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## Comparison of supercritical carbon dioxide and supercritical propane as mobile phases in supercritical fluid chromatography

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### SUMMARY

Comparisons of supercritical propane and supercritical carbon dioxide eluents were made on bare silica and octadecylsilane-derivatized silica using substituted and unsubstituted aromatic hydrocarbons as test solutes. The greater elution strength of carbon dioxide relative to propane for these solutes on underivatized silica is indicated to be largely the result of more effective competitive adsorption by carbon dioxide rather than enhanced mobile phase solubility. The effects of the addition of methanol modifier on solute retention were more pronounced in propane for both polar and non-polar solutes. An increase in the retention of polar aromatics on silica was observed with increasing density in methanol modified propane. This is apparently the result of a concomitant increase in the availability of stationary phase adsorption sites.

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### INTRODUCTION

The choice of a mobile phase solvent in supercritical fluid chromatography (SFC) depends to a large extent on the nature of the samples to be analyzed. Solute retention and selectivity are determined in part by mobile phase solvent strength which is a result of dispersive and specific interactions between solute and solvent. Direct comparisons of mobile phases can be used to gain insight into the nature and relative magnitude of solvent-solute interactions which can be useful for selecting an appropriate mobile phase.

Several comparisons of supercritical fluid mobile phases have been reported in the literature. Leyendecker et al.<sup>1</sup> examined the influence of density on the chromatographic behavior of lower alkanes as mobile phases in SFC. Chrysene was eluted more quickly in supercritical pentane than in supercritical propane at the same reduced density and reduced temperature. Lauer et al.<sup>2</sup> reported the retention behavior of a number of model compounds in carbon dioxide and in nitrous oxide as

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a function of temperature at equal densities. Leyendecker *et al.*<sup>3</sup> have compared the retention of several aromatic hydrocarbons in a number of SFC mobile phases at equal pressures and at equal reduced pressures. Retention results obtained at equal pressures varied considerably from those obtained at equal reduced pressures as was anticipated based on the differences in solvent critical pressures. Wright *et al.*<sup>4</sup> compared capacity factors of a polarity test mixture in supercritical carbon dioxide, nitrous oxide and ethane at equal reduced temperatures and reduced pressures. Leyendecker *et al.*<sup>5</sup> compared the capacity factors of aromatic hydrocarbons in supercritical diethyl ether and dimethyl ether under isobaric conditions.

Since comparisons of mobile phases may be conducted in a number of different ways and because the experimental parameters chosen for a comparison can greatly alter solute retention, care must be taken in drawing conclusions as to the relative solvent strength of the mobile phases. For instance, a comparison made at equal reduced temperatures of two mobile phases which have different critical temperatures may require greatly different operating temperatures. Differences in solute retention measured under these conditions may be due in part to differences in solute volatility resulting from variations in operating temperature rather than differences in the solvating strengths of the mobile phases. Since the solvating strength should depend on the distance between molecules, comparisons made at equal density should be more informative than those based on equal pressure. However, equal densities do not account for differences in molecular weights which may influence solvent strength. Klesper *et al.*<sup>6</sup> have suggested comparisons of mobile phases at equal free volumes in order to best evaluate the relative dissolution power of the solvents. In their report, the free volume,  $V_f$ , was calculated from the fluid density at pressure and temperature  $T$ ,  $\rho_{p,T}$ , and from the reference state density,  $\rho_0$ , of the crystalline state at the melting point and atmospheric pressure:

$$V_f = \frac{\rho_0}{\rho_{p,T}} - 1 \quad (1)$$

A comparison at equal free volumes is similar to one based on equal reduced densities. As an experimental consideration, it should be noted that equal reduced pressures do not necessarily result in equal reduced densities for two fluids at either the same temperature or at the same reduced temperature. In the report by Klesper *et al.*<sup>6</sup>, capacity factors of chrysene and pyrene measured on a LiChrosorb Si 100 column were found to be much larger in supercritical carbon dioxide than in supercritical pentane at equal free volumes and equal reduced temperatures. However, on the same column at equal free volumes and equal temperatures, the capacity factor of pyrene was found to be approximately the same in both solvents as reported by Schmitz<sup>7</sup>. Capacity factors for pyrene determined at equal free volumes in supercritical carbon dioxide and in several supercritical alkane eluents were found to fall on a common curve when plotted *versus* temperature. These similarities decreased at higher free volumes (lower densities), but good correlation was found<sup>7</sup> at free volumes as high as 1.7. In a comparison of the same solvents at equal densities, the capacity factor of chrysene was found to be much larger in carbon dioxide than in propane at the same temperature. This would be anticipated based on the previous results since the density of carbon dioxide is more than twice that of propane at equal free volumes.

In this report, the retention behavior of several substituted and unsubstituted aromatic hydrocarbons is presented in supercritical carbon dioxide and in supercritical propane on silica and octadecylsilane (ODS)-derivatized silica stationary phases. Aromatic hydrocarbons with polar functionalities were included in order to examine differences in the specific interactions of the solvents with various functional groups. The effects of a small amount of methanol modifier on the solvent strength of each mobile phase was also determined and adsorption isotherm measurements were made for methanol in each solvent in an attempt to correlate relative modifier surface coverage with the retention data.

## EXPERIMENTAL

The experimental set-up for the measurement of solute capacity factors is illustrated in Fig. 1. Methanol was mixed with the solvents by adding a known volume to the syringe reservoir of a Varian 8500 syringe pump and filling the balance with the mobile phase solvent. The volume percent modifier was calculated from the total reservoir volume during pressurization at the point at which the operating pressure was obtained. The determination of adsorption isotherms was carried out in the same manner as described previously<sup>8</sup>. For both types of measurements, additional safety precautions were implemented to minimize the possibility of propane combustion. A steady flow of argon at cu. 100 ml/min was introduced into the column oven to prevent build-up of an explosive atmosphere in the event of column leakage. The propane effluent was collected after it passed through the back pressure regulator by allowing it to expand into a 20-lbs. refillable propane cylinder (Charmglow). A 4 cm x 4.6 mm I.D. column packed with 60–200-mesh silica (Fisher) was placed in line from

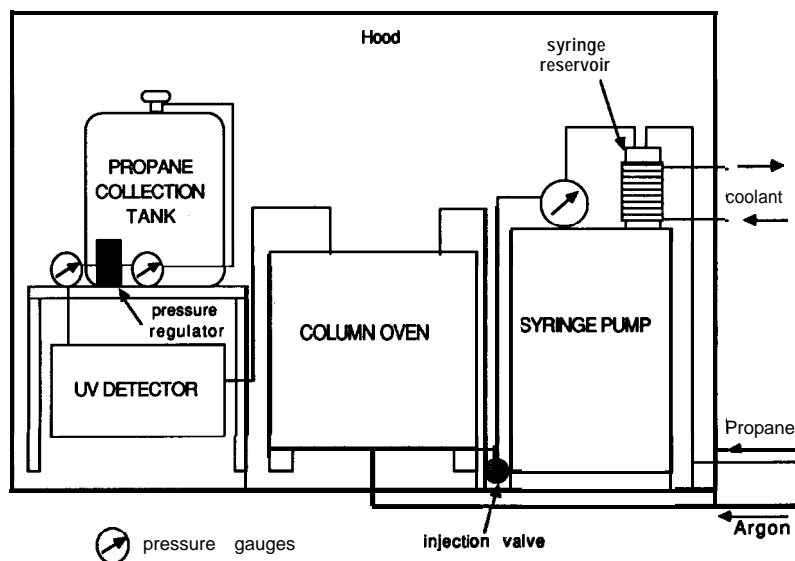


Fig. 1. Experimental set-up for retention studies.

the fluid cylinders to the solvent pump to remove impurities from the solvents. Identical conditions were maintained for carbon dioxide with the exception that the carbon dioxide effluent was vented into the hood rather than collected.

The underivatized silica column was 10 cm x 4.6 mm I.D. and packed with **Whatman** Partisil-10. The ODS-derivatized silica column was 4 cm x 4.6 mm I.D. and packed with **Whatman** Partisil-10 chlorotrimethylsilane endcapped ODS-2. Free volumes were calculated from eqn. 1 using values of  $\rho_0$  of 0.75 g/ml for propane and 1.56 g/ml for carbon dioxide<sup>9</sup>. The carbon dioxide was supercritical fluid grade from Scott Speciality Gases. The propane was C. P. grade and also obtained from Scott. Mobile phase densities were calculated from published temperature-pressure-density relationships for propane<sup>10</sup> and carbon dioxide<sup>11</sup>.

All capacity factor measurements were made in the usual manner from the retention time,  $t_R$ , and the column dead time,  $t_0$ , determined using benzene<sup>1</sup>

$$k' = \frac{(t_R - t_0)}{t_0} \quad (2)$$

and were reproducible to  $\pm 1.5\%$ . All measurements were made at 100°C.

The solutes used in this study are listed in Fig. 2. The solutes are numbered in the same order throughout this paper.

## RESULTS AND DISCUSSION

### *Capacity factors on underivatized silica*

The capacity factors for solutes 1-7 measured on the underivatized silica column (Partisil 10) in carbon dioxide and in propane at equal free volumes of 1.55 are shown graphically in Fig. 3. A free volume of 1.55 corresponds to a propane density of 0.29 g/ml and a carbon dioxide density of 0.61 g/ml. The capacity factors of solutes 8-11 were too large to be measured in propane under these conditions. In contrast to the results of **Schmitz**<sup>7</sup>, pyrene (solute 2) exhibited significantly greater retention in propane than in carbon dioxide. As shown in Fig. 3, the capacity factors measured in propane are more than twice those measured in carbon dioxide. Solvent selectivities for each solute were determined from capacity factor ratios

$$\alpha_{\text{CO}_2/\text{C}_3\text{H}_8} = \frac{k'_{\text{CO}_2}}{k'_{\text{C}_3\text{H}_8}} \quad (3)$$

<sup>a</sup> The retention time of benzene decreased slightly in propane on the underivatized silica column with the addition of 1% methanol modifier indicating that benzene was not unretained in unmodified propane under these conditions. The retention time of hexane measured at 200 nm in unmodified propane on this column was found to be slightly less than that of benzene measured under the same conditions and to correspond with the retention time of benzene in methanol-modified propane. This value was used as a measure of  $t_0$  for unmodified propane on the bare silica column.

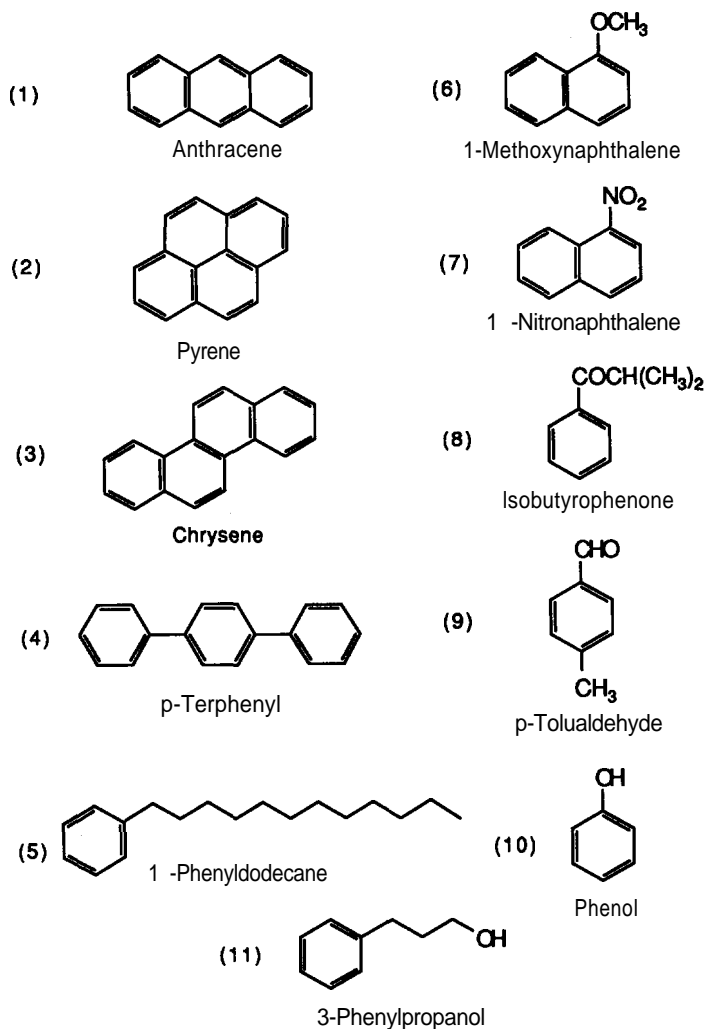


Fig. 2. Test solutes.

and are listed in the first column of Table I. The greatest relative difference in retention is seen for nitronaphthalene (solute 7) which suggests that specific interactions are an important factor in the greater elution strength of carbon dioxide. Among the unsubstituted polycyclic aromatics, solutes 14, p-terphenyl (solute 4) exhibited the greatest relative difference in retention and pyrene (solute 2) the smallest difference. The polarizabilities of the unsubstituted aromatics were calculated according to the method of Miller and Savchik<sup>12</sup> and are listed in Table II. Van der Waals volumes were calculated using the method of Bondi<sup>13</sup> and are also listed in Table II. A strong correlation was found between solute polarizabilities and the logarithms of the capacity factors in carbon dioxide as indicated by the correlation coefficient ( $r = 0.990$ ) for a linear least squares fit to the data. Poor correlation ( $r = 0.786$ ) was

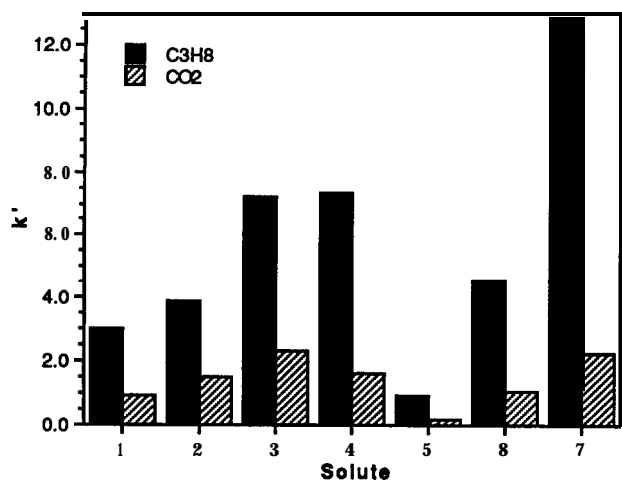


Fig. 3. Capacity factors ( $k'$ ) in propane and in carbon dioxide at equal free volumes of 1.55 on underderivatized silica.

TABLE I

SOLVENT SELECTIVITIES AT 100°C

Stationary phase	Partisil-10	Partisil-10	ODS-2	Partisil-10	ODS-2
$V_f(\text{CO}_2)$	1.55	3.25	1.55	1.55	1.55
$V_f(\text{C}_3\text{H}_8)$	1.55	0.88	1.55	1.55	1.55
Methanol (%g/ml)	0.0	0.0	0.0	1.0	1.0

Solute	$\alpha_{\text{CO}_2/\text{C}_3\text{H}_8}$				
1	0.311	1.02	2.07	0.813	1.37
2	0.392	1.25	2.73	0.882	1.76
3	0.323	1.26	2.89	0.804	1.86
4	0.223	0.849	2.81	0.969	1.83
5	0.217	1.59	6.50	1.86	1.83
6	0.238	0.660	1.59	0.671	1.18
7	0.181	0.505	0.844	0.494	0.710
8	—	0.316	0.691	0.348	0.974
9	—	0.356	0.417	0.292	0.524
10	—	0.310	0.416	0.246	0.327
11	—	—	0.558	0.246	0.476

TABLE II

PHYSICAL CONSTANTS OF UNSUBSTITUTED POLYCYCLIC AROMATICS

Solute	Molecular weight	Polarizability ( $\text{\AA}^3$ )	Van der Waals volume ( $\text{cm}^3/\text{mol}$ )
Anthracene	178.2	25.8	99.56
Pyrene	202.3	30.1	109.0
Chrysene	228.3	33.5	125.2
p-Terphenyl	230.3	29.7	131.8

observed between these measurements in propane. Conversely, a good correlation was observed between the solute Van der Waals volumes and the logarithms of the capacity factors in propane ( $r = 0.985$ ) but not in carbon dioxide ( $r = 0.774$ ). Although the exact nature of the above correlations **cannot** be determined from these results, a difference in solute molecular interactions in these two solvents is indicated.

In an attempt to compare the two mobile phases under **iso-elutropic** conditions, the density of the carbon dioxide mobile phase was lowered and the density of the propane mobile phase was raised until roughly equivalent capacity factors were obtained on the average for the unsubstituted aromatic hydrocarbons as shown in Fig. 4a. The trend in solvent selectivities for solutes 1-7 at equal free volumes is shifted as at

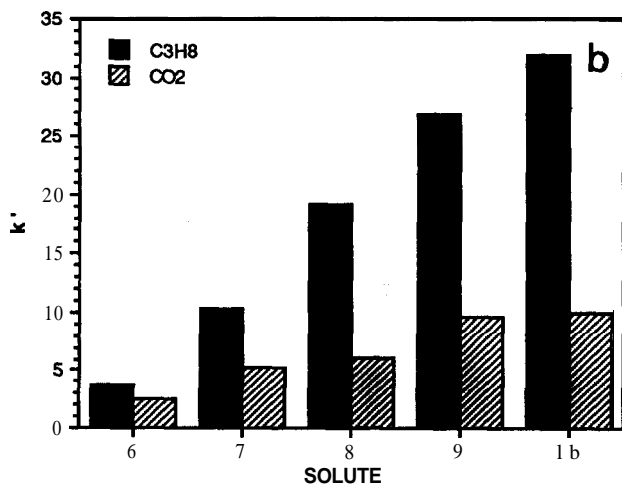
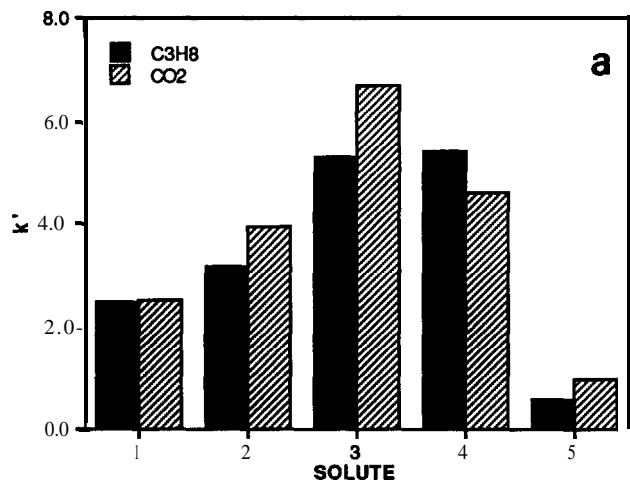


Fig. 4. Capacity factors in propane at 0.40 g/ml and in carbon dioxide at 0.48 g/ml on underivatized silica: (a) solutes 1-5 and (b) solutes 6-10.

these new densities as can be seen in the second column of Table I. Chrysene (solute 3) has the largest value of solvent selectivity of the unsubstituted aromatics with shorter retention in propane than carbon dioxide. p-Terphenyl (solute 4) still exhibits shorter retention in carbon dioxide than in propane under these conditions resulting in a much smaller value of solvent selectivity. Phenyldecane (solute 5) exhibited the largest change in solvent selectivity with changing density showing a sharp increase in retention in carbon dioxide with decreasing density. The capacity factors of the polar-substituted aromatics at these same densities are plotted in Fig. 4b. 3-Phenylpropanol (solute 11) was not eluted in propane at this density. Unlike the unsubstituted aromatics, the capacity factors of these solutes are much smaller in carbon dioxide than in propane. This result is not unexpected since, unlike propane, carbon dioxide possesses bond dipoles which should increase its specific interactions with the more polar solutes. As indicated by the solvent selectivity values in the second column of Table I, the capacity factors of these solutes in carbon dioxide relative to propane tend to decrease as the retention of the solutes increases. Apparently, as the magnitude of the specific interactions of the solutes with the polar adsorption sites on the silica surface increases, the greater chemical effect of carbon dioxide relative to propane becomes more pronounced.

#### ***ODS column at equal free volumes***

Capacity factors for all of the test solutes were measured in carbon dioxide and in propane at an equal free volume of 1.55 on an ODS-derivatized column. These capacity factors are shown graphically in Fig. 5. In contrast to the results shown in Fig. 3, which were obtained under these same conditions on the underivatized column, the retention of solutes 1-6 is much shorter in this case in propane than in carbon dioxide. The greater elution strength of propane indicates a greater distribution of these solutes into the mobile phase from the alkyl-bonded stationary phase. It can be assumed that this is the result of greater solubility of these solutes in propane relative to carbon

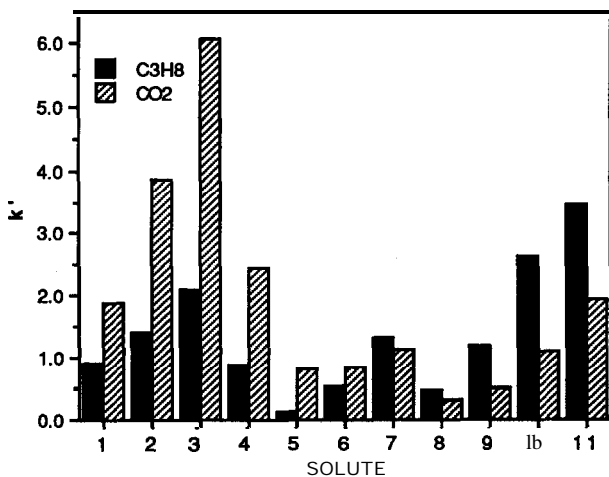


Fig. 5. Capacity factors in propane and in carbon dioxide at equal free volumes of 1.55 on ODS-derivatized silica.



dioxide since the potential for competitive adsorption is essentially eliminated by chemical derivatization of the silica surface. On the other hand, this argues that the greater eluent strength of carbon dioxide for these solutes on the underivatized silica column is the result of its ability to interact more strongly with the stationary phase surface and not the result of greater solubility of the solutes in the mobile phase. Carbon dioxide can apparently interfere more effectively with solute adsorption onto the silica surface thus reducing retention by competitive adsorption or through a mechanism of the type described by Snyder and Glajch<sup>14</sup> as site-competition delocalization. Therefore, the nature of the stationary phase must be considered in making comparisons of mobile phase solvent strength. The results reported by Schmitz<sup>7</sup> which indicated equal capacity factors for pyrene (solute 2) in carbon dioxide and in propane at equal free volumes on a LiChrosorb Si 100 column apparently represent an intermediate case in which competitive adsorption by carbon dioxide just balances the greater solubility of pyrene in propane.

As indicated by the mobile phase selectivities in the third column of Table I, phenyldodecane (solute 5) exhibits a much greater solubility in propane than in carbon dioxide as compared to the other solutes. This may be the result of the greater aliphatic character of this solute providing for better solubility in the hydrocarbonaceous solvent, however the same selectivity difference is not seen on the underivatized column. This might be explained by more effective competitive adsorption of carbon dioxide with this solute as compared to the unsubstituted polycyclic aromatics which would result in a smaller value of solvent selectivity for phenyldodecane than would otherwise be anticipated. The solvent selectivities of solutes 1-4 are similar and result in a good correlation between the corresponding capacity factors in each solvent ( $r = 0.989$ ). This suggests similar types of molecular interactions of these solutes in the two solvents in contrast to the differences observed on the underivatized silica column.

In comparison to solutes 1-5, the polar-substituted aromatics exhibit shorter retention in carbon dioxide than in propane on the ODS column with the exception of methoxynaphthalene (solute 6) as also illustrated in Fig. 5. This is expected based on the potential for greater specific interactions between the polar functionalities of the substituted aromatics and the bond dipoles of carbon dioxide. It also suggests that the shorter retention of these solutes in carbon dioxide relative to propane on the underivatized silica column is not solely the result of more effective competitive adsorption.

#### *Column selectivities*

Another interesting comparison can be made by examining the relative change in retention of the solutes in each mobile phase as a function of column type. Column selectivities were calculated from the capacity factors of the solutes on the underivatized Partisil-10 column and the ODS column:

$$\alpha_{\text{Partisil-10/ODS}} = \frac{k'_{\text{Partisil-10}}}{k'_{\text{ODS}}} \quad (4)$$

As indicated in Table III, the retention of solutes 1-5 in carbon dioxide is greater on the underivatized column as compared to the ODS column. The opposite is true in

TABLE III

COLUMN SELECTIVITIES IN CARBON DIOXIDE AND IN PROPANE AT  $V_i = 1.55$ 

Solute	$\alpha_{\text{Partisil-1 O/ODS}}$	
	Carbon dioxide	Propane
1	0.502	3.34
2	0.395	2.75
3	0.386	3.46
4	0.672	8.48
5	0.256	7.66
6	1.28	8.56
7	1.99	9.28
8	9.78	—
9	14.5	—
10	4.48	—
11	12.2	—

propane. This supports the idea that competitive adsorption plays an important role in determining the retention of solutes 1-5 on the underivatized column. If solubility of these solutes in carbon dioxide was the only contribution to its greater elution strength relative to propane, then carbon dioxide should compete more effectively for solute distribution with the hydrocarbon-ODS phase than does propane. As a result, the retention of these solutes in carbon dioxide should decrease, as in propane, rather than increase on going from the underivatized to the ODS-derivatized column.

In contrast, solutes 6 and 7, methoxynaphthalene and nitronaphthalene, exhibit shorter retention on the ODS column relative to the underivatized column in both carbon dioxide and in propane. Unlike solutes 1-5, the interaction energy of these polar solutes with the hydrophobic bonded phase is apparently less than their interaction energy with the underivatized silica surface in both of these solvents.

#### Modifier effects on underivatized silica

A further comparison of propane and carbon dioxide was made by examining the effects on solute retention of the addition of 1.0% g/ml methanol to each mobile phase at equal free volumes of 1.55 on both the underivatized and ODS-derivatized columns. The effect of modifier addition on free volume is small at this concentration and was neglected.

Using the underivatized silica column, the addition of methanol to carbon dioxide resulted in a relatively small decrease in the capacity factors of solutes 1-5 in comparison to unmodified carbon dioxide as shown in Fig. 6a. The polar substituted aromatics, on the other hand, exhibited substantial decreases in retention, particularly in the case of isobutyrophenone (solute 8) and tolualdehyde (solute 9). The large percentage decrease in retention for these solutes relative to methoxynaphthalene (solute 6) and nitronaphthalene (solute 7) may be the result of stronger localized interactions of the solutes with the silica surface which would magnify the observed effect on retention resulting from displacement of the solutes from active sites by methanol. The smaller percent change in retention seen for phenol (solute 10) may be

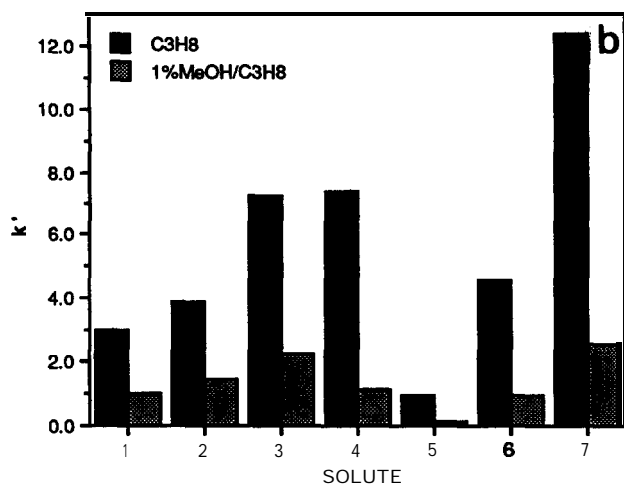
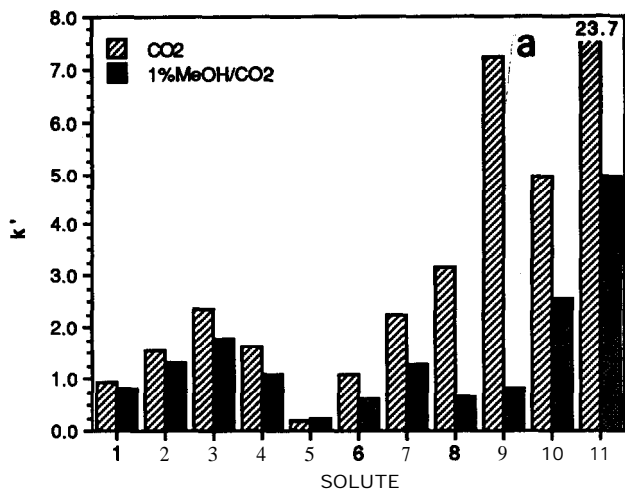


Fig. 6. Capacity factors in unmodified and methanol (MeOH)-modified solvents at equal free volumes on underivatized silica: (a) carbon dioxide and (b) propane.

due to the ability of this solute to displace rather than compete with methanol for adsorption sites<sup>15</sup>.

In propane on this same column, solutes 1-5 exhibit much larger decreases in retention with the addition of methanol, as shown in Fig. 6b, than was observed in carbon dioxide. Since the solubility of these solutes was indicated to be greater in propane than in carbon dioxide at these conditions, greater enhancement of mobile phase solubility in propane relative to carbon dioxide with the addition of modifier is unlikely. Therefore, for propane, competitive adsorption by methanol appears to be a more important factor for reducing solute retention. This follows from the previous

assumption that carbon dioxide competes more effectively with solutes 1-5 for adsorption sites without the aid of a modifier. Therefore, the effect of the modifier on the retention of these solutes in carbon dioxide due to competitive adsorption should be less pronounced, as was observed. In addition, it was determined from adsorption isotherm measurements that the stationary phase concentration of methanol was greater in propane than in carbon dioxide by nearly a factor of two at equal free volumes. Therefore, the effects of the modifier due to competitive adsorption should be enhanced in propane relative to carbon dioxide because of a greater concentration of modifier on the surface. For more polar solutes, such as nitronaphthalene (solute 7)

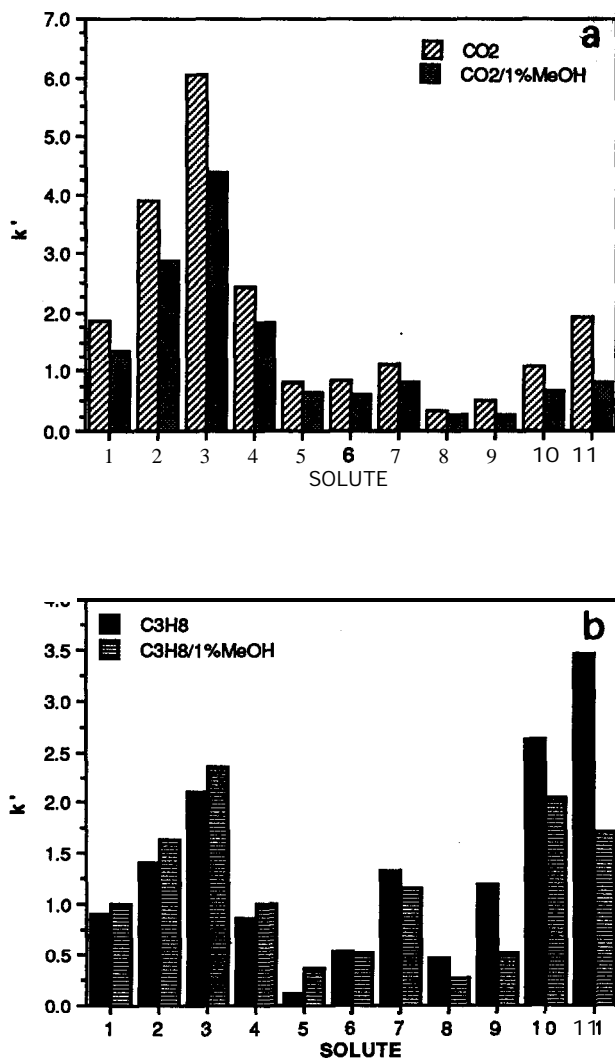


Fig. 7. Capacity factors in unmodified and methanol-modified solvents at equal free volumes on ODS-derivatized silica: (a) carbon dioxide and (b) propane.

which exhibited greater solubility in carbon dioxide than in propane based on the results obtained on the ODS column, a greater enhancement of mobile phase solubility in propane relative to carbon dioxide as a result of modifier addition should also be expected.

Comparison of the solvent selectivities in Table I for the solutes in methanol-modified (fourth column) and -unmodified fluids (first column) at equal free volumes on the underivatized column indicates a much larger increase in solvent selectivity with the addition of modifier for phenyldodecane (solute 5) relative to the other solutes. This result is similar to that obtained in the earlier comparison of solvent selectivities for phenyldodecane on the underivatized and ODS-modified columns, and is consistent with the earlier argument that phenyldodecane competes with carbon dioxide for adsorption sites less effectively than the other solutes.

### *Modifier effects on ODS-derivatized silica*

The effects on solute retention of the addition of methanol modifier to carbon dioxide on an ODS-modified silica column are illustrated in Fig. 7a. As indicated by the solvent selectivities of the modified and unmodified solvents on the ODS column listed in Table IV, the largest relative decrease in retention in carbon dioxide occurs for solutes 9-11. This is likely the result of a greater enhancement of their mobile phase solubility relative to the other solutes which is expected based on the ability of solutes 9-11 to interact strongly with methanol through hydrogen bonding.

A similar effect is observed for these solutes with the addition of methanol to propane on the ODS column as illustrated in Fig. 7b. In contrast to the results obtained in carbon dioxide, however, isobutyrophenone (solute 8) and tolualdehyde (solute 9) exhibit considerably larger changes in retention in propane with the addition of modifier on the ODS column as indicated in Table IV. This may result because of the poorer solvent strength of propane relative to carbon dioxide which would magnify the contribution of the modifier to mobile phase solubility.

TABLE IV

SELECTIVITIES OF MODIFIED AND UNMODIFIED SOLVENTS ON UNDERIVATIZED AND ODS-DERIVATIZED SILICA

Solute	$\alpha_{CO_2/CO_2/MeOH}$		$\alpha_{C_3H_8/C_3H_8/MeOH}$	
	<i>Partisil-10</i>	<i>ODS</i>	<i>Part&amp;I-10</i>	<i>ODS</i>
1	1.18	1.37	3.08	0.903
2	1.18	1.34	2.66	0.865
3	1.30	1.38	3.24	0.889
4	1.53	1.33	6.67	0.867
5	0.916	1.24	7.85	0.347
6	1.77	1.39	4.99	1.03
7	1.76	1.36	4.81	1.15
8	4.79	1.18	—	1.67
9	8.84	1.83	—	2.31
10	1.92	1.64	—	1.29
11	4.78	2.37	—	2.02

A difference in the effect of the modifier on the retention of solutes 1-5 in propane and in carbon dioxide is also observed in Fig. 7a and b. With the addition of methanol, the capacity factors of these solutes are reduced in carbon dioxide but are increased in propane. This suggests an enhancement of solubility in carbon dioxide and a reduction of solubility in propane with the addition of modifier. If the masking of residual adsorption sites by the modifier on the ODS column contributed significantly to the reduction of retention of these solutes in carbon dioxide, then a reduction in retention would also be anticipated in propane. The increased retention in propane is most significant for phenyldodecane (solute 5), which exhibits nearly a three-fold change in retention. Once again, methoxynaphthalene (solute 6) appears to be intermediate in its response exhibiting almost no change in retention.

The solvent selectivities for the modified solvents on the ODS column are given in the fifth column of Table I. Although the capacity factors of solutes 1-5 increased in propane and decreased in carbon dioxide relative to the unmodified solvents, the capacity factors are still larger in carbon dioxide. However, the solvent selectivities were reduced by ca. 35% for solutes 1-4 and by over 70% for phenyldodecane (solute 5) in comparison to the selectivity obtained in the unmodified solvents on the same column. Of the polar-substituted aromatics, nitronaphthalene (solute 7), phenol (solute 10), and 3-phenylpropanol (solute 11) exhibited an increase in the difference in retention in the two solvents on the ODS column with the addition of modifier.

The difference in the modifier effect on each solvent on the underivatized and ODS-derivatized columns can be observed by comparing the selectivities of the modified and unmodified solvents which were given in Table IV. In carbon dioxide and in propane on the ODS column, solutes 1-4 exhibit approximately the same value of modifier selectivity. In contrast, these values vary considerably for these solutes on the underivatized column. This suggests that the differences in modifier selectivity for these solutes on the underivatized column result from differences in competitive adsorption with the modifier rather than changes in their relative mobile phase solubilities.

### ***Comparison of ODS and methanol-modified silicas***

As shown in the previous results, the capacity factors of the polar-substituted aromatics were found to decrease substantially in both solvents on underivatized silica with the addition of a small amount of methanol modifier. This was further indicated to be the result of competitive adsorption and to some extent enhanced mobile phase solubility. The ability of the methanol modifier to effectively reduce solute-stationary phase interactions by masking adsorption sites on the surface can be examined by comparing the retention results in methanol-modified solvents on the underivatized column with the results obtained in the unmodified solvents on the ODS column. These results are compared for propane in Fig. 8b. It is clear that even with the additional solvent strength afforded by the presence of the modifier, the underivatized silica surface covered at more than 90% of its maximum methanol concentration still interacts much more strongly with these solutes than does the ODS-bonded phase. A similar result is obtained for carbon dioxide, as shown in Fig. 8a, although the difference in retention is much smaller.

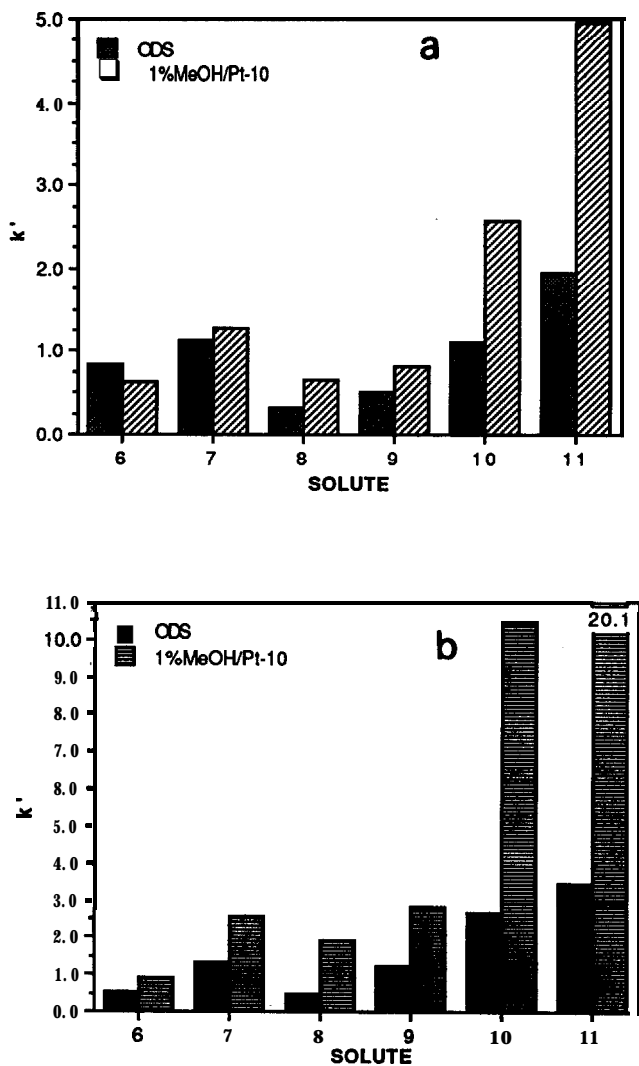


Fig. 8. Capacity factors in unmodified solvents on ODS-derivatized silica, and in modified solvents on underivatized silica: (a) carbon dioxide and (b) propane. Pt-10 = Partisil-10.

#### Density effects in methanol-modified solvents

A final comparison was made to examine the effects of increased mobile phase density on the retention of the test solutes in the methanol-modified solvents on the underivatized silica column. The retention results in carbon dioxide with 1.0% methanol modifier are illustrated in Fig. 9a. The capacity factors of all of the solutes decrease with increasing density. The relative change in retention is approximately the same for all solutes, as indicated by the density-selectivity values given in Table V. The effect of increased interactions in the mobile phase resulting from increased density appears to be nearly the same for all solutes.

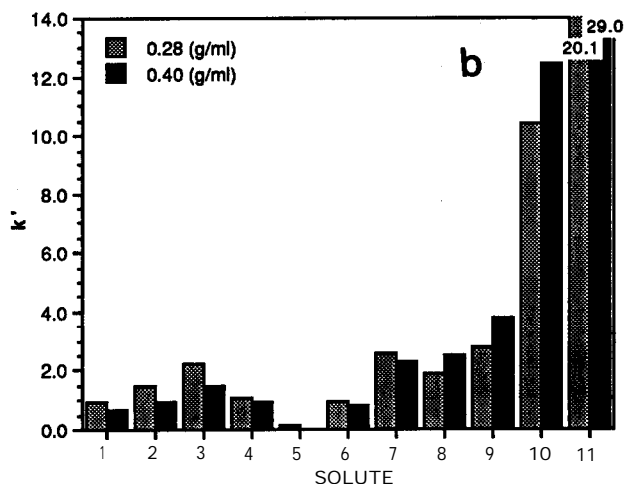
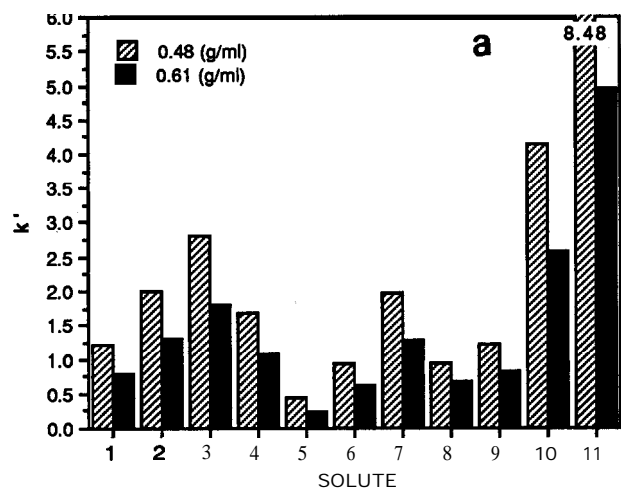


Fig. 9. Capacity factors in methanol-modified solvents at two densities on underivatized silica: (a) carbon dioxide and (b) propane.

In propane, the capacity factors of solutes 1-7 also decrease with increasing density as shown in Fig. 9b. In this case, however, the density selectivity values vary considerably for each solute. In addition, solutes 8-11 exhibit an unexpected increase in retention with increasing density. Since the methanol concentration is held constant, and the interactions of the mobile phase increase with increasing density, the increased retention of solutes 8-11 must be due to increased interactions of the solutes with the silica surface. A comparison of the adsorption isotherms of methanol on the same column was made in order to determine the extent of the change in modifier surface



TABLE V

DENSITY SELECTIVITIES OF METHANOL-MODIFIED SOLVENTS ON UNDERIVATIZED SILICA

Densities 0.28, 0.40, 0.48 and 0.61 g/ml are indicated in parentheses.

Solute	$\alpha_{CO_2(0.48/0.61)}$	$\alpha_{C_3H_8(0.28/0.40)}$
1	1.54	1.40
2	1.54	1.50
3	1.57	1.51
4	1.57	1.20
5	1.90	-
6	1.52	1.17
7	1.55	1.11
8	1.42	0.761
9	1.50	0.738
10	1.62	0.841
11	1.71	0.694

coverage. The isotherms are given in Fig. 10. The methanol concentration on the adsorbent from propane was calculated to decrease by 23% with increasing density. The resulting increase in the availability of adsorption sites apparently more than compensates for the increase in mobile phase solubility of these solutes which results from increased density.

In carbon dioxide, the methanol concentration on the adsorbent changes less with decreasing density, increasing by 13% with an absolute change in surface

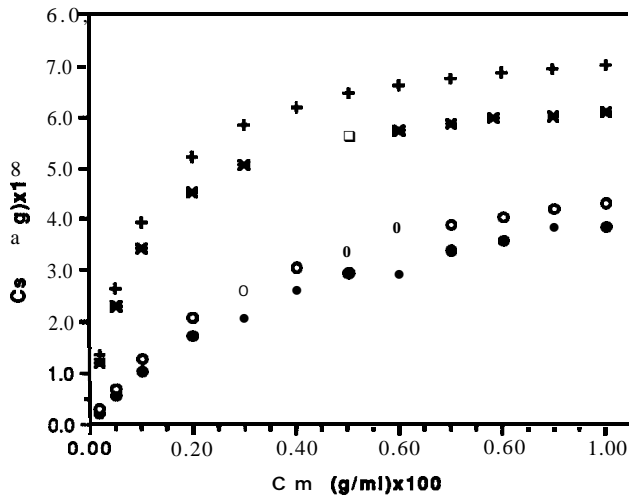


Fig. 10. Methanol adsorption isotherms at 100°C on underivatized silica from carbon dioxide and from propane at two densities. + = Propane, 0.28 g/ml ( $V_f = 1.55$ ); \* = propane, 0.40 g/ml; o = carbon dioxide, 0.48 g/ml; ● = carbon dioxide, 0.61 g/ml ( $V_f = 1.55$ ); Cs = stationary phase concentration, Cm = mobile phase concentration.

coverage ca. one third of that calculated from propane. This, in combination with the greater solvent strength of carbon dioxide for these solutes that was indicated previously, may explain why a reversal in the anticipated elution strength is not observed in carbon dioxide.

## CONCLUSIONS

The results presented herein indicated a number of differences in the factors that influence solute retention in carbon dioxide and propane mobile phases and in the effects of modifier addition on these solvents:

(1) The logarithms of the capacity factors of unsubstituted polycyclic aromatic hydrocarbons exhibited a good correlation with molar volume in propane and with polarizability in carbon dioxide on an underivatized silica column. This suggests a difference in the nature of the molecular interaction of these solutes in each of these solvents.

(2) At equal free volumes and equivalent temperatures, carbon dioxide and propane were found to have different solvent strengths for unsubstituted aromatic hydrocarbons which varied with the nature of the adsorbent surface.

(3) Although studies on a non-polar bonded phase column indicated greater solubility of unsubstituted aromatic hydrocarbons in propane, carbon dioxide exhibited a greater elution strength for these solutes on silica. This was attributed to its ability to compete more effectively with the solutes for non-specific adsorption sites on the silica surface.

(4) The greater elution strength of carbon dioxide for polar substituted aromatics was indicated to be the result of greater mobile phase solubility as well as more effective competitive adsorption onto silica.

(5) Although earlier results<sup>16</sup> indicated that unsubstituted aromatics do not compete with methanol for direct adsorption onto surface silanols, the modifier effect in carbon dioxide on underivatized silica appears to be largely the result of displacement of these solutes from stationary phase surface by the modifier. Both surface interactions and changes in mobile phase solvent strength appear to contribute to the modifier effect for more polar solutes.

(6) The modifier effect was more pronounced for both types of solutes in propane as a result of propane's inability to compete with the solutes for stationary phase adsorption sites and to solvate more polar solutes in the mobile phase without the aid of a modifier. The retention dependence of the more polar solutes on competitive modifier adsorption was sufficient in propane to result in an increase in retention with increasing mobile phase density due to the accompanying decrease in modifier stationary phase coverage.

The exact nature of the interactions of non-localizing solutes with the surface of silica is unclear. Although non-localized adsorption is apparently the case for unsubstituted aromatic hydrocarbons, it does not preclude effects on solute retention that results from competitive adsorption by the mobile phase solvent and modifier. This supports the model of Snyder and Glajch<sup>14,17</sup> which suggests that both localizing and non-localizing solutes should exhibit a retention dependence on the concentration of adsorbed modifier. Mobile phase contributions, however, still appear to play a role in the modifier effect. The nature of the interaction between carbon dioxide and the silica surface should be investigated further.

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