide produces high homolog selectivity at the expense of excessive retention. Pure HFC-134a results in decreased retention at the expense of decreased selectivity. A mixture of 60:40 HFC-134a/CO<sub>2</sub> results in a compromise between high selectivity and low retention.

The alkylbenzene series and alkylphenone series show comparable behavior despite the difference in polarity and hydrogen bond accepting ability between the phenyl and phenone “end group” [16]. Because of the similarity in selectivity and retention

as a function of mobile phase composition and temperature, further discussions will be limited to alkylphenones for simplicity.

Attempts to correlate the observed Martin rule slopes with various physicochemical properties of the mobile phase have met with limited success. When the Martin rule slope is compared to the calculated mobile phase densities listed in Table 1, very poor correlations are observed. In particular, the pure HFC-134a mobile phase is very poorly modeled. This is despite the fact that density is most often described as the primary factor governing retention in near-critical systems.

### 3.1. Carbon dioxide/conventional modifiers vs temperature

The phase behavior of conventional modifiers places many more restrictions on the range of temperature, pressure and mobile phase composition

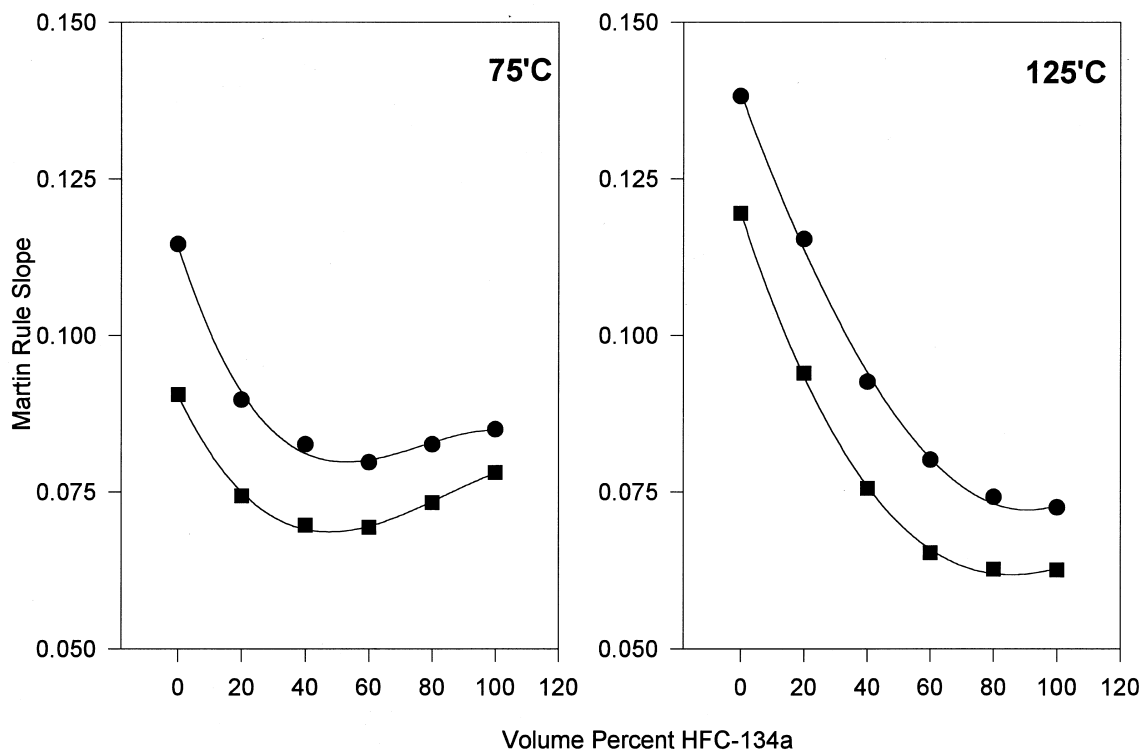


Fig. 3. Martin rule slope as a function of mobile phase composition at: (left) 75°C and (right) 125°C. Slopes are for: (●) alkylbenzenes and (■) alkylphenones. Chromatographic conditions as in Fig. 1.

which may be used than with HFC-134a [14]. In general, conventional mobile phase modifier concentrations must be held fairly low for a number of reasons. First, since the critical temperature of conventional mobile phase modifiers is usually quite high [11], addition of small amounts of these modifiers to carbon dioxide results in a relatively large increase in the mixture critical temperature of the mixed mobile phase. Often, the mixture critical pressure is also elevated significantly even though most modifiers have critical pressures lower than that of carbon dioxide. A second concern arises as a consequence of the elevation of the critical temperature and pressure of the binary mobile phases. When conventional mobile phase modifier concentration is raised to high levels at a fixed temperature and pressure, the system may undergo a phase transition to a biphasic system [14]. The consequence of this is irreproducible retention properties of the system.

Because of these concerns, conventional modifiers are generally added to carbon dioxide in low con-

centrations. With this in mind, the Martin rule slopes for a number of conventional mobile phase modifiers were compared at a constant molar concentration (11.7 mol%) as a function of temperature. The results obtained over the range of 10–90°C are shown in Fig. 5. Alcohol modifiers showed remarkably similar behavior. Relatively high Martin rule slopes were observed at low temperatures followed by a decrease in slope as temperature was increased, indicating a loss of selectivity. At higher temperatures, the Martin rule slope again increased, but did not reach the values obtained at the lower temperatures. Interestingly, the minima in the plots in Fig. 5 (left) do not correspond to the mixture critical temperatures (Table 2). Trifluoroethanol and 2-methoxyethanol appear to deviate from the other alcohols in their behavior. Acetonitrile and tetrahydrofuran also showed marked shifts in the minima for slope versus temperature. Again, the relative magnitude of the Martin rule slopes at any temperature do not appear to correlate with any of the

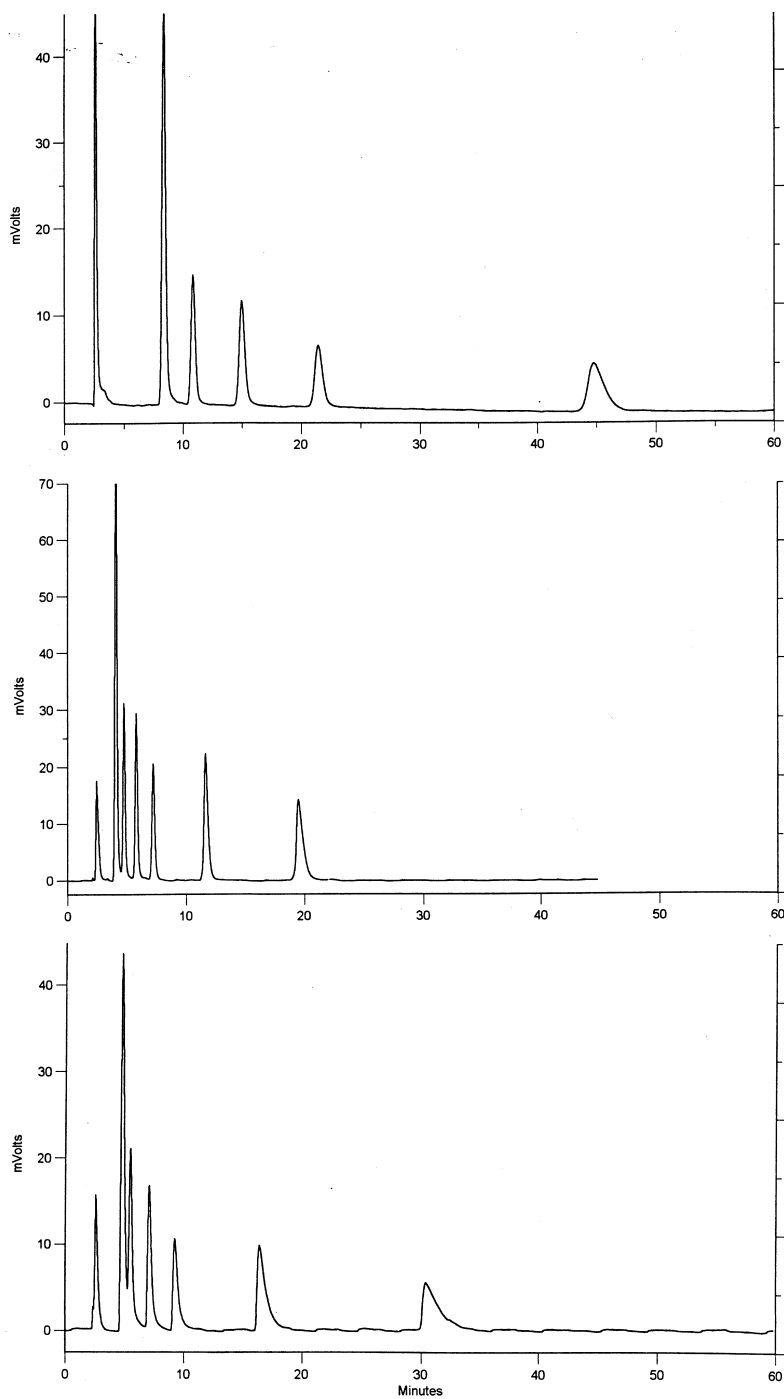


Fig. 4. Separation of acetophenone, butyrophenone, hexanophenone, octanophenone, dodecanophenone and hexadecanophenone using: (top) carbon dioxide; (middle) 60:40 HFC-134a/CO<sub>2</sub>; and (bottom) HFC-134a as the mobile phase at 75°C and 200 bar pressure. Flow-rate was 1.0 ml/min. Note: hexadecanophenone does not elute under 60 min using pure carbon dioxide.

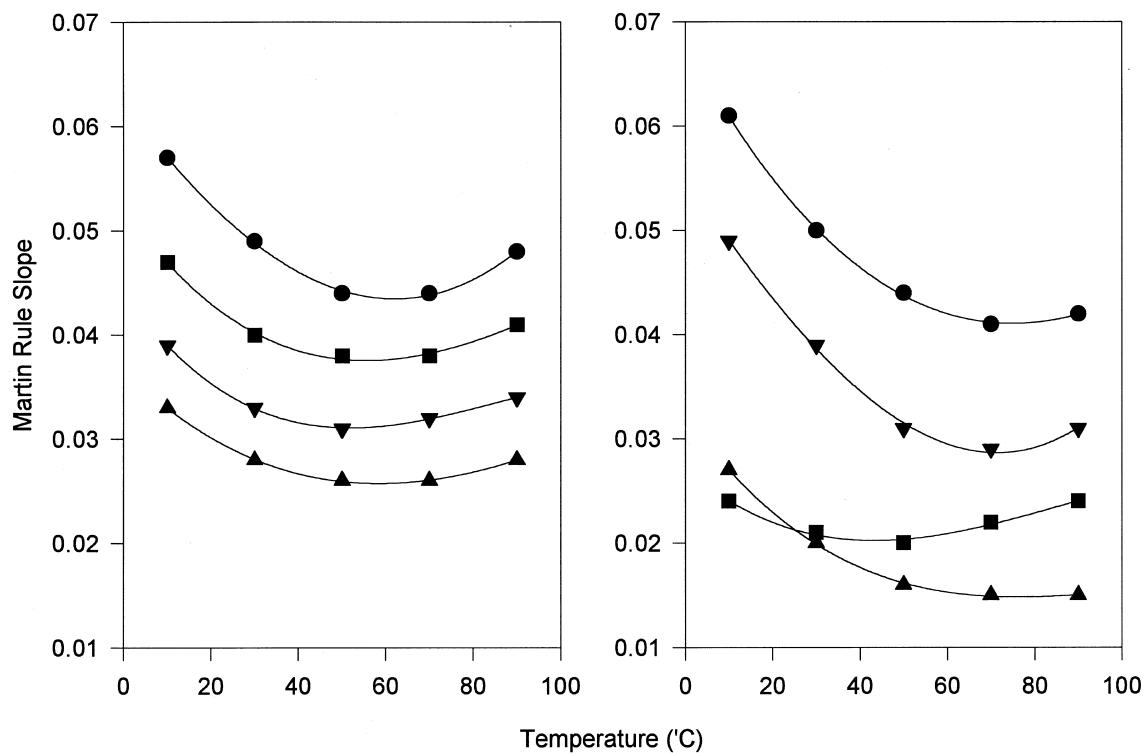


Fig. 5. Martin rule slopes for alkylphenones as a function of mobile phase modifier in carbon dioxide. Mobile phase consists of 11.7 mol% of: (left) (●) methanol, (■) ethanol, (▲) *n*-propanol and (▼) iso-propanol; (right) (●) acetonitrile, (■) tetrahydrofuran, (▲) 2-methoxyethanol and (▼) trifluoroethanol. Flow-rate was 1.5 ml/min using a Jordi Gel RP-C<sub>18</sub> column (250×4.6 mm) at 200 bar backpressure.

physicochemical properties of the mobile phase modifiers given in Tables 3 and 4. The only generality which may be derived by these comparisons is that methylene group selectivity appears to be uniformly better at lower temperatures.

The extent to which the behavior observed here is due to the nature of the polymeric stationary phase was examined by chromatographing the alkylphenones in a variety of mobile phases using a silica-based C<sub>18</sub> column. The results of these experiments

Table 3  
Solvent properties for mobile phase modifiers

Modifier	$\pi$	$\alpha$	$\beta$	Dielectric constant [17]	Dipole moment [17]
Methanol	0.60	0.93	0.62	33.0	1.70
Ethanol	0.54	0.83	0.77	25.3	1.69
<i>n</i> -Propanol	0.52	0.78	na	20.8	1.57
iso-Propanol	0.48	0.76	0.95	20.2	1.58
2-Methoxyethanol	0.71	na	na	17.2	2.36
Trifluoroethanol	0.73	1.51	0.00	27.7	2.03 [18]
Acetonitrile	0.75	0.19	0.31	36.6	3.92
Tetrahydrofuran	0.58	0.00	0.55	7.5	1.75

na: indicates values are not available.

Values from Ref. [16] except where noted.



Table 4  
Mobile phase densities at 200 bar with 11.7 mol% modifier

Modifier	(g/ml)				
	10°C	30°C	50°C	70°C	90°C
Methanol	0.9925	0.9060	0.8053	0.6901	0.5696
Ethanol	0.9998	0.9198	0.8268	0.7206	0.6063
<i>n</i> -Propanol	1.0044	0.9299	0.8444	0.7468	0.6402
iso-Propanol	0.9987	0.9247	0.8394	0.7422	0.6361
2-Methoxyethanol	na	na	na	na	na
Trifluoroethanol	na	na	na	na	na
Acetonitrile	0.9474	0.8826	0.8086	0.7246	0.6313
Tetrahydrofuran	1.0298	0.9551	0.8698	0.7732	0.6676

na: indicates density not calculable due to a lack of a binary interaction parameter.

are shown in Fig. 6. When carbon dioxide alone was used as the mobile phase, the correlation between  $\log k'$  and homolog number was highly skewed. At 10°C, the lower homologs (hexanophenone–octanophenone) appear to have a significantly different slope than the higher homologs (tetra-

canophenone–octadecanophenone). As the temperature was increased, this difference in slope decreased, but remains significant at 90°C. When HFC-134a was used as the mobile phase, similar behavior was observed. However, when 5 vol.% of methanol was added to the carbon dioxide mobile phase, the

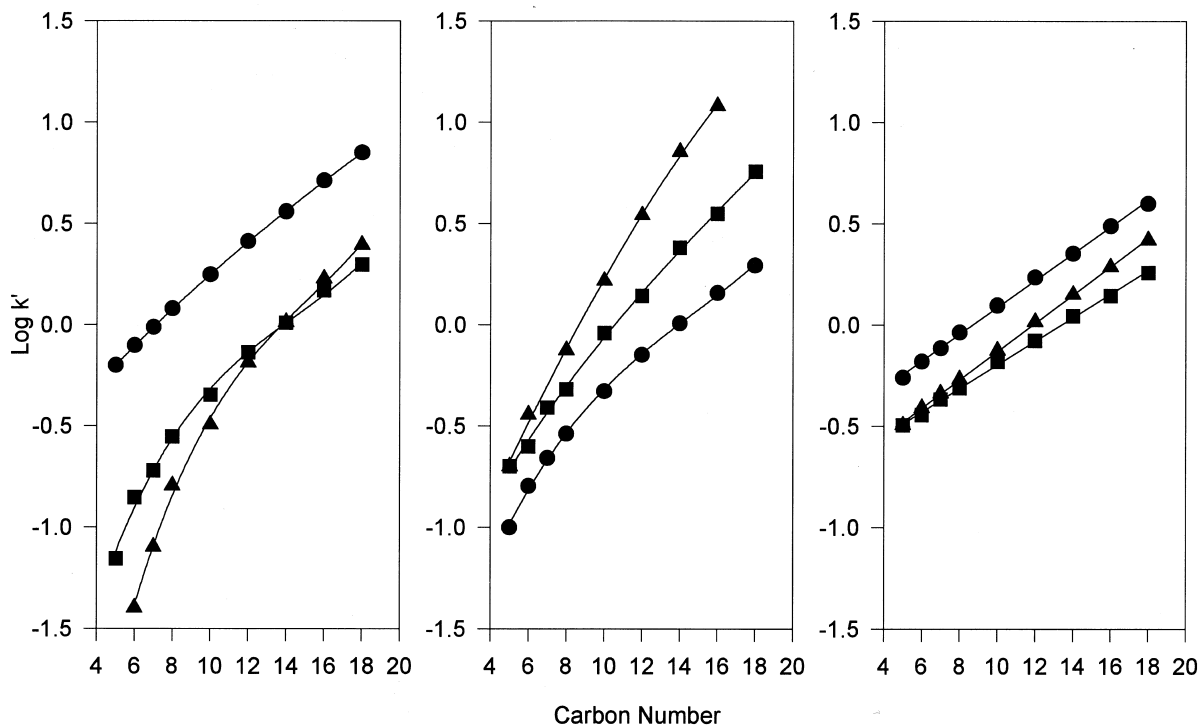


Fig. 6. Martin rule slopes for alkylphenones as a function of mobile phase composition. Mobile phase consists of: (left) (●) carbon dioxide at 90°C, (■) carbon dioxide at 50°C and (▲) carbon dioxide at 10°C; (middle) (●) HFC-134a at 90°C, (■) HFC-134a at 50°C and (▲) HFC-134a at 10°C; (right) (●) carbon dioxide/5 vol.% methanol at 90°C, (■) carbon dioxide/5 vol.% methanol at 50°C and (▲) carbon dioxide/5 vol.% methanol at 10°C. Flow-rate was 1.0 ml/min using a Zorbax SB-C<sub>18</sub> column (150×4.6 mm) at 200 bar backpressure.

correlation between  $\log k'$  and homolog number became much more linear. To a certain extent, the curvature of these plots may be artifactual due to the difficulty in determining the true void volume of the system. However, significant curvature is observed in Fig. 6 (left, middle) at retention factors which show linear behavior in Fig. 6 (right). These deviations suggest that if silica-based stationary phases are used for homologous compound characterization, conventional modifiers should be used to minimize non-ideal retention behavior.

### 3.2. Relative eluotropic strength

An additional consideration for the characterization of homologous compounds under near-critical conditions is the relative eluotropic strength of the various mobile phases. Operating a system with excellent methylene group selectivity is fruitless if the eluotropic strength of the mobile phase is insufficient to elute all of the components of a sample. Fig. 7 shows the retention factors obtained for decylphenone using carbon dioxide/HFC-134a mixed mobile phases. At 75°C, a mobile phase composition of approximately 70% volume HFC-

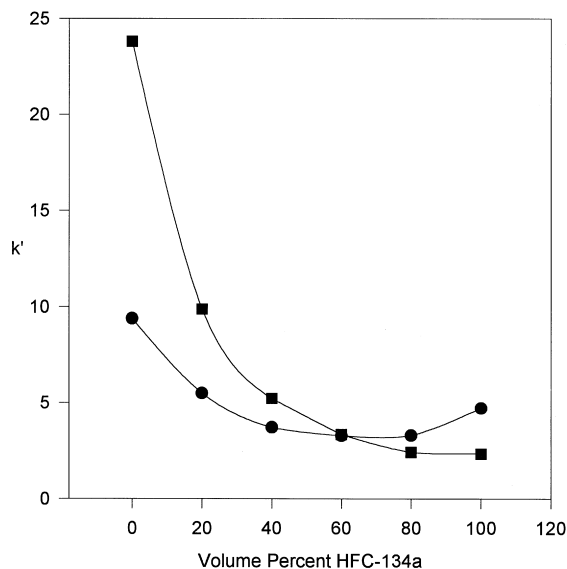


Fig. 7. Retention of decylphenone as a function of mobile phase composition at: (●) 75°C and (■) 125°C. Chromatographic conditions as in Fig. 1.

134a showed a higher eluotropic strength than either pure fluid alone. These results are consistent with those obtained earlier for a wide range of compounds [8]. Raising the temperature shifted this “optimal” HFC-134a concentration towards pure HFC-134a.

Carbon dioxide-based mobile phases containing conventional modifiers showed retention behavior consistent with that described earlier by Leyendecker [19] and Janssen [20]. Retention decreases and reached a minima somewhere near the mixture critical temperature, as shown in Fig. 8. At higher temperatures, retention began to increase, reaching a maxima at a temperature dictated by the analyte heat of adsorption on the stationary phase, heat of solution in the mobile phase and the isothermal compressibility of the mobile phase [21]. Beyond this temperature, retention decreases. Each of the conventional modifiers showed their own optimal temperature with respect to eluotropic strength towards decylphenone.

At 75°C, all of the mobile phases may be quantitatively compared with respect to eluotropic strength. Under these conditions, trifluoroethanol showed the highest eluotropic strength, followed by tetrahydrofuran, 2-methoxyethanol, *n*-propanol, iso-propanol, ethanol, acetonitrile and finally methanol. Earlier studies have shown this relative eluotropic strength to be dictated by a number of specific intermolecular interactions between the analyte, mobile phase and stationary phase rather than by any one physicochemical parameter [22]. At 75°C, the conventional modifiers proved stronger in eluotropic strength than any of the HFC-134a/carbon dioxide mobile phases. This is not expected to be maintained at higher temperatures, since HFC-134a increases in eluotropic strength at higher temperatures while the conventionally modified mobile phases lose eluotropic strength.

## 4. Conclusions

The polymeric reversed phase column used in this study showed the highest methylene group selectivity for homologous compounds using unmodified carbon dioxide. Addition of low concentrations of HFC-134a significantly decreased methylene group selectivity. Increasing the mobile phase concentration of

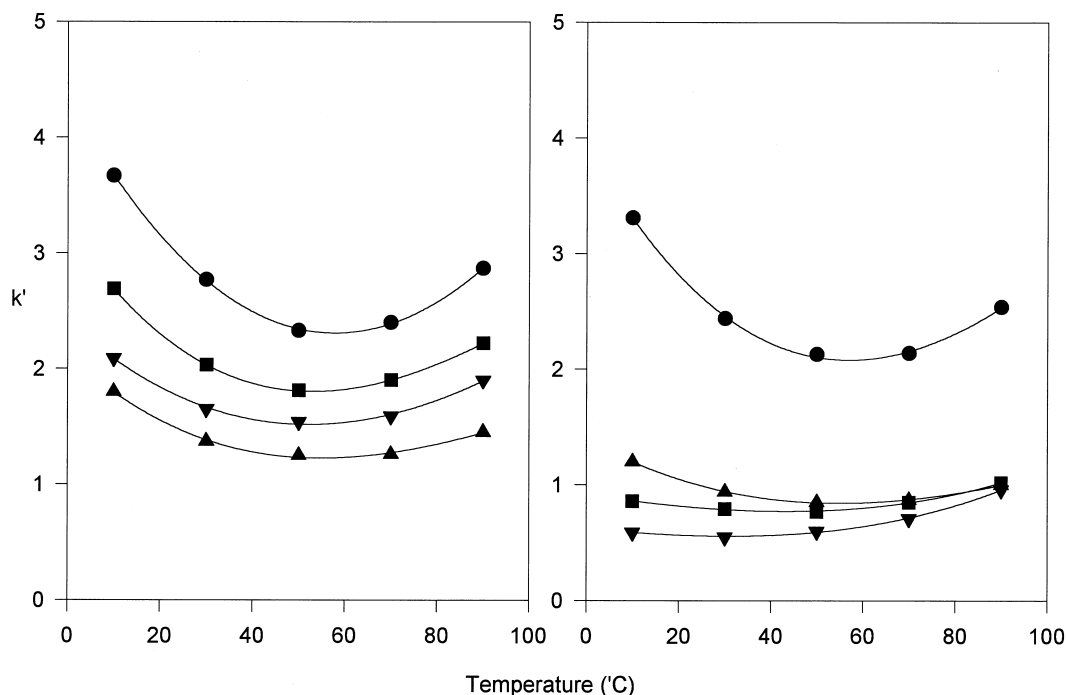


Fig. 8. Retention of decylphenone as a function of mobile phase modifier in carbon dioxide. Mobile phase consists of 11.7 mol% of: (left) (●) methanol, (■) ethanol, (▲) *n*-propanol and (▼) iso-propanol; (right) (●) acetonitrile, (■) tetrahydrofuran, (▲) 2-methoxyethanol and (▼) trifluoroethanol. Flow-rate was 1.5 ml/min using a Jordi Gel RP-C<sub>18</sub> column (250×4.6 mm) at 200 bar backpressure.

HFC-134a to very high levels began to increase the selectivity, but the resulting selectivity did not approach that of pure carbon dioxide. The eluotropic strength of the mobile phase increased as the concentration of HFC-134a increased. At low temperatures, a binary mixture of carbon dioxide/HFC-134a produced a higher eluotropic strength than either component alone.

When conventional modifiers were added to carbon dioxide, the methylene group selectivity also decreased. The resulting selectivity was very temperature dependent with low temperatures producing superior selectivities compared to higher temperatures. Eluotropic strength of these binary mobile phases was also very temperature dependent.

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