

## **Behaviour of phenols under supercritical fluid chromatographic conditions in relation to the pyrolysis of lignocellulosic materials**

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### **ABSTRACT**

A supercritical fluid chromatographic (SFC) study of five phenols (phenol, guaiacol, 2,4-dimethylphenol, eugenol and vanillin) was performed on a methylpolysiloxane column. The ultimate purpose was to apply the information obtained to the fractionation of oils, from pyrolysis of lignocellulosic materials, using packed columns and to the extraction of phenolic compounds. The supercritical conditions employed ranged from 45 to 120°C and from 73.2 to 120 atm for carbon dioxide (density ranging from 0.125 to 0.355 g ml<sup>-1</sup>). For each phenol, the temperature  $T(k'_{\max})$ , for which the retention factor is maximum, at a given pressure, was determined. The selectivity and resolution of the chromatographic separations were also examined; it was found that, for a pair of compounds, the resolution seems to be maximum at a temperature between the  $T(k'_{\max})$  of the two compounds at a given pressure. Enthalpies of volatilization and solvation and entropy of transfer were also calculated.

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### **INTRODUCTION**

Lignocellulosic materials are composed of three main macromolecules: two polysaccharides (cellulose and hemicelluloses) and an amorphous substance (lignin). Cellulose, which is the most abundant natural substance, consists of a linear arrangement of glucose units. Hemicellulose are branched chains of various hexose and pentose monomers. Lignin, the second most abundant and important polymeric substance in the plant world, is composed of phenylpropane units linked into a three-dimensional structure through a variety of different chemical bonds [1]. At moderate temperatures above 200°C, lignin degrades into three main fractions: gas, liquid tar and solid char. The tar fraction generally contains water, alcohols, acetic and other carboxylic acids, ketones and aldehydes and a wide variety of compounds related to phenol, guaiacol and syringol [2]. These phenols can be analysed by gas chromatography (GC) [3,4] and liquid chromatography (LC) [5,6].

Four of the five phenolic compounds examined in this study were obtained as the major components of a single fraction obtained by sequential solvent elution chromatography (SESC) on silica gel [7] on the bench scale. Supercritical fluid chromatography (SFC) would therefore appear to be an additional separation

technique able to isolate each individual phenolic compound following SESC fractionation.

SFC can exhibit a GC- or LC-like behaviour depending on the operating conditions (temperature, pressure, density). SFC can be carried out using either high-performance liquid chromatographic (HPLC) or capillary (less than 100  $\mu\text{m}$  I.D.) GC columns [8,9]; preparative columns have also been developed [10]. Supercritical fluids have reasonably high solvent strengths and can dissolve many different types of solutes. The solvent strength is related mainly to the fluid density; at a given temperature the solvent strength increases as the fluid density increases. For this reason, the fluids employed as carrier solvents in SFC have also been applied to supercritical fluid extraction (SFE) [11]. Supercritical extraction offers several advantages over conventional separation techniques: the solvent is in general easily separated from the extracted material; the solvent strength can be varied by changing the density; and the higher diffusion coefficients found in supercritical fluids allow shorter equilibration times in extraction. This technique can also be applied to thermally labile compounds by using low temperatures; moreover, when using carbon dioxide, no residual toxic solvent remains in the extracted materials. SFE has some drawbacks, however, in particular the need for high pressure and the limited choice of substances with low critical points [12].

A problem in both SFE and SFC is the paucity of fundamental data on supercritical fluid systems [9]. Only a few phenol analyses using SFC have been reported [13–15]. In this paper, results on the SFC analysis of a series of phenols produced during the thermal degradation of lignocellulosic materials are reported.

## EXPERIMENTAL

The separation by SFC of four methylene chloride (Fisher, HPLC grade) solutions was studied: A (phenol, guaiacol and eugenol); B (2,4-dimethylphenol and vanillin); C (phenol, eugenol and vanillin); and D (guaiacol and 2,4-dimethylphenol). Solutes were supplied by Aldrich and used as received. Concentrations ranged from 0.45 to 1  $\text{mg ml}^{-1}$ .

SFC experiments were performed using a Series 600 SFC/GC system from Lee Scientific, equipped with a high-pressure syringe pump, a time-sliced injector and a 5 m  $\times$  100  $\mu\text{m}$  I.D. column with a 0.25- $\mu\text{m}$  film of methylpolysiloxane. A flame ionization detector was connected to the column with a frit restrictor, which gave a velocity of *ca.* 1  $\text{cm s}^{-1}$  at 50°C, 75 atm and a detector temperature of 325°C and with carbon dioxide (Matheson, SFC grade) as mobile phase. All chromatographic runs were performed above the critical point of carbon dioxide ( $T_c = 31.3^\circ\text{C}$  and  $P_c = 72.9$  atm). Some GC experiments were also performed for comparison, using a DB-1 methylsilicone capillary (30 m  $\times$  0.32 mm I.D.) on a Hewlett-Packard HP-5890 gas chromatograph equipped with a cold on-column injector and a flame ionization detector. The initial column temperature was 50°C, held for 1 min, then increased to 250°C at 5°C  $\text{min}^{-1}$ . All chromatograms (SFC and GC) were recorded on an HP-3396A integrator (Hewlett-Packard).

The three-dimensional representations were made using the program Surfer (Golden Software, Golden, CO, U.S.A.), which creates regularly spaced grid data from irregularly spaced experimental data (Kriging method) and generated high-resolution plots on an HP-7475A plotter (Hewlett-Packard).

## RESULTS AND DISCUSSION

Tables I–IV give the experimental conditions used to elute the five solutes; temperatures from 45 to 120°C and pressures from 73.2 to 120 atm, corresponding to a variation in mobile phase density from 0.125 to 0.355 g ml<sup>-1</sup>. The capacity factor,  $k'$ , is related to the retention times of the solute,  $t_r$ , and of an unretained solute (here methylene chloride),  $t_m$ , according to the equation

$$k' = (t_r - t_m)/t_m \quad (1)$$

The three-dimensional representation of the so calculated  $k'$  as a function of pressure  $P$  and temperature  $T$  for eugenol is shown in Fig. 1a.

*Retention at constant pressure and temperature*

Fig. 1a shows that the capacity factors at constant pressure increase with temperature to a maximum value,  $T(k'_{\max})$ , then decrease. This point corresponds to weak solvation of the solute by the mobile phase but at the same times its volatilization from the stationary phase is not yet important. The existence of such an optimum temperature is unique to SFC. Above  $T(k'_{\max})$  there is an increase in the vapour pressure of the substrate, which results in its faster elution. The retention increase that

TABLE I

CAPACITY FACTORS ( $k'$ ) AND RESOLUTION ( $R$ ) FROM SFC ON A METHYLPOLYSILOXANE COLUMN (5 m × 100 μm I.D., 0.25 μm FILM) USING CO<sub>2</sub> AS MOBILE PHASE

Co-injection of (1) phenol, (2) guaiacol and (4) eugenol (solution A).

CO <sub>2</sub> conditions			$k'_1$	$k'_2$	$k'_4$	$R_{2,1}$	$R_{4,1}$	$R_{4,2}$
$T$ (°C)	$P$ (atm)	Density (g ml <sup>-1</sup> )						
45	80	0.255	0.66	0.89	3.14	—	—	—
	88	0.34	—	0.45	1.46	—	—	—
50	80	0.226	0.73	1.02	3.68	3.0	22.2	12.2
	88	0.283	0.41	0.53	1.60	1.8	15.6	6.8
	95	0.36	—	0.31	0.83	—	—	—
55	80	0.208	0.97	1.37	4.88	5.8	21.6	19.6
	88	0.249	0.60	0.83	2.73	4.6	23.0	21.6
	95	0.301	0.36	0.47	1.34	2.3	18.7	8.3
65	80	0.185	0.94	1.40	4.86	7.9	32.2	29.5
	88	0.215	0.55	0.82	2.85	6.4	27.8	26.1
	95	0.248	0.38	0.52	1.61	3.2	19.1	17.6
75	80	0.170	0.73	1.13	4.06	8.3	32.4	29.6
	88	0.193	0.50	0.78	2.75	7.1	30.6	27.9
	95	0.220	0.36	0.54	1.74	4.5	22.6	20.8
85	80	0.159	0.48	0.79	2.88	6.3	29.7	27.2
	88	0.179	0.41	0.66	2.30	5.3	26.0	23.7
	95	0.202	0.33	0.52	1.68	3.9	20.0	18.5
100	80	0.144	0.45	0.75	2.53	—	—	23.4
	95	0.180	0.24	0.39	1.23	3.3	17.0	14.3

TABLE II

CAPACITY FACTORS ( $k'$ ) AND RESOLUTION ( $R$ ) FROM SFC ON A METHYLPOLYSILOXANE COLUMN (5 m  $\times$  100  $\mu$ m I.D., 0.25  $\mu$ m FILM) USING CO<sub>2</sub> AS MOBILE PHASE

Co-injection of (3) 2,4-dimethylphenol and (5) vanillin (solution B).

CO <sub>2</sub> conditions			$k'_3$	$k'_5$	$R_{5,3}$
$T$ (°C)	$P$ (atm)	Density (g ml <sup>-1</sup> )			
45	80	0.255	1.21	3.31	—
	88	0.337	0.66	1.53	—
55	80	0.208	1.40	4.03	18.5
	88	0.249	0.87	2.22	9.92
	95	0.301	0.44	1.24	—
65	80	0.185	1.35	4.02	15.0
	88	0.215	0.96	2.61	8.71
	95	0.248	0.61	1.53	—
75	80	0.170	1.19	3.58	21.9
	88	0.193	0.93	2.65	18.5
	95	0.220	0.66	1.77	13.7
	120	0.326	—	0.31	—
85	80	0.159	1.05	3.19	20.1
	88	0.179	0.85	2.45	17.6
	95	0.202	0.61	1.66	13.8
	120	0.289	—	0.51	—
100	80	0.144	0.83	2.50	17.1
	95	0.180	0.51	1.44	10.9
	120	0.248	0.17	0.47	—
110	95	0.169	0.43	1.21	8.67
	120	0.228	0.17	0.50	—
120	77.6	0.125	—	1.61	—
	95	0.159	0.30	0.95	—
	102.7	0.175	—	0.77	—
	114.4	0.200	—	0.52	—

occurred below  $T(k'_{\max})$  is associated with the decrease in the density of carbon dioxide which reduces the solubility of the substrate and favours absorption on and in the stationary phase [16]. A behaviour similar to that shown by eugenol was also observed with the four other phenols (Fig. 1b–e). Such a behaviour, which is probably general in SFC, was found to be almost independent of the type of both the mobile [17,18] and stationary [17–21] phases.

At constant temperature, (Fig. 1a) the retention increases when the pressure decreases because the density of the mobile phase, and hence its solvent strength, decrease under these conditions. The closer the temperature is to  $T(k'_{\max})$ , the higher is the rate of retention increase. Note that the retention seems to reach a maximum only at a temperature close to  $T(k'_{\max})$ . Similar variations of the retention as a function of pressure were also observed for the other phenols (Fig. 1b–e).

Fig. 2 shows the logarithm of the capacity factor of eugenol as a function of reciprocal temperature for three constant pressures. It shows clearly that  $T(k'_{\max})$  shifts to higher values when the pressure increases. For the three pressures used, *i.e.*, 80, 88

TABLE III

CAPACITY FACTORS ( $k'$ ) AND RESOLUTION ( $R$ ) FROM SFC ON A METHYLPOLYSILOXANE COLUMN (5 m  $\times$  100  $\mu$ m I.D., 0.25  $\mu$ m FILM) USING CO<sub>2</sub> AS MOBILE PHASE

Co-injection of (1) phenol, (4) eugenol and (5) vanillin (solution C).

CO <sub>2</sub> conditions			$k'_1$ <sup>a</sup>	$k'_4$ <sup>a</sup>	$k'_5$ <sup>a</sup>	$R_{4,1}$	$R_{5,1}$	$R_{5,4}$
$T$ (°C)	$P$ (atm)	Density (g ml <sup>-1</sup> )						
75	73.2	0.15	(0.78)	4.41	5.3	26.5	30.1	4.34
100	82.5	0.15	(0.36)	1.88	2.24	19.3	17.4	2.70
120	90.3	0.15	—	1.00	1.20	—	—	1.97
55	78.5	0.20	0.89	4.28	5.05	28.0	24.6	3.47
65	83.7	0.20	0.66	3.15	3.72	22.8	25.4	3.66
75	89.3	0.20	0.47	2.19	2.59	19.6	19.6	2.91
85	94.3	0.20	0.34	1.54	1.82	16.0	16.2	2.48
100	103.1	0.20	—	0.93	1.11	—	—	1.77
55	87.7	0.25	0.51	2.00	2.30	7.25	13.8	1.97
65	95.3	0.25	0.36	1.37	1.58	13.2	11.7	1.72
75	102.7	0.25	0.26	0.99	1.16	—	—	1.65
100	120.8	0.25	—	0.47	0.56	—	—	1.33
55	94.9	0.30	0.31	(1.01)	(1.10)	6.8	7.7	0.73
75	114.3	0.30	—	(0.50)	(0.50)	—	—	—

<sup>a</sup> Values in parentheses were not used in  $\Delta H_{TOT}$  calculation.

TABLE IV

CAPACITY FACTORS ( $k'$ ) AND RESOLUTION ( $R$ ) FROM SFC ON A METHYLPOLYSILOXANE COLUMN (5 m  $\times$  100  $\mu$ m I.D., 0.25  $\mu$ m FILM) USING CO<sub>2</sub> AS MOBILE PHASE

Co-injection of (2) guaiacol and (3) 2,4-dimethylphenol (solution D).

CO <sub>2</sub> conditions			$k'_2$ <sup>a</sup>	$k'_3$ <sup>a</sup>	$R_{3,2}$
$T$ (°C)	$P$ (atm)	Density (g ml <sup>-1</sup> )			
75	73.2	0.15	0.96	1.57	8.72
85	76.8	0.15	0.76	1.08	3.82
100	82.5	0.15	0.51	0.71	2.17
120	90.4	0.15	0.26	0.36	—
50	74.9	0.20	(0.79)	(1.33)	8.79
55	78.2	0.20	0.91	1.64	4.34
65	83.7	0.20	0.84	1.50	4.34
75	89.3	0.20	0.57	1.04	3.12
85	94.3	0.20	0.42	0.58	1.94
100	103.1	0.20	0.26	(0.33)	1.94
45	79.3	0.25	0.70	1.12	5.13
50	83.5	0.25	0.56	0.85	5.67
55	87.7	0.25	0.50	0.72	2.90
65	95.3	0.25	0.39	0.54	2.35
75	102.7	0.25	0.27	(0.39)	2.59

<sup>a</sup> Values in parentheses were not used in  $\Delta H_{TOT}$  calculation.

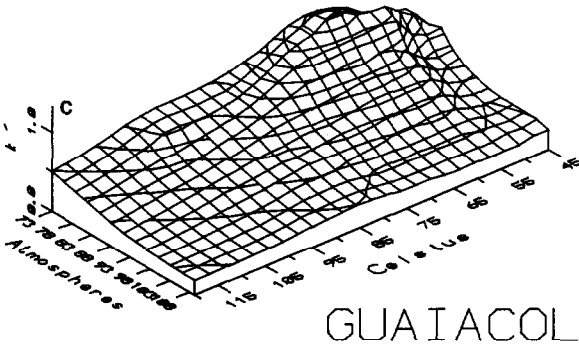
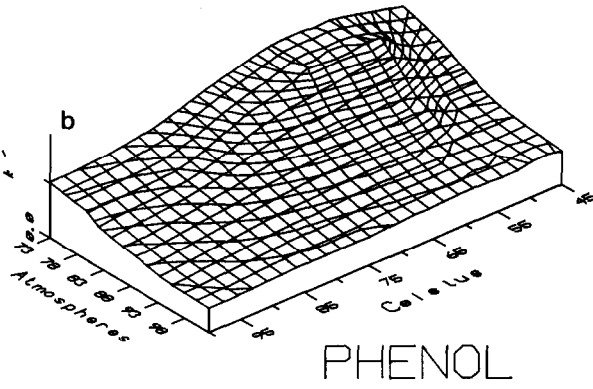
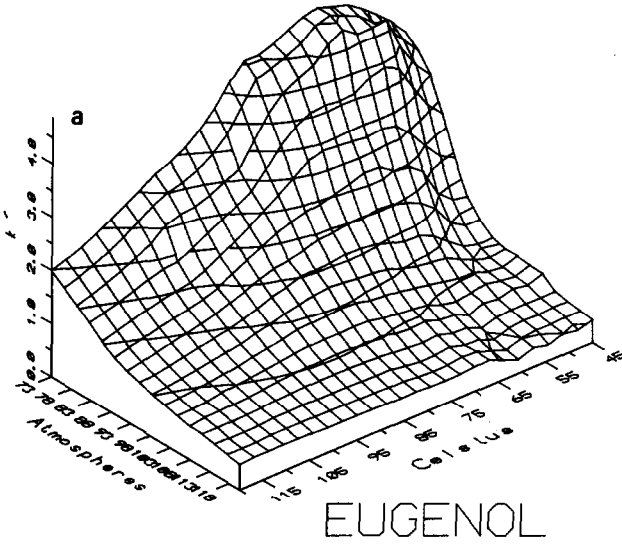


Fig. 1.

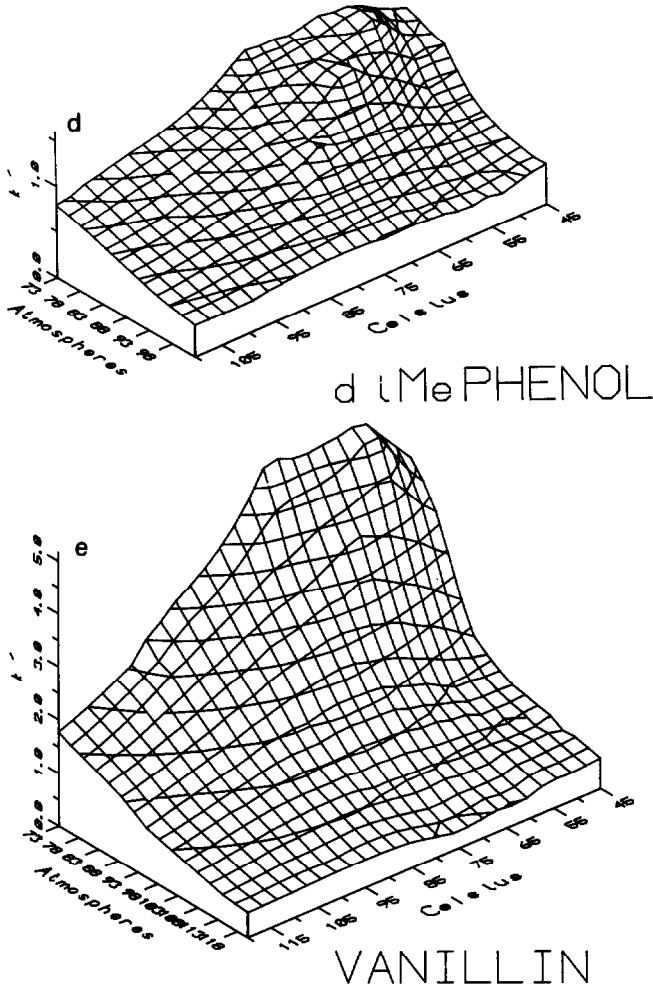


Fig. 1. Three-dimensional representation of capacity factors,  $k'$ , of (a) eugenol, (b) phenol, (c) guaiacol, (d) 2,4-dimethylphenol and (e) vanillin as a function of temperature ( $^{\circ}\text{C}$ ) and of pressure (atm).

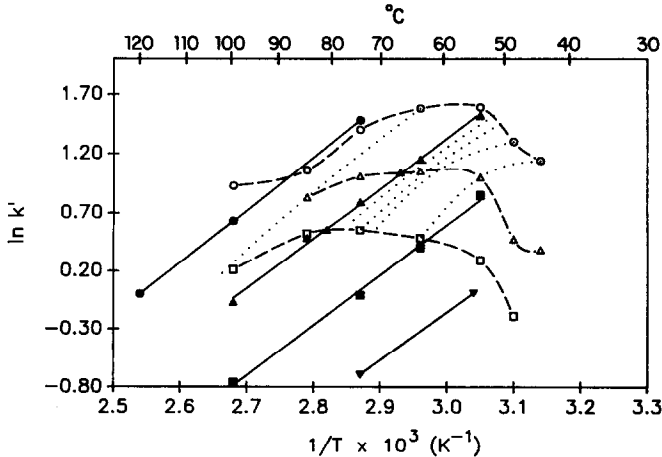


Fig. 2. Capacity factor,  $k'$ , of eugenol as a function of temperature ( $\text{K}^{-1}$ ) (constant pressure and density curves).  $\circ = 80$ ;  $\triangle = 88$ ;  $\square = 95$  atm. Dotted lines, estimated.  $\bullet = 0.15$ ;  $\blacktriangle = 0.20$ ;  $\blacksquare = 0.25$ ;  $\blacktriangledown = 0.30$

TABLE V

APPROXIMATE TEMPERATURES ( $^{\circ}\text{C}$ ) [AND CORRESPONDING DENSITIES ( $\text{g ml}^{-1}$ ) IN PARENTHESES] OF  $T(k'_{\text{max}})$  FOR FIVE PHENOLS AS A FUNCTION OF PRESSURE

Phenol	Pressure (atm)			
	80	88	95	120
Phenol	55 (0.208)	55 (0.249)	65 (0.248)	—
Guaiacol	55 (0.208)	65 (0.215)	65 (0.248)	—
2,4-Dimethylphenol	55 (0.208)	65 (0.215)	75 (0.220)	85 (0.289)
Eugenol	55 (0.208)	65 (0.215)	75 (0.220)	—
Vanillin	55 (0.208)	75 (0.193)	75 (0.220)	85 (0.289)

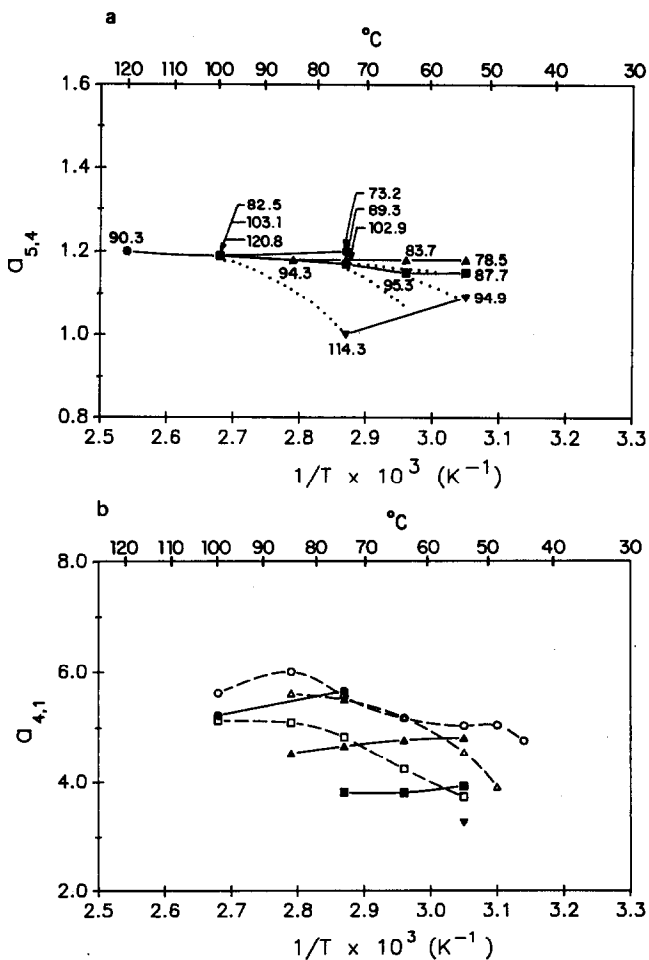


Fig. 3. (a) Selectivity of (5) vanillin-(4) eugenol as a function of temperature ( $\text{K}^{-1}$ ) for different densities; numbers designate pressures (atm).  $\bullet$  = 0.15;  $\blacktriangle$  = 0.20;  $\blacksquare$  = 0.25;  $\blacktriangledown$  = 0.30  $\text{g ml}^{-1}$ . Dotted lines, constant pressures. (b) Selectivity of (4) eugenol-(1) phenol as a function of temperature ( $\text{K}^{-1}$ ) for different pressures.  $\bullet$  = 0.15;  $\blacktriangle$  = 0.20;  $\blacksquare$  = 0.25;  $\blacktriangledown$  = 0.30  $\text{g ml}^{-1}$ .  $\circ$  = 80;  $\triangle$  = 88;  $\square$  = 95 atm.



and 95 atm, the  $T(k'_{\max})$  values were found to be *ca.* 55, 65 and 75°C, respectively. Note that the density also undergoes a slight increase from 0.208 g ml<sup>-1</sup> at 80 atm and 55°C to 0.220 g ml<sup>-1</sup> at 95 atm and 75°C. Table V gives approximate  $T(k'_{\max})$  values for the other phenols.

Fig. 2 also shows the logarithm of the capacity factor of eugenol as a function of reciprocal temperature for various constant densities (experimental data in Tables I and III and estimated values were used). It shows that, at constant density, the logarithm of the capacity factor varies linearly as a function of the reciprocal temperature and shows a slight decrease in slope when the density increases. This applies for densities ranging from 0.15 to 0.20 g ml<sup>-1</sup> for all pressures employed; for higher densities, at low pressures, the curves remain non-linear. Comparable results are obtained with the other phenols. It has been reported [22] for the fluoranthene-carbon dioxide-methylsilicone system that at densities higher than 0.20 g ml<sup>-1</sup>, all the constant-density lines show a major change in slope at some low pressure and low temperature. This could be related to the fact that the heat capacity of carbon dioxide,  $C_p$ , exhibits a maximum in this region [23].

### Selectivity

The chromatographic selectivity,  $\alpha$ , between two compounds 1 and 2 is related to their retention times or their capacity factors [24]:

$$\alpha = \frac{t_{r_2} - t_m}{t_{r_1} - t_m} = \frac{k'_2}{k'_1} \quad (2)$$

with  $t_{r_2} \geq t_{r_1}$  and therefore  $\alpha \geq 1$ . Fig. 3a shows the variation in selectivity between vanillin and eugenol and Fig. 3b that between eugenol and phenol. The choice of these two binary systems is such that in the former instance (Fig. 3a) the two compounds have very similar chromatographic behaviours (similar retention times) whereas in the latter (Fig. 3b) eugenol and phenol display different retention times. In Fig. 3a, constant-pressure lines were plotted from approximate pressure values and it appears that, for a constant pressure, the selectivity reaches a maximum with increasing temperature. In addition, for a given temperature, the selectivity slightly increases when the density or pressure decreases. The effect of pressure or density is only significant at low temperatures.

In contrast to the vanillin-eugenol system, the selectivity for the eugenol-phenol pair (Fig. 3b) is sensitive to pressure, regardless of temperature, because eugenol and phenol do not exhibit the same similar chromatographic behaviour as do vanillin and eugenol. As for the previous system, the sensitivity of the chromatographic selectivity to pressure tends to disappear at high temperatures as the three constant-pressure curves in Fig. 3b tend to converge as the temperature increases.

### Resolution

The chromatographic resolution,  $R$ , between two compounds 1 and 2 is also related to their retention times. In addition,  $R$  depends on the base peak widths,  $w_i$ , of both peaks as follows [24]:

$$R = \frac{t_{r_2} - t_{r_1}}{\frac{1}{2}(w_2 + w_1)} \quad (3)$$

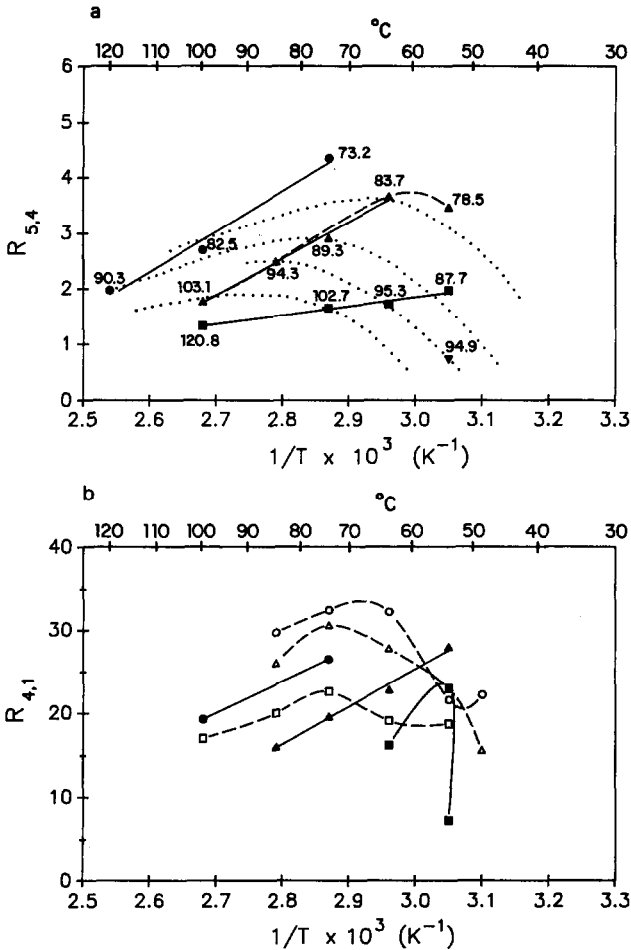


Fig. 4. (a) Resolution of (5) vanillin-(4) eugenol as a function of temperature ( $K^{-1}$ ) for different densities; numbers designate pressure (atm). (b) Resolution of (4) eugenol-(1) phenol as a function of temperature ( $K^{-1}$ ) for different pressures. Symbols as in Fig. 3.

Here the measured widths at half-height are used as estimates of  $\frac{1}{2}(w_2 + w_1)$ , which is only valid for symmetrical and non-tailing peaks.

For the range of temperature used, it is clear that the resolution between the phenol pairs (Fig. 4a and b) at constant pressure reaches a maximum value at a given temperature  $T(R_{\max})$ , and this maximum shifts towards high temperatures as the pressure increases. The values observed for  $T(R_{\max})$  seem to be fairly close to those determined for  $T(k'_{\max})$ . A similar observation was made during the analysis of oligostyrenes using pentane as the supercritical fluid [25]. In fact, the  $T(R_{\max})$  value seems to lie between the  $T(k'_{\max})$  values of the two compounds at a given pressure.

At constant density, it appears that the resolution increases linearly with decrease in temperature, but that there is a temperature above which the resolution decreases.

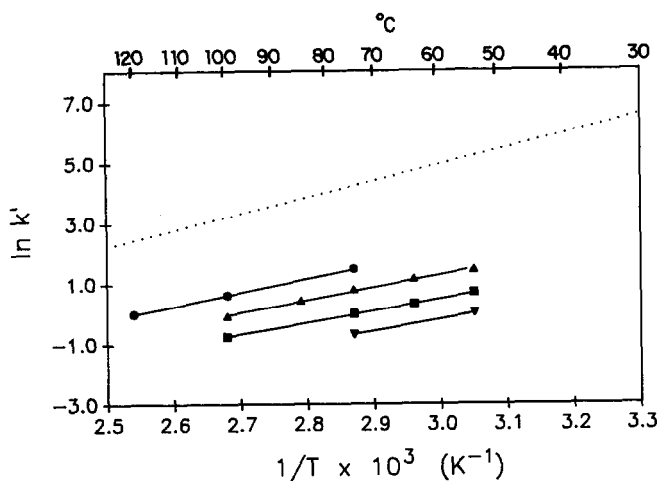


Fig. 5. Logarithm of capacity factor,  $k'$ , of eugenol as a function of reciprocal temperature ( $K^{-1}$ ) for different densities of the mobile phase. Dotted line,  $0.00 \text{ g ml}^{-1}$  (calculated).  $\bullet = 0.15$ ;  $\blacktriangle = 0.20$ ;  $\blacksquare = 0.25$ ;  $\blacktriangledown = 0.30 \text{ g ml}^{-1}$ .

Comparison between Figs. 3a and 4a shows that at high temperature, both the resolution and selectivity between vanillin and eugenol converge towards limiting values that do not depend on density or pressure. It should be noted that at high temperature, the solvation effect is less significant and the elution follows GC-like behaviour. This property of the chromatographic resolution has significant practical consequences, because it shows that the maximum resolution will be reached by operating at low pressure and at a temperature between the  $T(k'_{\max})$  values for the two compounds under consideration.

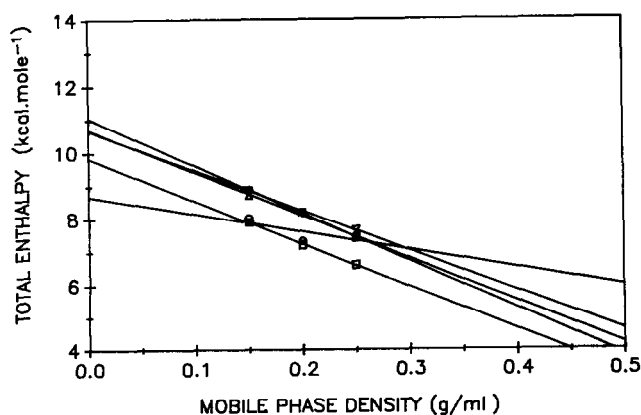


Fig. 6. Total enthalpies of phenols as a function of density of the mobile phase.  $\circ = \text{Phenol}$ ;  $\square = \text{guaiacol}$ ;  $\triangle = 2,4\text{-dimethylphenol}$ ;  $\nabla = \text{eugenol}$ ;  $\diamond = \text{vanillin}$ .

*Enthalpies of interactions at constant density*

Chester and Innis [21] and Yonker and Smith [26] suggested a thermodynamic approach to the representation of the variations of  $\ln k'$  with  $1/T$  at constant density in SFC:

$$\ln k' = \frac{-\Delta H_{\text{TOT}}}{RT} + \frac{\Delta S_{\text{TOT}}}{R} - \ln \beta \quad (4)$$

where  $\Delta H_{\text{TOT}}$  is measured from the slope of the van 't Hoff plot of  $\ln k'$  as a function of  $1/T$  and represents the difference between the standard enthalpy of solution of the solute in the stationary phase and its standard enthalpy of solvation in the mobile phase. This last term in fact contains both volatilization and solvation contributions, the last being a function of the mobile phase density.  $\Delta S_{\text{TOT}}$  is the entropy of transfer.  $\beta$  is the phase volume ratio and is considered, to a first approximation, to be constant; possible swelling of the stationary phase will modify this value [27].

When  $\ln k'$  is plotted against  $1/T$  at constant density, the slope of the linear part of the curves yield calculated values for  $\Delta H_{\text{TOT}}$  (Fig. 5).

Berger [22] proposed the following empirical equation:

$$\Delta H_{\text{TOT}} = \Delta H_{s-sp} - d(\Delta H_{s-sp} + \Delta H_{mp-sp}) \quad (5)$$

TABLE VI

ENTHALPY<sup>a</sup> OF VOLATILIZATION, ENTHALPY<sup>a</sup> OF SOLVATION AND ENTROPY<sup>a</sup> OF TRANSFER FOR PHENOLS IN THE CO<sub>2</sub>-METHYLPOLYSILOXANE SYSTEM WITH THE VOLUME PHASE RATIO  $\beta$  ESTIMATED TO BE 100.25

Phenol	Parameter	Mobile phase density (g ml <sup>-1</sup> )			
		0.25	0.20	0.15	0.00 <sup>b</sup>
Phenol	$\delta H_{\text{TOT}}$	7.5	7.3	8.0	8.7
	$\delta H_{s-mp}$	4.9	6.9	4.5	0.0
	$\delta S_{\text{TOT}}$	15.0	13.4	14.4	
Guaiacol	$\delta H_{\text{TOT}}$	6.6	7.2	7.9	9.7
	$\delta H_{s-mp}$	12.5	12.5	12.5	0.0
	$\delta S_{\text{TOT}}$	13.4	12.8	12.4	
2,4-Dimethylphenol	$\delta H_{\text{TOT}}$	7.4	8.2	8.7	10.8
	$\delta H_{s-mp}$	13.7	12.9	13.9	0.00
	$\delta S_{\text{TOT}}$	15.0	14.7	13.9	
Eugenol	$\delta H_{\text{TOT}}$	7.7	8.2	8.9	10.7
	$\delta H_{s-mp}$	12.0	12.4	11.9	0.0
	$\delta S_{\text{TOT}}$	12.9	12.9	13.4	
Vanillin	$\delta H_{\text{TOT}}$	7.4	8.2	8.9	11.1
	$\delta H_{s-mp}$	14.5	14.5	14.5	0.0
	$\delta S_{\text{TOT}}$	12.0	12.5	13.1	

<sup>a</sup> Enthalpies are in kcal mol<sup>-1</sup> and entropies in kcal mol<sup>-1</sup> K<sup>-1</sup> ( $R = 1.98$  cal mol<sup>-1</sup> K<sup>-1</sup>).

<sup>b</sup>  $\delta H_{\text{TOT}}$  for density 0.00 g ml<sup>-1</sup> represents  $\delta H_{s-sp}$ .

where  $\Delta H_{s-mp}$  is the enthalpy of interaction between the solute and mobile phase and  $\Delta H_{mp-sp}$  is the enthalpy of interaction between mobile phase and stationary phase; the latter value is considered to be small and negligible. Both refer to the solute at infinite dilution. The density  $d$  is the carrier fluid density with reference to a standard state of  $1 \text{ g ml}^{-1}$ . The zero density intercept value from the plot of  $\Delta H_{TOT}$  versus  $d$  represents  $\Delta H_{s-sp}$ , the standard enthalpy of interaction between the solute and stationary phase. Berger [22] found that there is only a slight difference between the  $\Delta H_{s-sp}$  value calculated by extrapolation at zero density and the  $\Delta H_{TOT}$  value determined from van 't Hoff plots under conditions of low pressure and high temperature where the GC approximation becomes valid.

Fig. 6 shows the variation of  $\Delta H_{TOT}$  as a function of density for the five compounds studied. From such graphs, values of  $\Delta H_{s-sp}$  may be calculated by extrapolation to zero density and point values of  $\Delta H_{s-mp}$  are then calculated using eqn. 5.

Table VI gives the interaction energies of the studied phenols in the supercritical carbon dioxide–methylpolysiloxane system. The  $\Delta H_{s-sp}$  values (given as  $\Delta H_{TOT}$  values at zero density in Table VI) would reflect the elution order of the phenols under SFC conditions where the pressure is low and the temperature is relatively high, and thus under conditions close to GC conditions (volatilization is prevailing). The same elution order was also observed in GC of the five compounds on a comparable column (DB-1, methylsilicone) and using helium as the mobile phase at low pressure.

The solvation energies ( $\Delta H_{s-mp}$ ) remain nearly constant for each solute (except phenol) and are about  $4.5\text{--}6.9 \text{ kcal mol}^{-1}$  for phenol and  $11.9\text{--}14.5 \text{ kcal mol}^{-1}$  for the other phenols. The entropy of transfer, calculated from eqn. 4, ranges from  $12.0$  to  $15.0 \text{ kcal mol}^{-1} \text{ K}^{-1}$  for the five phenols. All these values were calculated assuming that  $\Delta H_{s-sp}$  is an approximation of the GC contribution. Moreover, the phase ratio  $\beta$  is not necessarily constant; experimental determinations of  $\Delta H_{TOT}$  at only three densities were used to calculate the various interactions (Fig. 6). Finally, the elution of phenol is probably affected by the closeness of the solvent peak. It would be interesting to compare these interaction energies with those determined experimentally using other stationary phases.

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