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Addition of methanol to the mobile phase in packed capillary column supercritical fluid chromatography

Retention mechanisms from linear solvation energy relationships

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Abstract

Linear solvation energy relationships (LSERs) were used to verify previously proposed retention mechanisms when an organic modifier is used with an octyldecylsilane bonded phase in packed capillary column supercritical fluid chromatography. Supercritical fluid chromatographic retention data for a wide variety of compounds at different modifier concentrations were obtained using a 60 cm×200 μm I.D. ODS packed capillary column. Supercritical carbon dioxide at a pressure of 260 atm was used as mobile phase and methanol as modifier. The LSER regression equation used was $\log k' = SP_0 + l \log L^{16} + s \pi_2^H + a \alpha_2^H + b \beta_2^H + r R_2$, where k' represents the capacity factor and L^{16} represents the partition coefficient of the solute between the gas phase and *n*-hexadecane at 298 K, and l , s , a , b and r are the regression coefficients. By increasing the percentage of modifier added to the mobile phase, the l coefficient decreased gradually. The b and s coefficients were greatly decreased on moving from neat carbon dioxide mobile phase to 2% methanol modifier, thereafter showing a gradual decrease with increasing modifier concentration. From these observations, we substantiate the conclusion that when a small amount of modifier (up to 2%) is added, the predominant modifier effect on the ODS bonded phase is dynamic coating of free silanols on the surface of the stationary phase, and when more modifier is added, another effect, i.e. an increase in the density of the mobile phase leading to an increase in elution strength of the eluent, becomes more important.

Keywords: Linear solvation energy relationships; Organic modifiers; Mobile phase composition; Retention mechanisms

1. Introduction

As early as 1962 [1], the use of compressed (dense) gases and supercritical fluids as chromatographic mobile phases in conjunction with liquid

chromatographic (LC) packed columns was first reported. During its relatively short existence, supercritical fluid chromatography (SFC) has become an attractive alternative to GC and LC in certain industrially important applications. SFC often provides faster analysis times and better detector compatibility than LC, and extends the analyzable volatility range and lowers the analysis temperatures normally required for GC.

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Carbon dioxide, which is the preferred mobile phase in SFC, has limited solvating power for polar analytes. Owing to the limited number of alternative solvents possessing greater polarity with acceptable critical properties and safety requirements for SFC, the addition of polar modifiers to CO₂ is the best alternative when more polar fluids are needed.

Retention phenomena in SFC have been studied by many researchers [2–4] and a model for the prediction of retention in packed column SFC when using a mixed mobile phase has been developed [5]. Various effects of the addition of modifiers to the supercritical fluid mobile phase were observed by many authors, e.g., Engelhardt et al. [6], Heaton et al. [5], Blilie and Greibrokk [7], Janssen and Cramers [8] and Smith and Sanagi [9], to name a few. These authors showed that the addition of an organic modifier to the mobile phase decreased the retention times and improved the peak shapes for many polar compounds. They ascribed these observations to two contributing factors: the modifier helped to (a) deactivate the stationary phase and (b) increase the solvating power of the mobile phase. Janssen and Cramers claimed that the observations were additionally a result of specific interactions between the solute and the modifier in the mobile phase [8]. To date, the effects of modifiers on retention have not been fully substantiated.

For this purpose, we used a linear solvation energy relationship (LSER) model to determine the effects of adding a modifier to the mobile phase in SFC. The linear solvation energy relationship model has been very successful in describing numerous processes in which a series of solutes are distributed between two different phases. These processes include liquid–liquid chromatography [10], gas–liquid chromatography [11], gas–solid chromatography [12] and the partitioning of gases and vapors into polymers [13]. We investigated the following solvation equation to characterize the distribution of solute between the mobile and stationary phases in packed capillary column SFC:

$$\log k' = SP_o + l \log L^{16} + s\pi_2^H + a\alpha_2^H + b\beta_2^H + rR_2 \quad (1)$$

which was proposed and extensively used by Abraham [14]. The dependent variable in Eq. (1) can be

taken as the logarithm of the capacity factor or partition coefficient. SP_o is a solute-independent constant characteristic of the column under study, L^{16} is the partition coefficient of the solute between the gas phase and *n*-hexadecane at 298 K, π_2^H is the solute dipolarity/polarizability, α_2^H is the effective or summation solute hydrogen-bond acidity, and β_2^H is the effective or summation solute hydrogen-bond basicity. All of the constants, l , s , a , b and r , are dimensionless, empirically determined regression coefficients that characterize the partitioning between the mobile phase and the stationary phase in a given chromatographic system.

The advantages of packed column SFC include fast analysis speed, high sample capacity and high plate numbers per unit column length [15–18]. It is known that packed capillary columns can provide the same advantages of conventional packed columns, with much reduced mobile phase flow-rates [19]. This study was undertaken to provide greater understanding of the effects of adding modifiers to the supercritical mobile phase in packed capillary column SFC, using linear solvation energy relationships (LSERs).

2. Experimental

2.1. Chemicals

Thirty-five test compounds (laboratory grade) were obtained from a range of suppliers. SFC grade CO₂ (Scott Specialty Gases, Plumsteadville, PA, USA) was used as the mobile phase, HPLC grade acetone (Mallinckrodt, Paris, KY, USA) was used to mark the column void volume and HPLC grade methanol (Fisher, Fair Lawn, NJ, USA) was used as modifier.

2.2. Chromatographic system

The chromatographic system comprised a Model 600 SFC pump (Dionex, Sunnyvale, CA, USA) for pressure control of the carbon dioxide mobile phase and modifier, and a Model 600 GC/SFC oven (Dionex). This particular SFC instrument was equipped with a Valco C14W injection valve with a helium-powered pneumatic actuator. The modifier

mixing system used for this work was previously described [20]. In brief, the system uses an air actuated high-pressure prime/purge valve for on-line modifier introduction. This valve can deliver an accurate amount of modifier into the mobile phase. The column used was a 60 cm \times 200 μ m I.D. fused silica capillary, packed with 5 μ m ODS bonded silica [15]. The packing material (Inertsil ODS-2, 5 μ m diameter, 150 Å pore size, 350 m² g⁻¹ surface area) was obtained from Phenomenex (Torrance, CA, USA). The packed capillary column was connected directly to the injection valve and the detection of solutes occurred immediately after the bed support using the 200 μ m I.D. column as the flow cell. Detection for all experiments was accomplished with a Model 203 UV-Vis detector (Linear, Reno, NV, USA).

2.3. Method

Samples of test compounds were injected with timed split into the column and eluted with supercritical carbon dioxide at 100°C and 260 atm pressure (1 atm = 0.101325 MPa). Methanol was added as required. Capacity factors (k') were determined by using the relationship:

$$k' = (t_R - t_0)/t_0 \quad (2)$$

where t_R is the solute retention time and t_0 is the hold-up time of an unretained peak (acetone). The mean of triplicate injections was used in the calculations. The solute parameters used were taken from ref. [21] and are given in Table 1.

3. Results and discussion

Since the capacity factors in SFC are mostly influenced by the mobile phase density and the purpose of our work was to investigate the effect of modifiers on solute retention, all of the experiments in this study were performed at constant CO₂ pressure. The capacity factors of 35 test compounds were determined at 260 atm and 100°C, with increasing concentrations of methanol in the mobile phase (see Table 2). The two most polar solutes, heptanoic acid and nonanoic acid, were not eluted from the 5 μ m ODS column with neat carbon dioxide mobile

phase; however, they were eluted when four different concentrations (2 to 8%) of methanol was added. The correlation results from the SFC retention data, using Eq. (1) for a 60 cm packed capillary column, are given in Table 3. The standard deviations of the fit (S.D.) and the correlation coefficients (R) are also given in Table 3.

Upon inspection of Table 3 for each regression, the correlation coefficients (R) range from 0.9957 to 0.9987 and the standard deviations (S.D.) range from 0.0137 to 0.0230. The correlations of the capacity factor data (Table 2) with Eq. (1) are remarkably precise. Although we can observe that the fit quality decreased somewhat when the modifier was added, the overall correlations are better than those obtained in reversed-phase liquid chromatography [10].

Since the correlations are very precise, the various solvatochromic coefficients, SP_o , l , s , a , b and r are statistically significant and should be reasonable. In Fig. 1, the three most important coefficients (l , s and b) are plotted. The amount of methanol added is displayed on the x -axis and the coefficient values are plotted on the y -axis. Here, these three most important parameters show much greater variance than the other three coefficients (SP_o , a and r) when the modifier is added. In actuality, the SP_o , a and r coefficients do not vary much with modifier addition (see Table 3).

The most important finding in this study is the remarkable change in b coefficients when a small amount of modifier (2%) is added to the mobile phase. In the linear solvation energy relationship approach, the b coefficient has a distinct chemical interpretation. In GC, for example, it represents the hydrogen bond donor ability of the stationary phase. For a stationary phase that has no hydrogen bond donor group such as C₁₈ or squalane, the b coefficient should be zero. In contrast, if the stationary phase were to have an active hydrogen bond donor group, such as a hydroxyl group, then the b coefficient would be expected to be positive. In this case, as the solute basicity (β_2^H) increases, the retention increases.

In SFC, the b coefficient means the following:

$$b = b_{\text{stationary}} - b_{\text{mobile}} \quad (3)$$

where $b_{\text{stationary}}$ represents the hydrogen bond donor ability of the stationary phase and b_{mobile} represents

Table 1
Solute solvatochromic parameters

No.	Compound	Log L^{16}	π_2^H	α_2^H	β_2^H	R_2
1	Nitrobenzene	4.557	1.11	0.00	0.28	0.871
2	Ethyl benzoate	5.075	0.85	0.00	0.46	0.689
3	Benzyl alcohol	4.221	0.87	0.33	0.56	0.803
4	Benzonitrile	4.039	1.11	0.00	0.33	0.742
5	<i>m</i> -Nitrotoluene	4.878	1.11	0.00	0.27	0.866
6	Biphenyl	6.014	0.99	0.00	0.22	1.360
7	Naphthalene	5.161	0.92	0.00	0.20	1.340
8	<i>o</i> -Xylene	3.939	0.56	0.00	0.16	0.663
9	Butylbenzene	4.730	0.51	0.00	0.15	0.600
10	Acetophenone	4.501	1.01	0.00	0.48	0.818
11	Phenetole	4.242	0.70	0.00	0.32	0.681
12	Toluene	3.325	0.52	0.00	0.14	0.601
13	Benzaldehyde	4.008	1.00	0.00	0.39	0.820
14	<i>o</i> -Cresol	4.218	0.86	0.52	0.30	0.840
15	Methyl benzoate	4.704	0.85	0.00	0.46	0.733
16	<i>m</i> -Cresol	4.310	0.88	0.57	0.34	0.822
17	<i>p</i> -Cresol	4.312	0.87	0.57	0.31	0.820
18	Bromobenzene	4.041	0.73	0.00	0.09	0.882
19	Benzyl chloride	4.384	0.82	0.00	0.33	0.821
20	<i>o</i> -Dichlorobenzene	4.518	0.78	0.00	0.04	0.872
21	Pentamethylbenzene	5.798	0.66	0.00	0.20	0.850
22	1-Cyanononane	5.460	0.90	0.00	0.36	0.156
23	1-Cyanooctane	4.970	0.90	0.00	0.36	0.159
24	2-Undecanone	5.732	0.68	0.00	0.51	0.101
25	Octanal	4.361	0.65	0.00	0.45	0.160
26	Dibutyl ether	3.924	0.25	0.00	0.45	0.000
27	1-Bromohexane	4.130	0.40	0.00	0.12	0.349
28	1-Chlorooctane	4.772	0.40	0.00	0.10	0.191
29	1-Dodecyne	5.657	0.23	0.12	0.10	0.133
30	1-Dodecene	5.515	0.08	0.00	0.07	0.089
31	1-Decanol	5.628	0.42	0.37	0.48	0.191
32	1-Undecanol	6.130	0.42	0.37	0.48	0.181
33	1,4-Dibromobenzene	5.324	0.86	0.00	0.04	1.150
34	Heptanoic acid	4.460	0.60	0.60	0.45	0.149
35	Nonanoic acid	5.550	0.60	0.60	0.45	0.132

the hydrogen bond donor ability of the mobile phase. On inspection of Fig. 1, the 5 μm ODS bonded silica used as the stationary phase has a very large positive b coefficient when neat carbon dioxide is employed as the mobile phase. When 2% methanol is added to the mobile phase, the b coefficient decreases rapidly until at 4% methanol, the b coefficient becomes slightly negative, thereafter showing a gradual decrease with increasing modifier concentration. The signs and magnitudes of these b coefficients are reasonable. The large positive b coefficient with neat CO_2 indicates that the 5 μm ODS particles (Phenomenex) used in this study have some free silanol groups, even though they were deactivated by the

manufacturer. The rapid decrease in b , after adding 2% methanol, is due to the dynamic coating of the free silanols on the surface of the ODS packing material, which gives rise to a large decrease in $b_{\text{stationary}}$. The negative sign of the b coefficient indicates that the hydrogen bond donating ability of the mobile phase is greater than that of the stationary phase. This is especially true when a large amount of methanol exists in the mobile phase. As the amount of modifier in the mobile phase increases, the b_{mobile} value also increases. A gradual decrease in the b coefficient thereafter can be rationalized by an increase in b_{mobile} . These results strongly suggest that the b coefficient in Eq. (1) is closely related to

Table 2
Capacity factors of test compounds at different methanol concentrations^a

No.	Solute	Capacity factor				
		Methanol (% w/w)				
		0	2	4	6	8
1	Nitrobenzene	1.594	0.677	0.491	0.368	0.295
2	Ethyl benzoate	1.807	0.671	0.474	0.356	0.284
3	Benzyl alcohol	2.348	0.794	0.569	0.436	0.358
4	Benzonitrile	1.129	0.458	0.345	0.264	0.208
5	<i>m</i> -Nitrotoluene	1.932	0.798	0.556	0.409	0.326
6	Biphenyl	5.554	2.202	1.559	1.116	0.868
7	Naphthalene	3.098	1.350	1.090	0.812	0.654
8	<i>o</i> -Xylene	0.618	0.378	0.300	0.244	0.207
9	Butylbenzene	0.816	0.494	0.391	0.301	0.255
10	Acetophenone	1.753	0.611	0.442	0.333	0.269
11	Phenetole	0.978	0.452	0.343	0.271	0.228
12	Toluene	0.406	0.265	0.218	0.179	0.182
13	Benzaldehyde	1.341	0.493	0.368	0.284	0.224
14	<i>o</i> -Cresol	2.300	1.024	0.761	0.610	0.484
15	Methyl benzoate	1.584	0.602	0.431	0.328	0.266
16	<i>m</i> -Cresol	2.528	1.117	0.782	0.630	0.479
17	<i>p</i> -Cresol	2.547	1.117	0.824	0.646	0.512
18	Bromobenzene	0.839	0.518	0.360	0.357	0.326
19	Benzyl chloride	1.273	0.574	0.430	0.337	0.274
20	<i>o</i> -Dichlorobenzene	1.014	0.638	0.494	0.435	0.335
21	Pentamethylbenzene	1.009	1.082	0.791	0.578	0.470
22	1-Cyanononane	1.063	0.398	0.291	0.233	0.165
23	1-Cyanoctane	0.839	0.339	0.246	0.182	0.144
24	2-Undecanone	1.234	0.439	0.302	0.221	0.175
25	Octanal	0.710	0.261	0.190	0.155	0.124
26	Dibutyl ether	0.335	0.159	0.133	0.121	0.095
27	1-Bromohexane	0.411	0.276	0.225	0.182	0.157
28	1-Chlorooctane	0.452	0.307	0.241	0.188	0.158
29	1-Dodecyne	0.702	0.477	0.360	0.290	0.235
30	1-Dodecene	0.476	0.364	0.283	0.215	0.190
31	1-Decanol	1.776	0.716	0.557	0.379	0.309
32	1-Undecanol	2.213	0.877	0.585	0.461	0.342
33	1,4-Dibromobenzene	2.413	1.271	0.928	0.830	0.655
34	Heptanoic acid	–	0.545	0.480	0.317	0.262
35	Nonanoic acid	–	0.767	0.525	0.423	0.363

^a Conditions: 60 cm × 200 μm I.D. packed capillary column, 5 μm ODS; 100°C temperature; 260 atm pressure.

the deactivation of the free silanol groups on the surface of the stationary phase with the modifier.

The next most important LSER coefficient is the l coefficient, which reflects the combination of an endoergic cavity term and an exoergic solute–solvent general dispersion interaction term. The latter always dominates, giving rise to positive l constants [22]. In SFC, the l coefficient represents the following:

$$l = l_{\text{stationary}} - l_{\text{mobile}} \quad (4)$$

where $l_{\text{stationary}}$ is a measure of the strength of dispersion interaction between the solute and stationary phase and l_{mobile} is a measure of the strength of dispersion interaction between the solute and mobile phase. Fig. 1 shows that the l coefficients decrease inversely to the amount of methanol added. This is explained as follows. When a modifier is added to the mobile phase in SFC, an increase in l_{mobile} , i.e. an increase of solute–mobile phase dispersion interactions, is expected since an increase in the amount

Table 3
Regression coefficients^a based on solvatochromic parameters

Methanol in mobile phase (%)	n^b	Regression coefficient ^c							S.D. ^e
		SP_o	l	s	a	b	r	R^d	
0	33	-1.589 (0.022)	0.212 (0.004)	0.217 (0.018)	0.528 (0.016)	0.534 (0.024)	0.512 (0.013)	0.9987	0.0157
2	35	-1.530 (0.019)	0.188 (0.003)	0.046 (0.015)	0.521 (0.012)	0.013 (0.021)	0.513 (0.011)	0.9985	0.0137
4	35	-1.526 (0.031)	0.169 (0.005)	-0.005 (0.026)	0.518 (0.020)	-0.012 (0.035)	0.516 (0.018)	0.9957	0.0230
6	35	-1.512 (0.027)	0.151 (0.005)	-0.023 (0.023)	0.509 (0.018)	-0.084 (0.031)	0.516 (0.016)	0.9964	0.0202
9	35	-1.482 (0.026)	0.134 (0.005)	-0.084 (0.021)	0.502 (0.017)	-0.104 (0.029)	0.535 (0.015)	0.9967	0.0190

^aThe regression equation employed was $\log k' = SP_o + l \log L^{16} + s \pi_2^{11} + a \alpha_2^{11} + b \beta_2^{11} + r R_2$.

^bNumber of data points.

^cThe number in parentheses under each regression coefficient value is the standard deviation of the coefficient, which is generated from multiple linear regression calculations (see Ref. [25]).

^dCorrelation coefficient.

^eStandard deviation of the fit.

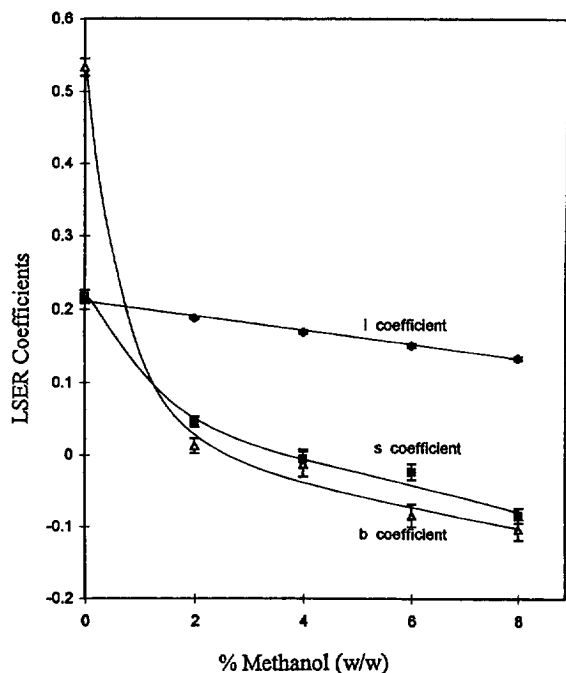


Fig. 1. Effect of the addition of methanol as a modifier on l , b and s coefficients. Conditions: 60 cm \times 200 μ m I.D. packed capillary column, 5 μ m ODS; 100°C temperature; 260 atm pressure.

of methanol added should lead to an increase in the mobile phase density which can, in turn, give rise to an increase in the overall solvating power of the mobile phase. Therefore, the magnitude of the l coefficient in Eq. (1) represents a measure of the overall elution strength of the eluent. A decrease in the l coefficient in Eq. (1) indicates an increase in l_{mobile} , which reflects an increased elution strength of the mobile phase.

As mentioned before, it is well known that the addition of an organic modifier to the mobile phase leads to a remarkable decrease in the capacity factors for polar compounds. The variances of the b and l LSER coefficients indicate that with a small amount of modifier (up to 2%) the predominant process is dynamic coating of free silanols on the surface of the stationary phase, and when more modifier is added, an increase in the density of the mobile phase (i.e. an increase in the solvating power of the eluent) is the important factor.

The third important coefficient is the s coefficient. Similarly, the s coefficient can be defined as follows for SFC:

$$S = S_{\text{stationary}} - S_{\text{mobile}} \quad (5)$$

where $S_{\text{stationary}}$ represents a measure of the strength of dipolarity–polarizability interactions between the

solute and the stationary phase and s_{mobile} represents the same interactions between the solute and the mobile phase. The s coefficients vary similarly to the b coefficients with increasing modifier concentration. This behavior can also be explained. With neat CO_2 , the s coefficient gives a large positive value since the dipole moment of neat CO_2 is zero (i.e. the value of s_{mobile} is nearly zero). As the concentration of modifier increases, the dipole–dipole interaction between the solute and mobile phase should increase, leading to an increase in the s_{mobile} coefficient. A rapid decrease in the s coefficient on moving from neat carbon dioxide mobile phase to 2% methanol modifier could also be explained by the dissolution of methanol and carbon dioxide in the stationary phase, which results in dilution of the stationary phase. It was reported in SFC that when a small amount of methanol (about 1–2%) was used as a modifier, there was extensive swelling of the stationary phase by methanol and carbon dioxide; however, higher methanol concentrations produced no significant further increase in methanol or carbon dioxide adsorption [23,24]. This diluted stationary phase could cause a rapid decrease in the $s_{\text{stationary}}$ value as well as the $b_{\text{stationary}}$ value.

When methanol was added as a modifier to the mobile phase using a packed capillary column, very similar modifier effects were observed. Throughout all of our experiments, we observed that for many polar compounds, peak shapes and retention times in packed capillary column SFC were greatly altered by the addition of an organic modifier to the mobile phase. Some polar compounds (e.g., *p*-cresol and benzaldehyde) gave broad, tailing peaks using packed capillary columns without a modifier; however, these compounds could be eluted as sharp, symmetric peaks with a modifier. The retention times of polar compounds were greatly decreased when 2% methanol was added, thereafter showing a gradual decrease with increasing modifier concentration.

The data presented in this paper regarding capacity factors at various concentrations of methanol in packed capillary SFC are very relevant to retention mechanism studies or related studies in the area of SFC. It could also be used for the characterization of packed capillary columns in comparison to conventional packed columns or open tubular columns in SFC.

In conclusion, the b and s coefficients decrease significantly when 2% methanol is added to the carbon dioxide mobile phase in packed capillary column SFC. This is explained by extensive adsorption of methanol on the surface of the chromatographic stationary phase. The gradual decrease in the l coefficient can also be understood by an increase in the solvating power of the mobile phase. We note that in SFC, a small amount of modifier (approximately 2%) is sufficient to elute most polar compounds with good peak shapes and reasonable speed. It should be noted that high modifier concentration in the mobile phase could cause a severe decrease in selectivity, especially, for the analysis of complex mixtures. When 8% methanol was added, the capacity factors for most compounds ranged from 0.15 to 0.50 (see the data under 8% in Table 2). A highly increased mobile phase solvent strength results in a great decrease in the retention times for most chemical compounds.

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