

# Some thermodynamic aspects of packed column supercritical fluid chromatography

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## Abstract

Packed column supercritical fluid chromatography (SFC) was employed in the investigation of the effects of density and packing surface silanol groups on the enthalpy and entropy of transfer of the solute between the mobile and stationary phases using  $\text{CO}_2$  as the mobile phase and solutes of various polarity. The solutes were aromatics, phenols and amines and the stationary phases were untreated silica gel Partisil-10, thermally treated Partisil-10 and Partisil-10 bonded with octadecylsilane. In the density range  $0.3\text{--}0.9\text{ g ml}^{-1}$ , the enthalpies decrease as the mobile phase fluid density increases while the entropies remain constant for well coated packings. A moderate pressure drop does not change this trend. The thermodynamic value obtained from a Van 't Hoff plot suggests a strong influence of the retention of polar solutes by surface silanol groups in the low-density region of SFC separation. In addition, a characteristic line of intersection points may be obtained from the extrapolated line of the Van 't Hoff plots. Tested with solutes and packings of various polarity, the characteristic line reveals the nature of the packing materials.

## 1. Introduction

The place of supercritical fluid chromatography (SFC) and supercritical fluid extraction (SFE) in chemical analysis is being established with the arrival of new and better SFC systems and some cases of acceptance of SFE methods as standard analytical procedures [1]. With simple control of the density of the mobile phase or addition of modifiers or additives, SFC and SFE offer chromatographers a wide range of choices of methods to tackle the ever demanding analytical problems. However, to achieve the same status as is enjoyed by GC or HPLC, SFC must not only have more validated application meth-

ods but also solve the problem of lack of suitable kinetic models to describe fully the retention process in SFC. The lack of a kinetic model is partly due to too many complex factors being involved, such as temperature, pressure drop, density, solutes, the nature of the mobile and stationary phases used and partly the paucity of fundamental data. Nevertheless, as supercritical fluids have the properties of both liquids and gases, depending on temperature and pressure, SFC also provides an ideal tool for the study of retention behaviour in chromatographic processes.

To take advantage of the liquid-phase-like and gas-phase-like properties of supercritical fluids, a number of papers have been published on a thermodynamic approach to retention behaviour

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in SFC [2–4]. Nevertheless, the application of the Van't Hoff equation in chromatographic studies was proposed and studied in the early stages of the development of chromatography [5]. Meyer [6] proposed a simple thermodynamic model and the concept of unit concentration to define the standard state for studying solute retention as a function of temperature at constant pressure. Later, Yonker and co-workers [7–9] studied the effects of density on the enthalpy and entropy of transfer for SFC and they developed a simple thermodynamic model to describe the retention process in capillary SFC systems. Chester and Innis [10] established an empirical thermodynamic model relating SFC retention to GC and HPLC retention. Combining the models of Yonker and co-workers and Chester and Innis, Berger [3] proposed an empirical equation based on experimental results and the Van't Hoff equation. This empirical equation was quickly adapted by Grandmaison and Kaliaguine [4] in their study of phenols under capillary column SFC conditions. The density range was narrow, however, owing to the limitations of the capillary column system. So far the relationship between enthalpy and the contribution of surface silanol groups and solutes of various polarity in packed column SFC systems has not been fully explored.

In recent years, packed column SFC has been experiencing renewed interest among the researchers working on SFC [11–13]. For example, Bartle *et al.* [14] used the Peng–Robinson equation of state (EOS) to develop a simple thermodynamic equation describing solute retention as a function of density and pressure in packed column SFC. Although open-tubular wall-coated capillary column SFC is much more popular because it offers more efficient separations of polar compounds owing to the large number of theoretical plates achievable, many reasons exist for developing packed column SFC technology, such as ease of transferring chromatographic data to preparative SFC, short analysis times and the choice of a wide range of packing materials developed for HPLC.

Packing surface activity creates a major obstacle to the wider use of packed column SFC,

because in many instances the surface activity of silica packing materials presents a serious limitation for packed column SFC when mobile phases of low polarity (*e.g.*, CO<sub>2</sub>) are used to elute polar analytes. An unmodified silica gel surface exhibits reversible adsorption of polar compounds owing to the presence of silanol groups, resulting in tailing peak shapes and extended retention times. Our test results show that many polar compounds were not eluted from an unmodified silica gel packed column, whereas non-polar compounds such as alkanes and aromatics eluted easily under similar experimental conditions [15]. To deal with this problem, polar organic modifiers such as methanol are often needed in both capillary and packed column SFC systems. These modifiers usually have dual functions, *i.e.*, to increase the solubility of polar solutes and to provide a dynamic coating of surface silanol groups. However, most of the modifiers are not compatible with flame ionization detection (FID), the most widely used universal detection method in SFC. In addition, the introduction of polar organic modifiers will also create many problems for SFC processes, *e.g.*, the toxicity of some modifiers and the complexity of the pumping and recovery systems. Therefore, much attention has been focused on improving surface modification methods in order to allow the elution of polar compounds when using CO<sub>2</sub> as the sole mobile phase [11–13].

Essentially, SFC is a water-free process and it is therefore possible to adopt different approaches other than the conventional HPLC column packing deactivation methods. A new deactivation method should produce not just well deactivated but also stable packing materials under SFC conditions. In this regard, thermal treatment of silica gel might yield useful information for the development of new chromatographic packing materials [16]. The method of preparation and the thermal treatment decide the composition of the silica gel surface. Scott and Kucera [17] studied the thermal treatment of silica gel and they concluded that at about 650°C the primary layer of strongly hydrogen-bound water is completely removed. They also reported

that at still higher temperatures (>900°C) sintering of the silica particles starts and the dehydration of silanol groups is complete, forming a hydrophobic surface covered with siloxane groups. Other researchers [16] have disputed the temperature range of dehydration and the existence of a hydrophobic surface, presenting evidence for the existence of free silanols that are hardly affected by thermal treatment at 600°C and below. Nevertheless, it is fairly obvious that thermal treatment of silica gel over a wide range of temperatures will provide silica gel surfaces with distinctly different characteristics in SFC studies.

Presumably, the retention time of polar solutes such as phenols is caused not only by the remaining silanol groups on the silica surface (silanophilic effects), but also by the long alkyl functional groups (solvophobic effects) introduced through reaction with chlorosilanes, which also play an important role in the adsorption and desorption in the separation process [18]. The thermal deactivation method, therefore, would provide some insight into the interaction of surface silanols with a particular fluid mobile phase–solute combination, as the method avoids using long alkyl groups and gives controlled concentrations of silanol groups on the silica gel surface. As the chromatographic process is closely associated with the free energy of transfer of the solute from the mobile to the stationary phase, any modification of the stationary phase should be reflected in the measurement of thermodynamic data. Hence a thermally treated surface free of silane groups and having a controlled amount of silanol groups provides an ideal material to study the correlation between silanol groups on a silica gel stationary phase and the solute in the mobile phase. The data obtained from the study of thermally modified silica gel surfaces would be useful in developing an accurate quantitative thermodynamic model, which is essential for extracting the maximum amount of information about the SFC systems and helping to make SFC become a mature and viable analytical technique. However, so far the thermal treatment of silica gel packings in SFC has not been reported.

As an integral part of the study of the pyrolysis of lignocellulosic materials [4], the purpose of this work was to investigate the retention behaviour of thermally treated silica gel under SFC conditions and to compare it with commercial silane-modified packings. An attempt was also made to measure the enthalpy and entropy of interaction between the mobile phase and the stationary phase as a function of density, in order to introduce quantitative aspects in the investigation of thermally treated silica gel and other packings being developed in our laboratory. It is also intended to demonstrate that the Van't Hoff plot can be further explored for characterizing packed columns in SFC systems.

## 2. Theoretical

The effect of density on retention in SFC has been well studied [3,9,19]. The adsorption and desorption processes between the mobile and stationary phases are associated with enthalpic and entropic effects. The free energy of transfer of the solute from the mobile to the stationary phase is considered to be the major factor governing retention [5]. Yonker and Smith [9] have shown that the enthalpy of solute transfer between the stationary and mobile phase at infinite dilution ( $\Delta H_T^0$ ) is a basic thermochemical parameter which can be used to understand and predict solute retention behaviour in SFC. Grandmaison and Kaliaguine [4] obtained the enthalpy and entropy of transfer of five phenols in their investigation of behaviour of phenols under SFC conditions, further demonstrating the usefulness of this approach in SFC studies.

The principle of this thermodynamic approach is to compare the enthalpy and entropy changes of different chromatography systems. These enthalpy and entropy data can be obtained from the well known Van't Hoff plot, which expresses the dependence of the capacity factor,  $k'$ , on temperature,  $T$ , as

$$\ln k' = -\frac{\Delta H_T^0}{RT} + \frac{\Delta S_T^0}{R} - \ln \beta \quad (1)$$

where  $k'$  is related to the retention times of the

solute,  $t_R$ , and of an unretained solute,  $t_0$ , according to the equation

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

$\Delta H_T^0$  and  $\Delta S_T^0$  are the enthalpy and entropy, respectively, associated with the transfer of the solute from the mobile to the stationary phase,  $R$  is the gas constant and  $\beta$  is defined as the phase ratio and is often considered to be constant [4].

The relationship between  $\ln k'$  and  $T^{-1}$  at constant density ( $\rho$ ) is linear whenever  $\Delta S_T^0$  and  $\beta$  are considered to be independent of temperature. If this is the case, from Eq. 1 we can write

$$\left[ \frac{d \ln k'}{d(1/T)} \right]_{\rho} = -\frac{\Delta H_T^0}{R} \quad (3)$$

Thus, when  $\ln k'$  is plotted against  $1/T$  at constant  $\rho$ , the slope of the linear part of the experimental curves yields estimated values for the enthalpy of transfer. Once the value of enthalpy has been obtained, we can calculate the entropy of transfer from the intercept of the plot of Eq. 3 provided that phase ratio  $\beta$  can be estimated. The standard state for both  $\Delta H_T^0$  and  $\Delta S_T^0$ , based on the concept of concentration units for the distribution coefficient [6], is  $1 \text{ g ml}^{-1}$  [3].

Chester and Innis [10] applied the Van 't Hoff equation to study the solute retention behaviour of a capillary SFC system. From the observation of GC data in the literature and limited experimental results, they suggested that for SFC systems the retention mechanism can be divided into GC-like (adsorption-like) and LC-like (partition-like) regions. This model is very interesting because it provides a clear picture of the solute retention mechanism in SFC and bridges the thermodynamic study of GC and LC through SFC. Nevertheless, tested only with a capillary column and over a narrow range of density, this model may not be applicable to packed-column SFC as the behaviour of packed column SFC is different from that of capillary column SFC in many ways, such as the presence on the packing surface of long alkyl groups, usually a larger amount of surface silanol groups and a high pressure drop.

Yonker and Smith [9] used the Van 't Hoff plots ( $\ln k'$  vs.  $1/T$ ) to determine the overall enthalpy of transfer between the mobile and stationary phase for  $n$ -alkanes and  $n$ -alkanols with two capillary columns of different polarity. Their experimental results of the enthalpy and entropy of transfer showed significant differences between two columns tested with the same solutes under identical experimental conditions, reflecting the important role played by the nature of stationary phase in determining  $\Delta H_T^0$  and  $\Delta S_T^0$ .

Based on the work of Chester and Innis [10] and Yonker and Smith [9], Berger [3] noted that in capillary SFC, the natural logarithm of the retention factor ( $\ln k'$ ) decreases linearly with increasing density at constant temperature. He also assumed that the stationary phase does not change much with the introduction of a supercritical carrier gas, and solute-stationary phase (s-sp) interaction should be the same in GC or SFC. Berger proposed the following empirical equation:

$$\Delta H_T^0 = \Delta H_{s-sp}^0 - \rho(\Delta H_{s-mp}^0) \quad (4)$$

where  $\Delta H_{s-sp}^0$  is obtained from  $\ln k'$  vs.  $1/T$  plots under GC conditions or by extrapolation of  $\Delta H_T^0$  at zero density, and  $\Delta H_T^0$  is obtained from Van 't Hoff plots in SFC at various fixed densities. This equation has been employed to study the behaviour of phenols in a capillary column SFC system [4], and seems to work very well at low densities and for capillary column SFC. The applicability of this equation to packed column SFC has not been tested. Here it must be noted that the assumptions made for this equation, *i.e.*,  $\Delta H_{s-sp}^0$  is constant (or changes negligibly) regardless of the mobile phase density and  $\Delta H_{s-mp}^0$  depends only on density, may not hold in packed column SFC as long as they are not tested experimentally. The simplified approach of this equation necessitates a prudent attitude when applying it under packed column SFC conditions, as packed column SFC usually employs much higher pressures than in capillary SFC and exhibits a higher surface polarity. In addition, the interactions of the solute with the mobile

phase depend not only on the density of the mobile phase but also on the nature of the solutes and the mobile phase. Hence, the  $\Delta H_{s-m}^0$  value should be decided accordingly. We believe that testing this simple thermodynamic model in packed column SFC warrants its applicability and would be useful in establishing a realistic model that takes the differences of packed column SFC into account.

### 3. Experimental

#### 3.1. Instrumentation

The SFC system (Lee Scientific 600) has been described elsewhere [4]. For packed column SFC experiments, some minor modifications were made to this SFC system. At the packed column outlet end, a tee column end-fitting (Valco TCET 441) is attached. One end of this tee is connected to a capillary restrictor (25 cm  $\times$  15  $\mu$ m I.D.) leading to a flame ionization detector, which gave a flow-rate of 1 ml s<sup>-1</sup> at 300 atm (1 atm = 101 325 Pa) and 80°C with SFC-grade CO<sub>2</sub> (Scott, Plumsteadville, PA, USA) as the mobile phase; the other end of the tee (at right-angles to the normal flow path) is used to accept the capillary splitter, which is a 15 or 25  $\mu$ m I.D. capillary tube having a length from 1 to 4 cm to adjust the splitting ratio. The column was packed at our laboratory using the supercritical fluid displacement method developed by Dean and Poole [12].

Taking the oven configuration and optimum operating parameters into consideration, we chose a 15 cm  $\times$  2.1 mm I.D.  $\times$  1/4 in. O.D. (1 in. = 2.54 cm) stainless-steel tube as a blank column for our SFC system. Standard Valco fittings (Valco Instruments, Houston, TX, USA), 2- $\mu$ m screens and precut, smooth-bore tubing from Anspec (Ann Arbor, MI, USA) were used for all columns. The packing materials were unmodified silica gel (Partisil 10, 10- $\mu$ m irregular particles) and modified silica gel ODS-1, ODS-2 and ODS-3 (Partisil-10 particles surface-bonded with octadecylsilane groups) from Whatman (Clifton, NJ, USA). In total six columns were

packed for this investigation. Packings of columns B and C were thermally treated at 660 and 900°C for 2 h, respectively. To avoid the drastic changes in the physical properties of the packings that may occur during sudden temperature changes, the packings were cooled gradually in a muffle furnace after heat treatment. Descriptions of these columns are given in Table 1 and the properties of the packing materials are given in Table 2.

#### 3.2. Chemicals

Naphthalene was obtained from BDH Chemicals (Ville St.-Laurent, Quebec, Canada). Dichloromethane (HPLC purity) was purchased from Aldrich (Milwaukee, WI, USA) and used for dead-time ( $t_0$ ) measurements. Eugenol (4-allyl-2-methoxyphenol) with a purity of 99%, pyridine, vanillin and 2,4-dimethylphenol with a purity of 97% were also bought from Aldrich.

Phenols were chosen as probes in this work because they have medium polarity, providing a means to observe interactions between active sites and solutes with a reasonable retention time and peak shape. Another probe in this work was pyridine, which is a very sensitive probe for silanol activity as observed by De Weerd *et al.* [20]. However, pyridine can only be used for very well coated packing materials, which limits its usefulness as a probe for packings of various polarity. Each probe was dissolved in HPLC-

Table 1  
Descriptions of packed columns

Column	Packing material	Treatment
A	Partisil-10	Unmodified
B	Partisil-10, thermally treated	Calcined at 660°C for 2 h
C	Partisil-10, thermally treated	Calcined at 900°C for 2 h
D	ODS-1	Silane treated, C <sub>18</sub> , 5% C <sup>a</sup>
E	ODS-2	Silane treated, C <sub>18</sub> , 15% C <sup>a</sup>
F	ODS-3	Silane treated and end-capped, C <sub>18</sub> , 10% C <sup>a</sup>

<sup>a</sup> Manufacturer's specification.

Table 2  
Properties of packing materials

Column	Stationary phase	Pore volume (ml g <sup>-1</sup> ) <sup>a</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	C (%) <sup>b</sup>	OH/nm <sup>2</sup> <sup>c</sup>
A	Partisil-10	0.897	373.5	0.44	3.61
B	T-660	0.926	304.1	N/A	2.52
C	T-900	0.559	159.3	N/A	1.92
D	ODS-1	0.774	300.0	4.75	2.73
E	ODS-2	0.485	212.5	17.32	1.75
F	ODS-3	0.559	267.7	10.75	1.05

<sup>a</sup> Measured by the BET technique.

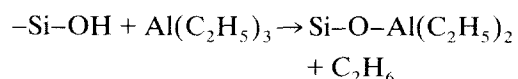
<sup>b</sup> CHN analysis results.

<sup>c</sup> OH analysis results.

grade dichloromethane prior to introduction on to the column. Sample size plays an important role in SFC [21]. In this work the concentration of samples per component was about 1–3 μg μl<sup>-1</sup>.

### 3.3. Surface hydroxyl groups

The concentration of hydroxyl groups on the surface of a silica gel packing has long been a research subject and many measurement techniques have been explored [22]. The general consensus is that there exist about 4–5 hydroxyl groups per nm<sup>2</sup> [23,24]. In this investigation the measurement was based on the work of Sato *et al.* [25] and Marcinkowska [24]. The basis of this method is the reaction of an organometallic reagent with the surface hydroxyl groups on silica gel. In this work, triethylaluminium was chosen as an organometallic reagent as it does not produce secondary reactions. Sato *et al.* [25] showed that one molecule of triethylaluminium reacts with one surface OH group and releases one molecule of ethane:



By measuring the volume of ethane released, one can calculate the concentration of surface hydroxyl groups of the silica gel. Duplicate measurements were performed for all samples

and the results were averaged. The precision of the hydroxyl group measurements for these samples was usually within the 5–10% (R.S.D.) range.

### 3.4. CHN elemental analysis

Elemental analysis data on unbonded and bonded-phase packings were obtained with a Model 1106 elemental analyser (Carlo Erba, Milan, Italy). Duplicate analyses for carbon, hydrogen and nitrogen were normally performed for all the samples. To verify the accuracy of the measurement, some of the bonded samples were sent to an independent analytical laboratory (INRS, Ste.-Foy, Quebec, Canada). The precision of the measurement was usually within the 4–5% range.

### 3.5. Nitrogen BET measurement

Surface areas, pore size distributions and pore volumes of the silica gels were measured by the BET method [26] using an Omnisorp 100 instrument from Omicron (Berkeley Heights, NJ, USA). The sample pretreatment involved heating the sample at 220°C for 8 h under a vacuum of 10<sup>-5</sup> mbar. Duplicate measurements were performed for selected samples. The precision of the surface area measurements for these samples was usually within the 4–5% range.

### 3.6. Experimental procedures

For each chromatographic experiment, approximately 10  $\mu\text{l}$  of a solution containing naphthalene in dichloromethane were injected. Eugenol, pyridine, vanillin and 2,4-dimethylphenol solution were prepared similarly. For fear of dynamic masking effects, a single solute solution was used in this study. The experiments were normally performed at  $\text{CO}_2$  densities ranging from 0.4 to 0.9  $\text{g ml}^{-1}$  and infrequently from 0.3 to 0.9  $\text{g ml}^{-1}$ . The density of carbon dioxide at different temperatures and pressures was calculated using the Peng–Robinson equation of state and checked against values given by a density calculation program of Lee Scientific.

All experimental measurements were made twice and averaged. In the event of divergence of the results, triplicate measurements were made and averaged. Although in column SFC systems the calculated  $\Delta H_T^0$  is a convenient approach for providing some chromatographic insight, it also has definite restrictions. The precision of  $\Delta H_T^0$  values is compromised by the working density range in both capillary and packed columns. With packed columns, our own laboratory results [15] and those of Lauer *et al.* [27] show that heavy peak tailing appeared with densities less than 0.5  $\text{g ml}^{-1}$ . In addition, the applicable density range of capillary columns can hardly exceed 0.5  $\text{g ml}^{-1}$  without a serious decrease in resolution. To overcome this limitation, three measurements instead of two were made and averaged for chromatograms taken when the density was less than 0.5  $\text{g ml}^{-1}$  in this work.

## 4. Results and discussion

### 4.1. Thermally treated silica gel

The retention of naphthalene and eugenol on columns A, D and F, three columns with different properties, was first studied under carefully controlled constant-density conditions and the results were plotted as  $\ln k'$  vs.  $1/T$  at each of a

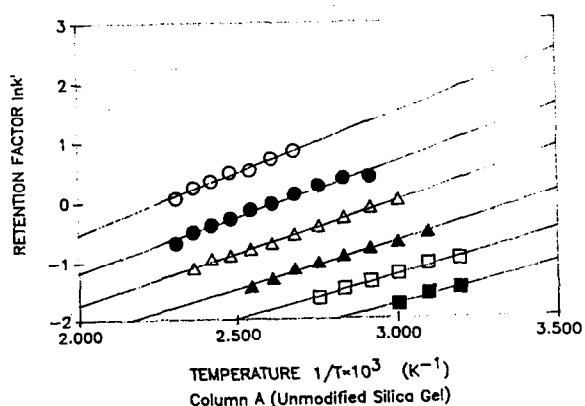


Fig. 1. Logarithm of capacity factor,  $k'$ , of naphthalene as a function of reciprocal temperature ( $\text{K}^{-1}$ ) for different densities of the mobile phase. Stationary phase, unmodified Partisil-10; mobile phase,  $\text{CO}_2$ . Density:  $\circ = 0.4$ ;  $\bullet = 0.5$ ;  $\triangle = 0.6$ ;  $\blacktriangle = 0.7$ ;  $\square = 0.8$ ;  $\blacksquare = 0.9 \text{ g ml}^{-1}$ .

number of constant densities. Selected plots of  $\ln k'$  vs.  $1/T$  are shown in Figs. 1, 2 and 3 for columns A, D and F, respectively. Generally, in Figs. 1–3 all the Van't Hoff plots yield straight lines (with some slight indication of “roll-over” at low temperatures for columns A and F) over the temperature range 40–160°C, the pressure range 148–415 atm or the  $\text{CO}_2$  density range 0.3–0.9  $\text{g cm}^{-3}$ .

The slopes of the lines in Figs. 1–3 yield

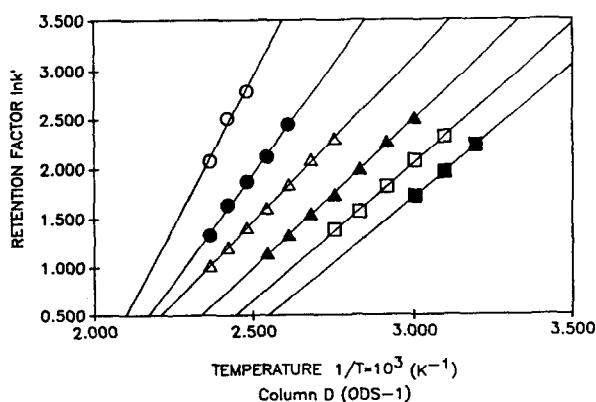


Fig. 2. Logarithm of capacity factor,  $k'$ , of eugenol as a function of reciprocal temperature ( $\text{K}^{-1}$ ) for different densities of the mobile phase. Stationary phase, Partisil-10 ODS-1; mobile phase,  $\text{CO}_2$ . Symbols as in Fig. 1.

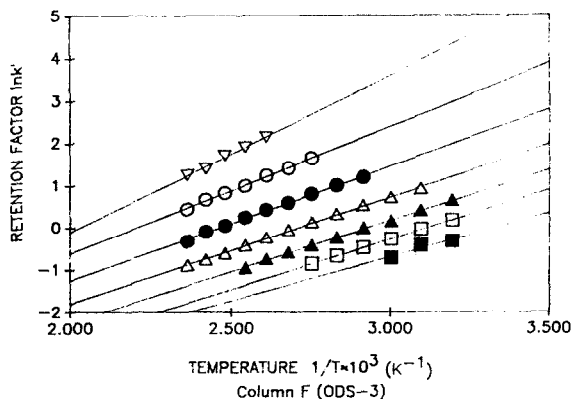


Fig. 3. Logarithm of capacity factor,  $k'$ , of eugenol as a function of reciprocal temperature ( $K^{-1}$ ) for different densities of the mobile phase. Stationary phase, Partisil-10 ODS-3; mobile phase,  $CO_2$ . Symbols as in Fig. 1;  $\nabla = 0.3 \text{ g ml}^{-1}$ .

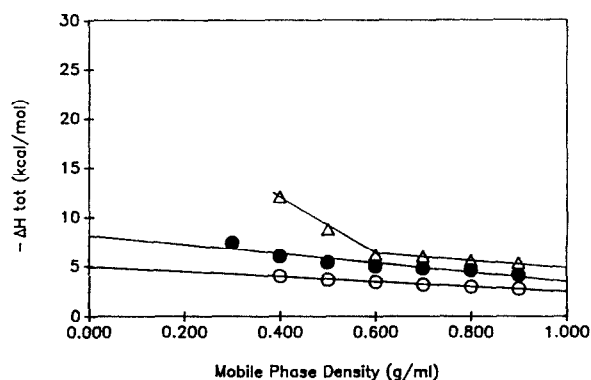


Fig. 4. Total enthalpies of transfer as a function of  $CO_2$  density of the mobile phase. Stationary phase:  $\circ$  = unmodified Partisil-10;  $\triangle$  = Partisil ODS-1;  $\bullet$  = ODS-3. Mobile phase,  $CO_2$ . Solute:  $\triangle$ ,  $\bullet$  = eugenol;  $\circ$  = naphthalene.

calculated values of enthalpy, which are plotted against density in Fig. 4. It is noted that the enthalpy values obtained from the curves in Fig. 4 (naphthalene line for column A and eugenol line for ODS-3) form nearly straight lines, while the eugenol curve for ODS-1 first follows a similar trend in the density range  $0.6\text{--}0.9 \text{ g ml}^{-1}$  but diverges in the low-density region. Similar data treatment was applied to all columns and the data obtained are presented in Tables 3–8.

The  $\Delta H_T^0$  values for naphthalene and 2,4-dimethylphenol on columns A, B and C are between 2 and 13  $\text{kcal mol}^{-1}$  ( $1 \text{ kcal} = 4.184 \text{ kJ}$ ), similar values having been reported for naphthalene, *n*-pentane and propane as mobile phases [14,28], and for 2,4-dimethylphenol in pure  $CO_2$  as eluent [4]. The  $\Delta H_T^0$  and  $\Delta S_T^0$  values reported for these solutes are also of similar magnitude to published results [3,8,9,29].

For all the solutes tested in this work, the data in Tables 3–5 show that the retention increases with decrease in density and  $\Delta H_T^0$  tends to become more negative. Grandmaison and Kaliaguine [4] reported that  $\Delta H_T^0$  also reflects the elution order of the polycyclic aromatics tested in their capillary SFC system, which is in agreement with the results of packed column SFC in this work [15]. As shown in Table 2, the surface geometry of the silica is also altered during the thermal treatment. The untreated silica gel has a large surface area, which generates low phase ratios, leading to high retention. The thermal treatment process decreased the surface areas and hence decreased the retention

Table 3

Enthalpy and entropy of transfer for column A (unmodified Partisil-10) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density ( $\text{g ml}^{-1}$ )					
		0.4	0.5	0.6	0.7	0.8	0.9
Naphthalene	$-\Delta H_T^0$	4.00	3.64	3.44	3.16	2.95	2.73
	$-\Delta S_T^0$	4.26	4.85	5.52	6.00	6.51	6.85
2,4-Dimethylphenol	$-\Delta H_T^0$	12.90	7.31	4.71	4.17	3.21	2.99
	$-\Delta S_T^0$	21.62	9.21	3.11	2.53	0.91	0.55

<sup>a</sup> Enthalpies are in  $\text{kcal mol}^{-1}$  and entropies in  $\text{cal mol}^{-1} \text{ K}^{-1}$  ( $R = 1.98 \text{ cal mol}^{-1} \text{ K}^{-1}$ ). The volume phase ratio  $\beta$  was estimated to be 11.2.



Table 4  
Enthalpy and entropy of transfer for column B (thermally treated at 660°C) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density (g ml <sup>-1</sup> )					
		0.4	0.5	0.6	0.7	0.8	0.9
Naphthalene	$-\Delta H_T^0$	4.99	3.99	3.65	3.05	2.79	2.75
	$-\Delta S_T^0$	6.44	5.31	5.64	5.05	5.31	6.18
2,4-Dimethyl-phenol	$-\Delta H_T^0$	13.10	8.91	7.33	7.11	6.96	6.10
	$-\Delta S_T^0$	22.12	13.15	10.38	11.76	12.26	10.89

<sup>a</sup> See Table 3.

Table 5  
Enthalpy and entropy of transfer for column C (thermally treated at 900°C) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density (g ml <sup>-1</sup> )					
		0.4	0.5	0.6	0.7	0.8	0.9
Naphthalene	$-\Delta H_T^0$	4.37	3.57	3.61	3.05	2.71	2.23
	$-\Delta S_T^0$	3.86	4.55	5.76	5.33	5.37	4.89
2,4-Dimethyl-phenol	$-\Delta H_T^0$	11.79	8.70	7.70	6.58	5.97	4.39
	$-\Delta S_T^0$	19.09	12.71	10.93	10.24	10.08	6.18

<sup>a</sup> See Table 3.

factors of polar compounds such as phenols. Therefore, the role of the physical properties of thermally treated silica gel should be taken into account. However, comparing the  $\Delta H_T^0$  data for columns A, B and C, we note that the  $\Delta H_T^0$  values for naphthalene are of similar magnitude. In addition, the thermally treated packings produced almost identical chromatograms for naphthalene although their physical properties were altered during thermal treatment, especially in

the case of column C. As naphthalene is a non-polar solute, the main retention mechanism with naphthalene in these three columns is predominantly physical adsorption and desorption. Small differences in  $\Delta H_T^0$  and  $\Delta S_T^0$  among these columns could mean that the column packing surface geometry plays a minor role in the SFC process.

The OH concentration measurement (Table 2) shows that the thermal treatment produced a

Table 6  
Enthalpy and entropy of transfer for column D (ODS-1) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density (g ml <sup>-1</sup> )					
		0.4	0.5	0.6	0.7	0.8	0.9
2,4-Dimethyl-phenol	$-\Delta H_T^0$	11.65	9.25	8.02	7.69	7.36	7.36
	$-\Delta S_T^0$	18.71	14.26	11.84	12.32	12.51	14.32
Eugenol	$-\Delta H_T^0$	12.03	8.75	6.12	5.97	5.54	5.29
	$-\Delta S_T^0$	19.46	13.23	7.62	8.16	7.76	7.70

<sup>a</sup> See Table 3.

Table 7  
Enthalpy and entropy of transfer for column E (ODS-2) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density (g ml <sup>-1</sup> )					
		0.4	0.5	0.6	0.7	0.8	0.9
2,4-Dimethylphenol	$-\Delta H_T^0$	10.46	9.90	9.57	7.69	6.71	6.45
	$-\Delta S_T^0$	15.09	15.74	15.88	12.32	11.17	11.46
Eugenol	$-\Delta H_T^0$	9.23	8.48	7.80	7.66	7.03	7.04
	$-\Delta S_T^0$	12.81	12.43	12.89	13.48	12.57	13.37

<sup>a</sup> See Table 3.

silica gel with less surface silanol groups in columns B and C, which would in turn yield less negative  $\Delta H_T^0$  values and a shorter retention time and peak shape improvement for 2,4-dimethylphenol compared with column A. In addition, in comparison with chromatographic data for column A packed with untreated silica gel, the retention time of a polar solute such as 2,4-dimethylphenol is much shorter and peak tailing is decreased to a certain extent for both columns B and C packed with silica gel thermally treated at 660 and 900°C, respectively. The most probable explanation is that the heat treatment produced an inert silica gel by removing the silanol groups from the packing surface, forming a more hydrophobic surface as expected. This improvement, however, cannot match that of a well coated packing such as ODS-3.

Nevertheless, the enthalpy values for 2,4-dimethylphenol indicate that other factors exist that contribute to  $\Delta H_T^0$  besides the amount of surface silanol groups. For example, there are different kinds of sites on the surface of a silica particle. According to Colin and Guiochon [30], five main types of sites are present: free or isolated silanol, silanol with physically adsorbed water, dehydrated oxide, germinal silanol and bound silanols. Of these sites, two different types of surface silanols, *i.e.* bound and isolated silanols, are predominantly responsible for the retention of hydroxyl-containing solutes. Solutes with hydroxyl groups are able to interact with the bonded silanols and are adsorbed on these sites. The retention of these solutes decreases with the removal of these hydroxyl groups or bonded silanols. It is generally accepted that

Table 8  
Enthalpy and entropy of transfer for column F (ODS-3) from Van 't Hoff plot

Solute	Parameter <sup>a</sup>	Mobile phase density (g ml <sup>-1</sup> )						
		0.3	0.4	0.5	0.6	0.7	0.8	0.9
2,4-Dimethylphenol	$-\Delta H_T^0$		7.82	7.75	6.94	5.84	5.50	5.24
	$-\Delta S_T^0$		14.30	13.29	13.17	11.19	11.13	11.01
Eugenol	$-\Delta H_T^0$	7.37	5.97	5.38	5.00	4.78	4.59	4.10
	$-\Delta S_T^0$	9.80	8.38	8.46	8.77	9.23	9.50	9.80
Pyridine	$-\Delta H_T^0$		7.41	6.37	6.30	6.17	6.12	6.28
	$-\Delta S_T^0$		11.37	9.46	9.60	9.94	10.16	11.04
Vanillin	$-\Delta H_T^0$		7.61	6.96	6.04	5.66	5.73	5.57
	$-\Delta S_T^0$		11.80	11.54	10.40	10.42	11.60	11.98

<sup>a</sup> See Table 3.

after heating silica gel over 600°C, only isolated OH groups still exist on the silica gel surface and that these isolated (free) OH groups are, nevertheless, very active [24]. Mauss and Engelhardt [16] pointed out that the reaction of silica with chlorosilanes takes place mainly at these isolated silanols, which may explain the significant differences in capacity factor for columns C and E for these two column packings having similar amounts of silanols on the silica gel surface. Other possible causes are impurities on the surface of the silica gel [31] and rehydration of the packing material [32].

Concerning the problem of rehydration of thermally treated silica gel, according to the competition model, the solutes must be able to displace these eluent molecules from the surface in order to be adsorbed. The selective adsorption of solutes on silica gel has been attributed exclusively to the surface silanols [20]. In this case, chromatographic retention and selectivity should be correlated with the surface silanol concentration. Therefore, rehydration of thermally treated silica gel would alter the retention time of a polar probe solute after a certain period of time under the chromatographic conditions. In fact, one of the thermally treated columns, column B, was in use for 3 months during one experimental run to elute 2,4-dimethylphenol without appreciable changes in the retention time, showing stable chromatographic characteristics. Rehydration of thermally treated silica gel can be preformed by boiling in water [16]. However, under pure CO<sub>2</sub> SFC conditions, the thermally treated packing would not be rapidly rehydrated.

It is *a priori* possible that a difference in  $k'$  might be caused by the differences in pressure drop due to the laboratory packing procedure. Although the outlet pressure of the columns at each mobile phase density was not measured, the retention factors of polycyclic aromatics on the three columns were carefully measured and found to be very similar under identical conditions, indicating that the pressure drop of the three columns does not affect the retention time of 2,4-dimethylphenol. In addition, the reproducibility of the packing procedure has been

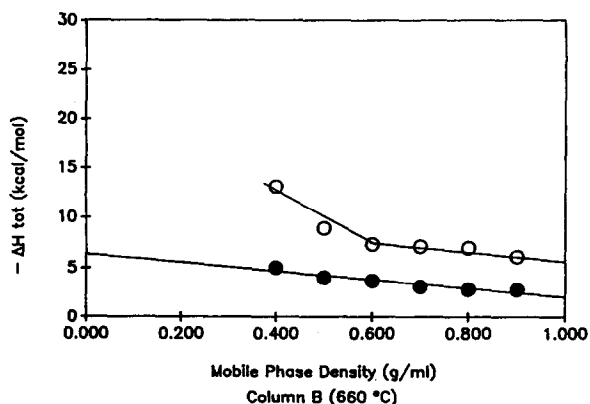


Fig. 5. Total enthalpies of transfer as a function of CO<sub>2</sub> density of the mobile phase. Stationary phase, thermally treated Partisil-10. Solute: ○ = 2,4-dimethylphenol; ● = naphthalene.

examined with unmodified Partisil-10 silica gel and polycyclic aromatics and found to be very good [15].

For both thermally treated and octadecylsilane (ODS)-treated silica gel, the study of  $\Delta S_T^0$  at constant density as a function of temperature provides another means of elucidating the retention mechanism of SFC. Figs. 5 and 6 give  $\Delta H_T^0$  and  $\Delta S_T^0$ , respectively, versus CO<sub>2</sub> density for column B. The  $\Delta H_T^0$  values of naphthalene in column B at different CO<sub>2</sub> densities lie on a straight line from 0.4 to 0.9 g ml<sup>-1</sup>, as do the  $\Delta S_T^0$  values, indicating a simple adsorption-like retention mechanism. However, the  $\Delta H_T^0$  values

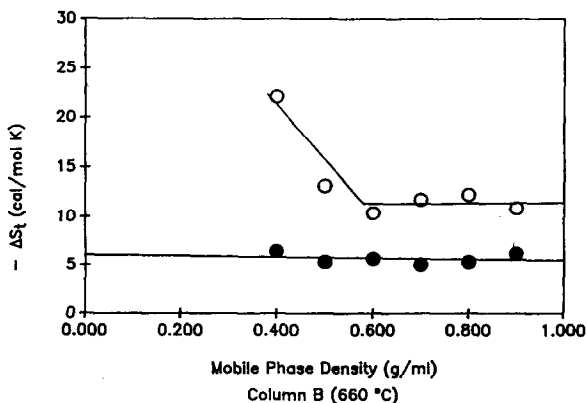


Fig. 6. Total entropies of transfer as a function of CO<sub>2</sub> density of the mobile phase. Stationary phase and solutes as in Fig. 5.

of 2,4-dimethylphenol follow a trend similar to that of naphthalene from 0.9 to 0.6 g ml<sup>-1</sup>, then diverge from 0.6 to 0.4 g ml<sup>-1</sup>, showing increasing interactions between surface silanol groups and hydroxyl groups of the solute. As shown in Fig. 6, the entropy values of 2,4-dimethylphenol change more dramatically than the enthalpy values, giving a clear indication of the silanophilic effects at low density. Similarly to the entropy study for thermally treated samples,  $\Delta S_T^0$  provides a useful tool in studying the nature of the packings.

#### 4.2. Octadecylsilane-bonded packings

ODS-1 and ODS-2 are octadecyl-bonded columns prepared without end-capping, and thus still have accessible hydroxyl groups on their surface (see Table 2). Employing pure CO<sub>2</sub> as the mobile phase, the ODS columns permitted phenols such as 2,4-dimethylphenol and eugenol to elute. However, the chromatographic peak shapes suggest in all instances strong interactions between the analyte and the stationary phase, as the phenols eluted with strong tailing. It was originally believed that the ODS-2 would exhibit little affinity for the phenols and fewer silanol groups on its surface, as the material had been extensively treated with silane as shown by its high hydrocarbon content (17.3% carbon). However, silanol group concentration measurement, poor chromatographic peak shape and failure to elute pyridine all indicate that maximum coverage of surface hydroxyl groups is not reached for the ODS-2 packing. For silica-based supports, Berendsen and De Galan [33] employed a geometrical model to demonstrate that unreacted hydroxyl groups still exist at the surface of silica gel even at maximum coverage of silane owing to steric constraints. Many workers have shown that conventional end-capping is not totally effective in that all silanol sites are not reacted [33,34]. However, our test results show that the ODS-3 column eluted pyridine with relative ease, indicating that end-capping is very effective in masking unreacted silanols. As the exact commercial silylation treatment process is not known, it would be pure speculation to state that

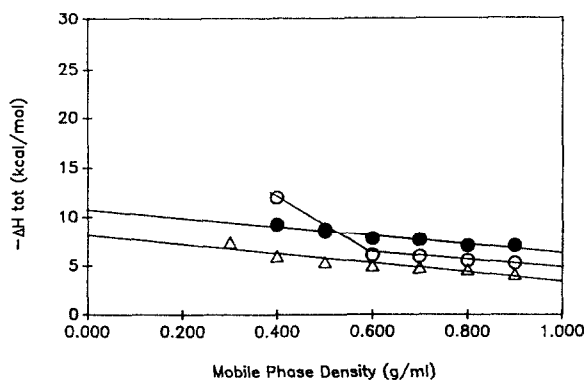


Fig. 7. Total enthalpies of transfer as a function of CO<sub>2</sub> density of the mobile phase. Stationary phase: ○ = Partisil ODS-1; ● = ODS-2; △ = ODS-3. Solute: eugenol.

the end-capping of ODS-3 is more successful in masking silanols than other similar packings used by other workers [20], as different ways exist to perform end-capping [35].

Using eugenol as a probe, characteristic plots of enthalpy and entropy as functions of density for low- and high-polarity packings can be established, as shown in Figs. 7 and 8. The well coated ODS-3 produces a linear plot and has the smallest enthalpy values, whereas ODS-1 shows a sudden increase in enthalpy and entropy values at low density. For the ODS-3 packing, this characteristic plot shows a typical adsorption and desorption process in a chromatographic column over a wide density region. For example, Fig. 9 shows the enthalpy of interaction between

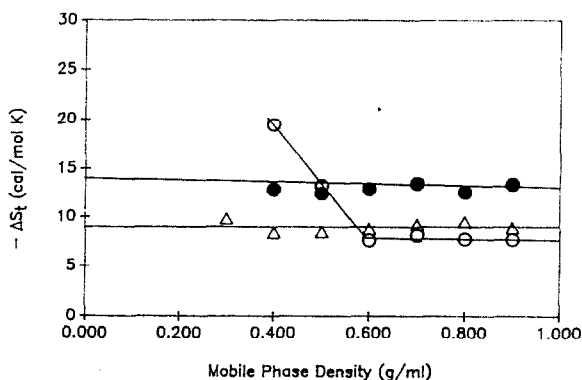


Fig. 8. Total enthalpies of transfer as a function of CO<sub>2</sub> density of the mobile phase. Stationary phases and solute as in Fig. 7.

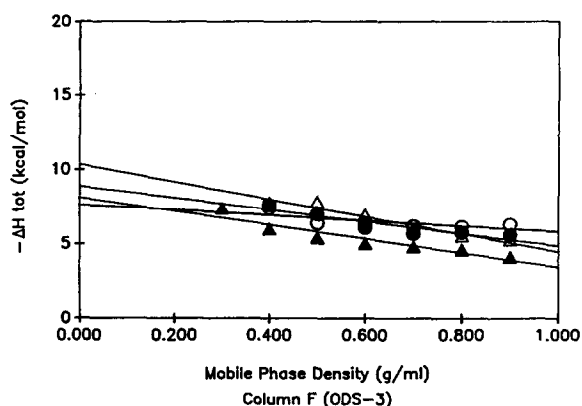


Fig. 9. Total enthalpies of transfer as a function of  $\text{CO}_2$  density of the mobile phase. Stationary phase: Partisil-10 ODS-3. Solute:  $\blacktriangle$  = eugenol;  $\bullet$  = vanillin;  $\triangle$  = 2,4-dimethylphenol;  $\circ$  = pyridine.

pyridine, carbon dioxide and the octadecylsilane-coated stationary phase ODS-3. Unlike phenols, pyridine interacts with the surface silanol groups mainly through dipole–dipole effects. Nevertheless, the pyridine enthalpy curve for ODS-3 demonstrates the same linear characteristic as for eugenol, which interacts with surface silanol groups mainly through hydrogen bonds. The linear characteristic of a well coated column is also supported by the vanillin enthalpy measurement results (see Table 8 and Fig. 9). As expected, changes in pressure drop or flow-rate have little impact on the linear characteristic of the ODS-3 packing [15]. Therefore, the retention behaviour in packed column SFC involves two different types of mechanisms. As shown in Figs. 7 and 8, with polar compounds low-polarity columns such as ODS-2 and ODS-3 show minor variations in  $\Delta H_T^0$  and no variation in  $\Delta S_T^0$  over the whole  $\text{CO}_2$  density range. The same behaviour is observed for high-polarity columns such as ODS-1 at high  $\text{CO}_2$  densities. Similar variations were also found for non-polar compounds such as naphthalene interacting with highly polar columns such as A and B (see Figs. 4, 5 and 6). As the  $\text{CO}_2$  density decreases, silanophilic effects begin to play a more important role, as illustrated by the significant contribution of interactions of eugenol with the residual silanols of ODS-1 (Figs. 7 and 8).

The difference in  $\Delta H_T^0$  and  $\Delta S_T^0$  between ODS-2 and ODS-3, as shown by Figs. 7 and 8, is probably caused by long alkyl chains on the densely coated ODS-2 packing surface, which make the elution of solutes with large alkyl groups difficult and thus increase the energy required. Horváth [36] and Schoenmakers *et al.* [21] proposed a dual retention mechanism, in which the bonded silane groups and the silanol groups contribute independently. The contribution of the silanol groups to retention is assumed to follow a Langmuir isotherm, whereas the chemically bonded alkyl groups on the surface are assumed to give rise to a linear isotherm. Our experimental results seem to be in good agreement with the dual retention mechanism. In addition to the silanol contribution, the ODS-2 packing has more densely bonded groups on the surface and thus has more contributions of aliphatic groups to the retention of solute. In the high-density region, the linear isotherm of bonded groups is predominant. This may explain why when packings without a bonded phase such as column C are tested with 2,4-dimethylphenol, the enthalpy of transfer is smaller at high density when compared with that of column E (compare Tables 5 and 7), even if both have very similar surface silanol concentrations. The reason is that there is no solvophobic effect for column C owing to the lack of a bonded hydrocarbonaceous surface.

In the low-density region, the situation is different as other factors are playing more and more important roles. Although supercritical carbon dioxide is usually considered to be a non-polar solvent, it has been shown to possess hydrogen bonding capabilities and some dipole selectivity. In fact, Phillips and Robey [37] compared the solvent strength and selectivity of supercritical carbon dioxide with those of liquid hexane. They found that  $\text{CO}_2$  is a Lewis base readily pairing with the Lewis acid phenol, making the solute, to a certain extent, unavailable for hydrogen bonding with the silanol groups. As the interaction of solute and solvent is closely related to the density of the mobile phase, a density decrease will lead to a decrease in solute–solvent interactions and a progressive

dominance of stationary phase–solute interactions in the retention process. However, for a well coated column packing material such as ODS-3, the stationary phase–solute interactions are limited even in the low-density region owing to the small concentration of reactive silanols left at the surface of silica gel prepared by reaction with organosilane. In addition, for packings such as ODS-1, increased stationary phase–solute interactions and easy access to active sites give the silanol groups at the surface of the silica gel more chances to absorb the solute and, thus, more energy is required to desorb the solute, which in turn is reflected in the absolute increase in enthalpy values. In other words, the lower the density, the greater is the role for silanol groups on the surface of the packing support.

#### 4.3. Intersection points of Van 't Hoff plots

The calculation of enthalpy of solute transfer from the slope of  $\ln k'$  vs.  $T^{-1}$  at constant density is well known. However, the data in Fig. 10 for eugenol eluted from a silane-modified silica gel (ODS-3) system demonstrate another interesting point, that may not have been previously studied. It is noted that when the linear relationships between  $\ln k'$  and  $T^{-1}$  are extrapolated, these lines seem to intersect at a common point around  $(-0.30 \pm 0.2, -7.50 \pm 0.5)$ . In fact, similar intersection points were observed for all other solute–stationary combinations investi-

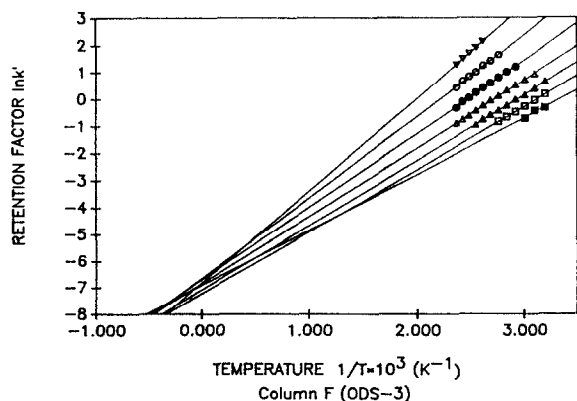


Fig. 10. Van 't Hoff plots as in Fig. 3, except the plots are extrapolated to show the intersection point.

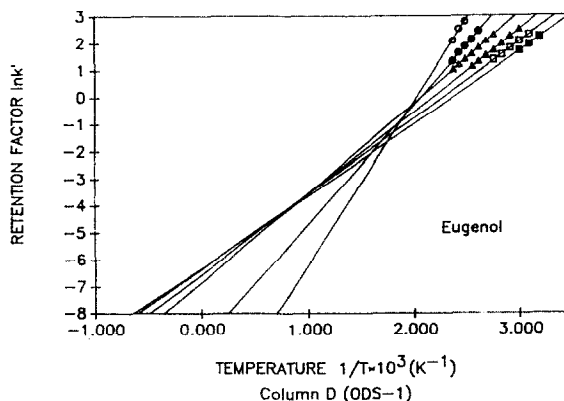


Fig. 11. Van 't Hoff plots ( $\ln k'$  vs.  $1/T$ ) for eugenol at different  $\text{CO}_2$  densities of the mobile phase. The plots are extrapolated to show the intersection point. Stationary phase: Partisil-10 ODS-1. Symbols as in Fig. 1.

gated in this work, as exemplified by eugenol eluted from ODS-1 (high-density region in Fig. 11) and naphthalene eluted from the unmodified silica gel Partisil-10 (Fig. 12). Capillary column SFC also exhibits similar phenomena. For example, the plots of  $\ln k'$  vs.  $1/T$  for octadecane in the density range  $0.3\text{--}0.4 \text{ g ml}^{-1}$  in the work of Yonker and Smith [9] show a perfect converging point. Similar cases can be found in many other works [3,4]. Nevertheless, each column system shows some specific characteristics. For example, for more polar columns such as ODS-1, only in the high-density region ( $0.6\text{--}0.9 \text{ g ml}^{-1}$ ) is this kind of intersection point observed, as shown in

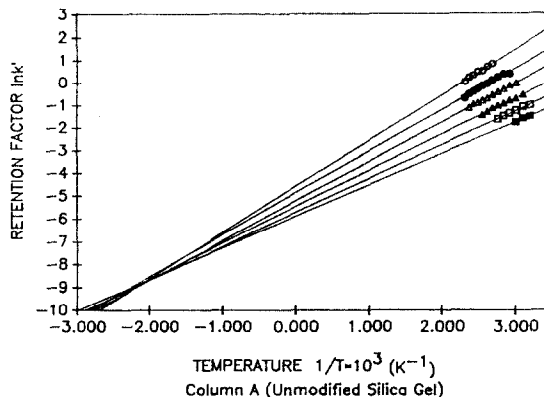


Fig. 12. Van 't Hoff plots as in Fig. 1, except the plots are extrapolated to show the intersection point.

Fig. 11. In the low-density region, the slope of  $\ln k'$  vs.  $1/T$  becomes very steep and the lines would not converge as they do when non-polar solutes elute from unmodified silica gel as shown in Fig. 12.

Table 9 lists our estimates of the values of  $\ln k'_{LP}$  and  $1/T_{LP}$  obtained at this intersection point for various solutes eluting from the six columns tested in this work. Note that as the values are extrapolated in the  $\ln k'$  vs.  $1/T$  diagram, negative values of  $1/T_{LP}$  are possible. These estimated values are plotted in Fig. 13, which shows some correlation between  $\ln k'_{LP}$  and  $1/T_{LP}$ . One line is obtained for 2,4-dimethylphenol eluting from the six columns and when two columns have similar OH concentrations their points are close to each other on this line (compare columns B and D or columns C and E). Large differences in intersection point positions are observed when different solutes are eluting from the same column. Note, for example, the points pertaining to naphthalene and 2,4-dimethylphenol in column A. This difference seems to be larger for more polar columns (compare naphthalene and 2,4-dimethylphenol for columns A, B and C).

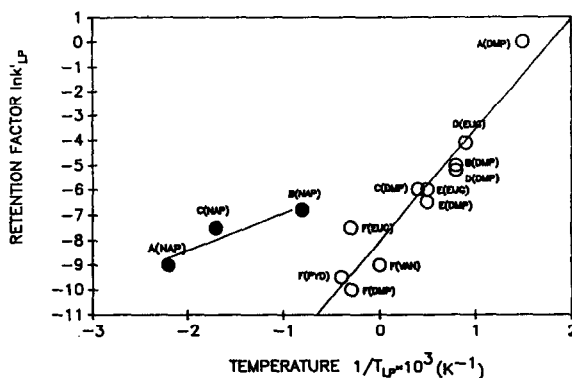


Fig. 13. Variation of the intersection points from extrapolated Van't Hoff plots. For abbreviations, see Table 9.

The values of  $\ln k'_{LP}$  obtained with 2,4-dimethylphenol and the six columns under study are plotted against OH surface concentration in Fig. 14. A linear correlation is observed, indicating that for one polar solute the coordinates of this intersection point on Van't Hoff plot are strongly depending on OH concentration.

From Eq. 1, these coordinates must satisfy

$$\ln k'_{LP} = -\frac{\Delta H_T^0}{RT_{LP}} + \frac{\Delta S_T^0}{R} - \ln \beta \quad (5)$$

Table 9

Converging points from Van't Hoff plot for treated and untreated packing materials

Column	Stationary phase	Solute	Retention factor, $\ln k'_{LP}$	Temperature $1/T_{LP} \cdot 10^3$ , (K <sup>-1</sup> )	Code
A	Partisil-10	2,4-Dimethylphenol	0.0	1.5	A(DMP)
		Naphthalene	-9.0	-2.2	A(NAP)
B	T-660	2,4-Dimethylphenol	-5.0	0.8	B(DMP)
		Naphthalene	-6.8	-0.8	B(NAP)
C	T-900	2,4-Dimethylphenol	-6.0	0.4	C(DMP)
		Naphthalene	-7.5	-1.7	C(NAP)
D	ODS-1	Eugenol	-4.1	0.9	D(EUG)
		2,4-Dimethylphenol	-5.2	0.8	D(DMP)
E	ODS-2	Eugenol	-6.0	0.5	E(EUG)
		2,4-Dimethylphenol	-6.5	0.5	E(DMP)
F	ODS-3	Eugenol	-7.5	-0.3	F(EUG)
		2,4-Dimethylphenol	-10.0	-0.3	F(DMP)
		Vanillin	-9.0	0.0	F(VAN)
		Pyridine	-9.5	-0.4	F(PYD)

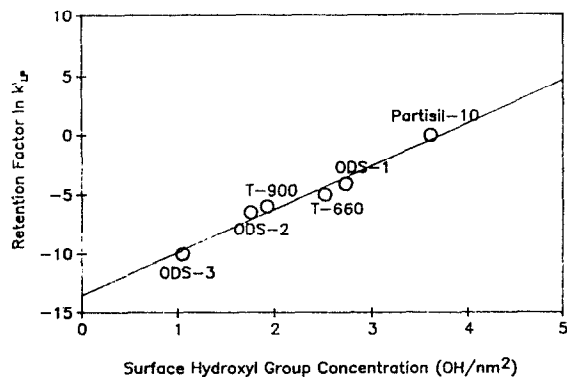


Fig. 14. Values of  $\ln k'_{LP}$  of the six columns for 2,4-dimethylphenol versus stationary phase surface OH concentration.

Because, as shown in Figs. 6 and 8, the  $\Delta S_T^0/R$  values are almost independent of  $\text{CO}_2$  density in instances where intersection points are found, Eq. 5 indicates that an intersection point of Van't Hoff plots is obtained whenever the variations of  $\Delta H_T^0/RT_{LP}$  in the density range of interest are negligible compared with  $\Delta S_T^0/R - \ln \beta$ . Fig. 15, in which the data points correspond to  $\Delta H_T^0$  and  $\Delta S_T^0$  of the various solutes used in this investigation eluting through the six columns under study at high  $\text{CO}_2$  density, shows that this is indeed the case and that Eq. 5 is roughly satisfied in this instance.

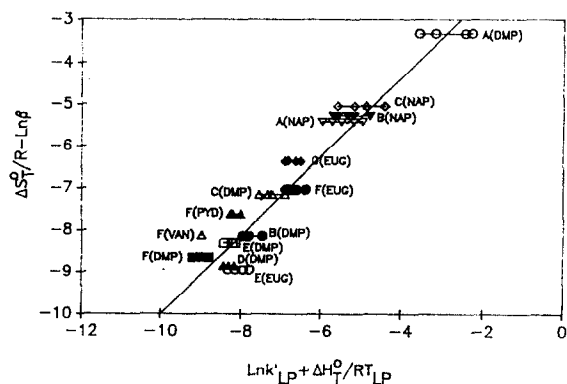


Fig. 15.  $(\Delta S_T^0/R) - \ln \beta$  versus  $\ln k'_{LP} + \Delta H_T^0/RT_{LP}$ . For abbreviations, see Table 9.

## 5. Conclusions

Retention in SFC is a complex function of temperature, pressure, density and surface chemical characteristics of the stationary phase. Therefore, a multi-dimensional approach was adopted, including thermodynamic parameters, BET and surface silanol OH group concentration measurements in the study of silica gel packing materials used in packed column SFC. This allowed us to establish certain relationships between the thermodynamic values and the number of silanol groups on the silica gel surface. The results can be summarized as follows:

(1) Enthalpy and entropy values obtained from Van't Hoff plots can be utilized as thermodynamic criteria to determine the polarity and to extract other information on stationary phases in packed column SFC.

(2) A characteristic slope of enthalpy vs. density for each category of packing may be obtained with certain low-polarity phenols such as eugenol and 2,4-dimethylphenol.

(3) The characteristic slope depends mainly on the nature of the packing. For a well coated packing such as ODS-3, moderate pressure drops and solutes of different polarity have little impact on the slope.

(4) At low  $\text{CO}_2$  density, interactions with silanol groups on the stationary phase surface become more significant as a result of the decrease in solute-solvent interactions.

(5) Extrapolated Van't Hoff plots have common intersection points. When plotted, these points produce a straight line. The coordinates of these points are correlated with the OH surface concentration and also with the  $\Delta H_T^0$  and  $\Delta S_T^0$  values.

## 6. Acknowledgements

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