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# Modifier effects in open tubular capillary column supercritical fluid chromatography

## Retention mechanisms from linear solvation energy relationships

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### Abstract

Recently, the solvatochromic comparison method was successfully applied to determine the effects of adding a modifier to the mobile phase in packed capillary columns, and we have extended this method to understand the modifier effect in open tubular capillary column supercritical fluid chromatography (SFC). SFC retention data for a wide variety of compounds at different modifier concentrations were obtained using a 10 m×50 μm I.D. SB-methyl-100 polydimethylsiloxane 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  $\log k' = SP_0 + l \log L^{16} + s\pi_2^H + a\alpha_2^H + b\beta_2^H + rR_2$ , 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. For open tubular column SFC, variation of the  $l$  and  $s$  coefficients showed a similar pattern to the packed capillary column SFC. However, the  $b$  coefficient showed a different pattern from packed capillary SFC, i.e., a gradual decrease with increasing modifier concentration. Based on these observations, the effects of a small amount of a modifier in the supercritical mobile phase and its effects on solute retention mechanisms have been discussed. For open tubular column SFC, the swelling of the chromatographic stationary phase by a modifier and carbon dioxide and the increase of dipolarity of the mobile phase are the most important contributing factors in substantiating the modifier effect on solute retention. © 1998 Elsevier Science B.V.

**Keywords:** Linear solvation energy relationships; Mobile phase composition; Modifier effects; Open tubular columns; Retention mechanisms

### 1. Introduction

The use of compressed (dense) gases and supercritical fluids as chromatographic mobile phases in conjunction with liquid chromatographic-type packed columns was first reported by Klesper et al. in 1962

[1]. During its relatively short history, supercritical fluid chromatography (SFC) has become an attractive alternative to gas chromatography (GC) and liquid chromatography (LC) in certain industrially important applications. SFC gives the advantage of high efficiency and allows the analysis of non-volatile or thermally labile mixtures.

In SFC, the effect of short intermolecular distances and the resulting increase in intermolecular

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interactions is an enhanced solubilizing capability of the solvent towards various solutes. Compounds with much higher molecular masses than normally separated in GC can therefore be chromatographed. However, the most commonly used mobile phases in SFC are all relatively non-polar fluids. Carbon dioxide, the most widely used fluid, is no more polar than hexane [2], even at high densities. Solute polarity should be between that of the stationary phase and the mobile phase in order to have a well behaved separation. Few real samples contain only non-polar solutes, so a major objective of research in SFC has been directed toward increasing the range of solute polarities that can be handled by the technique. To bring the SFC technique into routine use, mobile phases that are more polar than the commonly used carbon dioxide are necessary.

The solvent strength of supercritical CO<sub>2</sub>, even at high density, is not sufficient for the elution of polar solutes. Polar mobile phases such as NH<sub>3</sub> [3] exhibit useful properties, but a more practical way to extend the range of compounds separable by SFC is to use a mixed mobile phase. The solubility of the solute in the supercritical phase can be influenced considerably by adding modifiers to the mobile phase. The use of modifiers has been reported by, for example, Jentoft and Gouw [3] and by Novotny et al. [4]. The latter group showed that adding 0.1% 2-propanol to pentane as the mobile phase decreases the observed partition coefficient (*K*) values for many polynuclear aromatic hydrocarbons by 20–35%.

Retention phenomena in SFC have been studied by many researchers [5–7] and a model for the prediction of retention in packed column SFC when using a mixed mobile phase has been developed [8]. Various effects of the addition of modifiers to the supercritical fluid mobile phase were observed by many authors, e.g., Heaton et al. [8], Engelhardt et al. [9], Blilie and Greibrokk [10] and Janssen and Cramers [11]. 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 ob-

servations were additionally a result of specific interactions between the solute and the modifier in the mobile phase [11]. It is also known [12] that this modifier effect is much more noticeable in packed column SFC than in open tubular column SFC.

To determine the effects of adding a modifier to the mobile phase in open tubular column SFC, we used a linear solvation energy relationship (LSER) model. 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 phase. These processes include liquid–liquid chromatography [13], gas–liquid chromatography [14], gas–solid chromatography [15] and the partitioning of gases and vapors into polymers [16]. We investigated the following solvation equation to characterize the distribution of solute between the mobile and stationary phases in open tubular capillary column SFC:

$$\log k' = SP_0 + l \log L^{16} + s\pi_2^H + a\alpha_2^H + b\beta_2^H + rR_2 \quad (1)$$

which was proposed and extensively used by Abraham [17]. The dependent variable in Eq. (1) can be taken as the logarithm of the capacity factor or partition coefficient. *SP*<sub>0</sub> is a solute-independent constant characteristic of the column under study, *L*<sup>16</sup> is the partition coefficient of the solute between the gas phase and *n*-hexadecane at 298 K, *π*<sub>2</sub><sup>H</sup> is the solute dipolarity/polarizability, *α*<sub>2</sub><sup>H</sup> is the effective or summation solute hydrogen-bond acidity and *β*<sub>2</sub><sup>H</sup> 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.

To our knowledge, our previous paper [18] is the only reported application of a LSER using solute parameters to study the effects of adding a modifier to the mobile phase in SFC. In the previous work, we used a packed capillary column; however, in this work, we chose an open tubular capillary column to study different chromatographic retention mechanisms at modifier concentrations for different types of columns.

## 2. Experimental

### 2.1. Chemicals

Thirty-five test compounds (laboratory-grade) were obtained from a range of suppliers. SFC-grade CO<sub>2</sub> (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 the same one as for the previous work [18]. 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 capillary column used was a 10 m×50 μm I.D. SB-methyl-100 polydimethylsiloxane with 0.25 μm film thickness obtained from Dionex. 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 calcula-

tions. The solute parameters used were taken from Ref. [19] and are given in Table 1.

## 3. Results and discussion

The retentions in SFC are mostly influenced by the temperature and pressure of the mobile phase. As the temperature of the mobile phase increases, the capacity factor ( $k'$ ) decreases. Qualitatively this may be explained [20] by an increase of the vapour pressure of the solute which leads to a shift in partition in favour of the mobile phase. The pressure of the mobile phase also influences the retentions in SFC. As the pressure of the mobile phase is varied, the density of the mobile phase also changes, changing the solvent strength of the mobile phase. Since the purpose of the current work is to investigate the effect of modifiers in open tubular capillary SFC, all of the experiment in this study were performed at constant CO<sub>2</sub> pressure and temperature. To compare with our previous results obtained in packed capillary column SFC, we selected the same experimental conditions (260 atm and 100°C). The capacity factors of 35 test compounds were determined using different methanol-modified (0%, 2%, 4%, 6%, w/w) carbon dioxide mobile phase (see Table 2). The correlation results from the SFC retention data, using Eq. (1) for a 10 m×50 μm I.D. open tubular capillary column, are given in Table 3. The standard deviations (S.D.s) of the fit and the correlation coefficients ( $R$ ) are also given in Table 3. In each regression, the correlation coefficient ( $R$ ) exceeds 0.995, and the S.D. is less than 0.02. Clearly retention in SFC with methanol-modified carbon dioxide mobile phase, is remarkably well-correlated with Eq. (1). This goodness of fit strongly suggests that the LSER methodology is applicable in understanding the effects of modifiers on retention in SFC.

Recently, we [18] showed that among the various solvatochromic coefficients,  $SP_0$ ,  $l$ ,  $s$ ,  $a$ ,  $b$  and  $r$ , three coefficients ( $b$ ,  $l$ ,  $s$ ) are more significant than the others in influencing the effects of adding a modifier to the mobile phase in SFC. For the present work, these three coefficients also showed much greater variance than the others when 2%, 4%, 6% modifier is added.

Table 1  
Solute solvatochromic parameters

No.	Compound	Log $L^{16}$	$\pi_2^H$	$\alpha_2^H$	$\beta_2^H$	$R_2^H$
1	Nitrobenzene	4.557	1.11	0.00	0.28	0.871
2	Ethylbenzoate	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	Methylbenzoate	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	Benzylchloride	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-Cyanoctane	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	Dibutylether	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 most interesting observation in this study is the negative values of  $b$  coefficients, especially even when no modifier 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  $C_{18}$  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 ( $\beta_2^H$ ) 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  $b_{\text{mobile}}$  represents the hydrogen bond donor ability of the mobile phase.

The negative sign of the  $b$  coefficient with pure  $CO_2$  mobile phase implies that the  $CO_2$  is acting as a hydrogen bond donor, which, of course, is chemically impossible. However,  $CO_2$  is a hard, weak Lewis acid, so the  $b$  coefficient can be a measure of its electron accepting ability. The reversible chemical reaction between  $CO_2$  and ammonia or amines to form carbamates nicely demonstrates the electron

Table 2  
Capacity factors of 35 test compounds at different methanol concentrations<sup>a</sup>

No.	Solute	Capacity factor Methanol (% w/w)			
		0	2	4	6
1	Nitrobenzene	0.896	0.425	0.329	0.236
2	Ethylbenzoate	0.824	0.433	0.341	0.243
3	Benzylalcohol	0.628	0.344	0.297	0.217
4	Benzonitrile	0.619	0.301	0.237	0.179
5	<i>m</i> -Nitrotoluene	1.061	0.495	0.389	0.263
6	Biphenyl	2.485	1.189	0.892	0.599
7	Naphthalene	1.422	0.768	0.618	0.429
8	<i>o</i> -Xylene	0.387	0.265	0.226	0.181
9	Butylbenzene	0.553	0.375	0.309	0.223
10	Acetophenone	0.761	0.373	0.297	0.213
11	Phenetole	0.499	0.304	0.251	0.181
12	Toluene	0.243	0.167	0.138	0.130
13	Benzaldehyde	0.559	0.288	0.250	0.167
14	<i>o</i> -Cresol	0.752	0.433	0.358	0.251
15	Methylbenzoate	0.723	0.391	0.315	0.219
16	<i>m</i> -Cresol	0.847	0.434	0.344	0.254
17	<i>p</i> -Cresol	0.859	0.466	0.356	0.255
18	Bromobenzene	0.531	0.333	0.282	0.208
19	Benzylchloride	0.643	0.371	0.296	0.210
20	<i>o</i> -Dichlorobenzene	0.633	0.398	0.347	0.250
21	Pentamethylbenzene	1.276	0.748	0.582	0.405
22	1-Cyanononane	0.798	0.402	0.309	0.219
23	1-Cyanooctane	0.611	0.315	0.258	0.174
24	2-Undecanone	0.761	0.437	0.318	0.207
25	Octanal	0.366	0.224	0.180	0.134
26	Dibutylether	0.196	0.156	0.133	0.101
27	1-Bromohexane	0.317	0.236	0.207	0.153
28	1-Chlorooctane	0.411	0.310	0.257	0.182
29	1-Dodecyne	0.602	0.460	0.377	0.262
30	1-Dodecene	0.475	0.399	0.308	0.241
31	1-Decanol	0.773	0.505	0.378	0.263
32	1-Undecanol	0.995	0.631	0.491	0.313
33	1,4-Dibromobenzene	1.402	0.763	0.617	0.415
34	Heptanoic acid	0.514	0.331	0.264	0.194
35	Nonanoic acid	0.922	0.553	0.426	0.299

<sup>a</sup> Conditions: 10 m × 50 μm I.D. open tubular column, SB-methyl-100 polydimethylsiloxane with 0.25 μm film thickness; 100°C temperature; 260 atm pressure.

accepting ability of CO<sub>2</sub> [21]. The acidity of CO<sub>2</sub> likely plays a role in this negative *b* coefficient. The understanding of this negative *b* coefficient could be improved given a fundamental description of the Lewis acidity of CO<sub>2</sub> as a supercritical fluid. The Lewis acidity of CO<sub>2</sub> has been quantified based on Et(30) parameters, an empirical measure of solvent polarity [22], for supercritical CO<sub>2</sub> by Hyatt [23].

His results showed CO<sub>2</sub> [Et(30)=33.8 kcal/mol at 1000 p.s.i., 24°C; 1 p.s.i.=6894.76 Pa] to have a polarity close to benzene and toluene but significantly higher than those of aliphatic hydrocarbons (*n*-pentane, 31.0; *n*-hexane, 31.0).

When methanol is added to the mobile phase, the *b* coefficient gradually decreases with increasing modifier concentration. This can be rationalized by an increase in *b*<sub>mobile</sub>, i.e., an increase of the hydrogen bond donating ability of the mobile phase with increasing modifier concentration. The difference between packed capillary column [18] and open tubular column was that the rapid decrease in the *b* coefficient after adding 2% methanol in packed capillary column was not observed in open tubular column. This indicates that the 5 μm ODS particles used in packed capillary column have a much greater number of free silanol groups than the polydimethylsiloxane stationary phase in open tubular column (Fig. 1). The rapid decrease in *b*, in packed capillary SFC after adding 2% methanol, was considered a result of the dynamic coating of the free silanols on the surface of the ODS packing material, which gives rise to a large decrease in *b*<sub>stationary</sub> [18].

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 [24]. In SFC, the *l* coefficient represents the following:

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

where *l*<sub>stationary</sub> is a measure of the strength of dispersion interaction between the solute and stationary phase and *l*<sub>mobile</sub> is a measure of the strength of dispersion interaction between the solute and mobile phase. The *l* coefficient in open tubular column SFC decreases inversely to the amount of methanol added just like packed capillary column SFC (Fig. 2). In GC, the solute does not interact with the mobile phase, so *l*=*l*<sub>stationary</sub>. In SFC, however, a contribution (*l*<sub>mobile</sub>) from the mobile phase is very important. When a modifier is added to the mobile phase in SFC, an increase in *l*<sub>mobile</sub>, i.e., an increase of solute–mobile phase dispersion interactions, is expected since an increase in the amount of methanol added should lead to an increase in the mobile phase

Table 3  
Regression coefficients<sup>a</sup> based on solvatochromic parameters

Methanol in mobile phase (%)	$N^b$	Regression coefficient <sup>c</sup>							S.D. <sup>e</sup>
		$SP_0$	$l$	$s$	$a$	$b$	$r$	$R^d$	
0	35	-1.712 (0.018)	0.243 (0.003)	0.309 (0.015)	0.223 (0.012)	-0.062 (0.021)	0.256 (0.010)	0.9984	0.0134
2	35	-1.650 (0.019)	0.223 (0.004)	0.056 (0.016)	0.217 (0.012)	-0.114 (0.022)	0.259 (0.011)	0.9973	0.0142
4	35	-1.635 (0.024)	0.204 (0.004)	0.032 (0.020)	0.205 (0.016)	-0.129 (0.027)	0.267 (0.014)	0.9952	0.0179
6	35	-1.604 (0.020)	0.175 (0.004)	-0.010 (0.016)	0.202 (0.013)	-0.154 (0.022)	0.269 (0.011)	0.9961	0.0145

<sup>a</sup> The regression equation employed was  $\log k' = SP_0 + l \log L^{16} + s \pi_2^H + a \alpha_2^H + b \beta_2^H + r R_2$ .

<sup>b</sup> Number of data points.

<sup>c</sup> The number in parentheses under each regression coefficient value is the standard deviation of the coefficient, which is generated from multiple linear regression calculations.

<sup>d</sup> Correlation coefficient.

<sup>e</sup> Standard deviation of the fit.

density which can, in turn, give rise to an increase in the solvating power of the mobile phase. Therefore, the magnitude of the  $l$  coefficient in Eq. (4) represents a measure of the elution strength of the eluent. A decrease in the  $l$  coefficient in Eq. (4) indicates an

increase in  $l_{\text{mobile}}$ , which reflects an increased elution strength of the mobile phase.

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

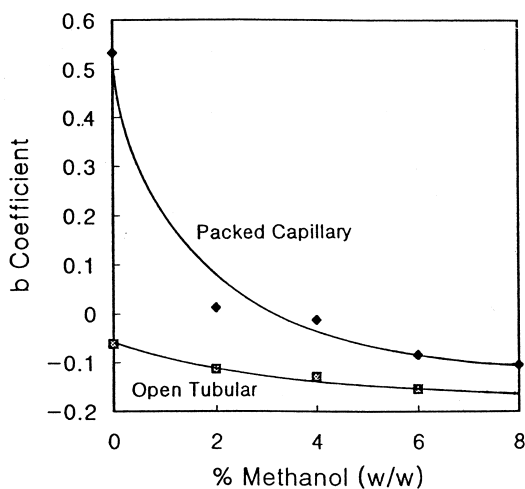


Fig. 1. Effect of the addition of methanol as a modifier on  $b$  coefficients. Conditions: 10 m  $\times$  50  $\mu$ m I.D. open tubular column, SB-methyl-100 polydimethylsiloxane with 0.25  $\mu$ m film thickness; 100°C temperature; 260 atm pressure.

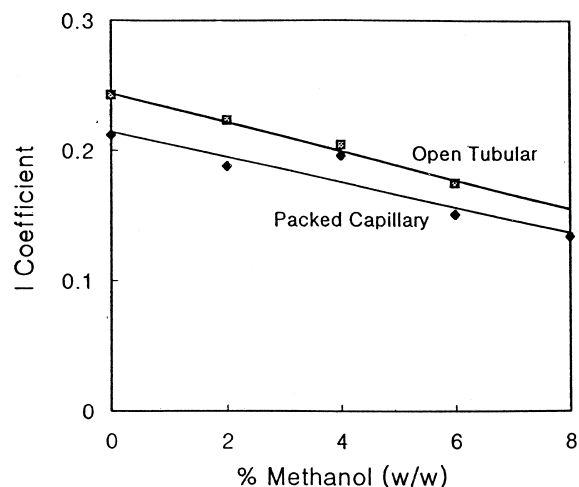


Fig. 2. Effect of the addition of methanol as a modifier on  $l$  coefficients. Conditions: 10 m  $\times$  50  $\mu$ m I.D. open tubular column, SB-methyl-100 polydimethylsiloxane with 0.25  $\mu$ m film thickness; 100°C temperature; 260 atm pressure.

$$s = s_{\text{stationary}} - s_{\text{mobile}} \quad (5)$$

where  $s_{\text{stationary}}$  represents a measure of the strength of dipolarity–polarizability interactions between the solute and the stationary phase and  $s_{\text{mobile}}$  represents the same interactions between the solute and the mobile phase. For the open tubular column SFC, the  $s$  coefficient is greatly decreased on moving from neat carbon dioxide mobile phase to 2% methanol modifier, thereafter showing a gradual decrease with increasing modifier concentration. This trend is very similar as in packed capillary column (Fig. 3).

A rapid decrease in the  $s$  coefficient with the 2% methanol modified mobile phase could be explained by an adsorption of both methanol and carbon dioxide on the chromatographic stationary phase [25] and an increase in the dipolarity of the mobile phase [26]. Studies of stationary phase solvation by supercritical fluids have been reported by several authors. For example, Strubinger and Parcher [26] have studied the surface excess adsorption isotherms of supercritical carbon dioxide on packed columns with octadecyl silica stationary phases. Selim and Strubinger [27] have studied the adsorption isotherms of supercritical pentane and methanol-modified supercritical pentane using bonded polymeric stationary

phase in capillary SFC. Yonker and Smith [28] studied the surface excess adsorption isotherms of 2-propanol from supercritical 2-propanol–CO<sub>2</sub> binary solutions using a bonded polymeric stationary phase in capillary SFC as a function of density, temperature and modifier mole fraction. It was also 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 absorption [29,30]. Based on these studies, it is clear that an adsorption of both methanol and carbon dioxide on the chromatographic stationary phase results in the dilution of that phase. This diluted stationary phase could cause a decrease of the  $s_{\text{stationary}}$  value. On the other hand, when modifier is added to the mobile phase the dipolarity of the mobile phase, i.e., the  $s_{\text{mobile}}$  value would be a non-linear function of modifier concentration. Namely, small additions of methanol (1–2%) to carbon dioxide produce a large increase in the dipolarity of the mobile phase, and at modifier concentrations above 2%, the dipolarity of the mobile phase increases slowly [26]. With 2% methanol, this rapid increase of the  $s_{\text{mobile}}$  value could cause a rapid decrease of the  $(s_{\text{stationary}} - s_{\text{mobile}})$  value. Above 2% modifier, the  $s_{\text{mobile}}$  value will increase gradually with increasing modifier concentration because the dipole–dipole interaction between the solute and mobile phase should increase as the concentration of modifier increases.

In conclusion, in open tubular column SFC, the  $b$  coefficient does not decrease rapidly when 2% methanol is added to the carbon dioxide mobile phase; however, the  $s$  coefficient decreases rapidly with 2% methanol. This indicates that for open tubular column SFC, the dilution of the chromatographic stationary phase by a modifier and carbon dioxide and the increase of dipolarity of the mobile phase play more important roles in explaining the modifier effect on solute retention than the covering of active free silanol groups by modifier although the latter is more important than the former in packed capillary column. The data presented in this paper regarding capacity factors at various concentrations of methanol using an open tubular capillary column

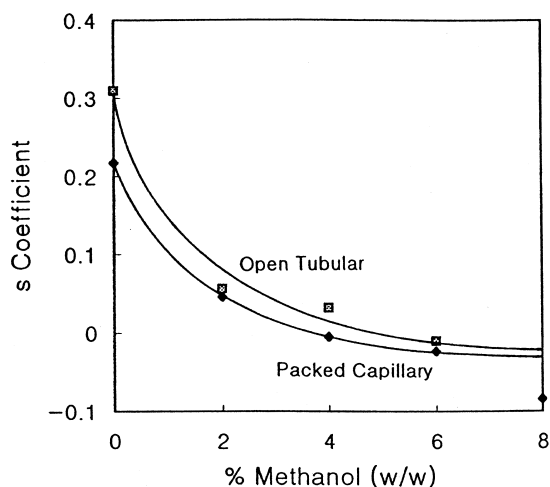


Fig. 3. Effect of the addition of methanol as a modifier on  $s$  coefficients. Conditions: 10 m × 50 μm I.D. open tubular column, SB-methyl-100 polydimethylsiloxane with 0.25 μm film thickness; 100°C temperature; 260 atm pressure.

are very relevant, and could be used for the retention mechanism studies or related studies in the area of SFC.

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