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## CHROMATOGRAPHY WITH SUB- AND SUPERCRITICAL ELUENTS: INFLUENCE OF TEMPERATURE, PRESSURE AND FLOW-RATE ON THE BEHAVIOUR OF LOWER ALKANES

DIETGER LEYENDECKER, FRANZ P. SCHMITZ\*, DAGMAR LEYENDECKER and ERNST KLESPER

*Lehrstuhl für Makromolekulare Chemie der RWTH Aachen, Worringer Weg 1, D-5100 Aachen (F.R.G.)*

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### SUMMARY

The chromatographic behaviour of *n*-pentane, *n*-butane, isobutane and propane was studied in the liquid, gaseous and supercritical gaseous states by running chromatograms of a mixture containing four polynuclear aromatic hydrocarbons. Both the capacity ratios and the resolutions reach maxima at temperatures above the boiling or the critical temperature at a given constant pressure. The maxima are the more pronounced the lower the alkane and the higher the molecular weight of the substrate. This temperature-dependent course of resolution at constant pressure is influenced mostly by changes in plate numbers. On increasing the pressure, the capacity ratios and resolution decrease.

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### INTRODUCTION

Although supercritical fluid chromatography (SFC) has been known for more than 20 years, it has attracted wider attention only recently. Interest has grown particularly since it became possible to modify conventional high-performance liquid chromatographic (HPLC) apparatus for use in SFC<sup>1-4</sup>. In the past, several reviews were published that showed the then current state of development<sup>5-11</sup>. Progress has been made in both the practical and theoretical aspects of SFC. Of special interest was how to influence the separation behaviour of SFC by varying the working conditions. Thus the dependence of retention and resolution on pressure and to a lesser extent on temperature and flow-rate has been described for different column materials, eluents and substrates.

The most commonly used column materials are alumina and silica gel and the most usual eluents are carbon dioxide, alkanes and ethers. As we reported earlier<sup>12</sup>, capacity ratios ( $k'$ ) and resolution ( $R$ ) may reach maxima at temperatures above the critical temperature of the eluents, which was demonstrated using diethyl and dimethyl ether and separating polynuclear aromatic hydrocarbons (PAHs) on a silica gel column. Similar results were obtained when using *n*-alkanes for elution<sup>13-16</sup>. For the interpretation of the behaviour of  $k'$  it is of interest that Smith and Udseth<sup>17</sup>

recently studied the solubility of substrates in supercritical fluids under several operating conditions.

In order to gather some more experimental data, we have studied the separation behaviour of propane, *n*-butane, isobutane and *n*-pentane and the results are reported in this paper.

## EXPERIMENTAL

The apparatus and columns were as described previously<sup>1,2</sup>.

*n*-Butane (99.5%), isobutane (99.5%) and propane (99.5%) (all from Linde, Höllriegelskreuth, F.R.G.) were used without further purification. *n*-Pentane was dried over sodium, distilled, filtered and degassed. Physical data of the eluents are listed in Table I. Because all the eluents are low-boiling, they must be pre-pressurized in order to be pumped while in the liquid state. The pre-pressures varied from 6 bar (*n*-pentane) to 16 bar (propane). *n*-Pentane also served as an inert substance to determine the dead times. When using *n*-pentane as the mobile phase, however, dead time measurements were carried out with *n*-heptane.

TABLE I  
PHYSICAL DATA OF THE ELUENTS<sup>1,3</sup>

Eluent	$T_b$ (°C)	$T_c$ (°C)	$p_c$ (bar)	$\rho_c$ (g cm <sup>-3</sup> )
<i>n</i> -Pentane	36.1	196.5	33.7	0.237
<i>n</i> -Butane	-0.5	152.0	38.0	0.228
Isobutane	-11.7	135.0	36.5	0.221
Propane	-42.1	96.7	42.5	0.217

As a test mixture, a solution of naphthalene, anthracene, pyrene and chrysene (each 0.01–0.001 *M*) in *n*-pentane was used, the concentrations being chosen such that comparable peak areas in UV detection were obtained. Approximately 20  $\mu$ l of the solution were injected for each chromatogram.

As a measure of pressure, the column end pressure  $p_e$  was always employed. Volumes were liquid volumes metered by the pumps, neglecting the different compressibilities of the four eluents.

The determination of the dead time,  $t_0$ , was carried out for calculation of the capacity ratios,  $k'$ , according to

$$k' = \frac{t_R - t_0}{t_0} \quad (1)$$

where  $t_R$  is the retention time of a given peak.

The selectivity of separation is expressed by the relative capacity ratio,  $\alpha$ , of neighbouring peaks,  $m$  and  $m + 1$ :

$$\alpha = \frac{k'_{m+1}}{k'_m} = \frac{t_{m+1} - t_0}{t_m - t_0} \quad (2)$$

Other characteristic quantities for characterizing the separation are the resolutions  $R_i$  and  $\bar{R}$ , which are given by

$$R_i = \frac{t_{m+1} - t_m}{w'_{m+1} + w'_m} \cdot \sqrt{\ln 4} \quad (3a)$$

and

$$\bar{R} = \frac{\sum_i^j R_i}{j} \quad (3b)$$

where  $R_i$  = resolution for the  $i$ th pair of peaks,  $\bar{R}$  = average resolution,  $t_m$  = retention time of the  $m$ th peak,  $w'$  = peak width at half-height,  $j = 3$  and  $i = 1, 2$  or  $3$ .

Plate numbers were obtained according to

$$n = 4 \ln 4 \left( \frac{t_R}{w'} \right)^2 \quad (4)$$

## RESULTS AND DISCUSSION

Supercritical gases can be considered as being above the critical temperature  $T_c$  and critical pressure  $p_c$ , whereas subcritical gases are above  $T_c$  but below  $p_c$  or else below  $T_c$  and  $p_c$ . Because the dissolution power of supercritical and subcritical gases strongly depends on density, which in turn depends on pressure, the solubility parameters given by Hildebrandt and Scott<sup>19</sup> were modified for application to supercritical gases by Giddings and co-workers<sup>20,21</sup>:

$$\delta = 1.25 p_c^{1/2} (\rho_{\text{gas}}/\rho_{\text{liq}}) \quad (5)$$

where  $\rho_{\text{gas}}$  = (reduced) density of the gas and  $\rho_{\text{liq}}$  = (reduced) density of the liquid at the boiling point.

The temperature and pressure dependence of the density have a characteristic behaviour, shown for  $n$ -butane in Fig. 1<sup>22</sup>. Additional data can be found in the literature<sup>22-24</sup>.

Because substances behave similarly at their critical points, their  $\rho(p)$  diagrams are also similar. At  $T = T_c$  the  $\rho(p)$  isotherm shows a point of inflection on the vertical part of the curve. Therefore, in the range near  $T_c$  a small decrease in pressure yields a considerable decrease in density and thereby in solution power.

Table II gives the temperature and pressure ranges and the ranges of the reduced temperature,  $T_r$ , and reduced pressure,  $p_r$ , applied in the chromatographic runs. The ranges of temperature and pressure used make a comparison between HPLC and SFC possible, and for  $n$ -pentane also between HPLC, SFC, gas chromatography (GC) and high-pressure GC. At a low column end pressure ( $p_e$ ), where

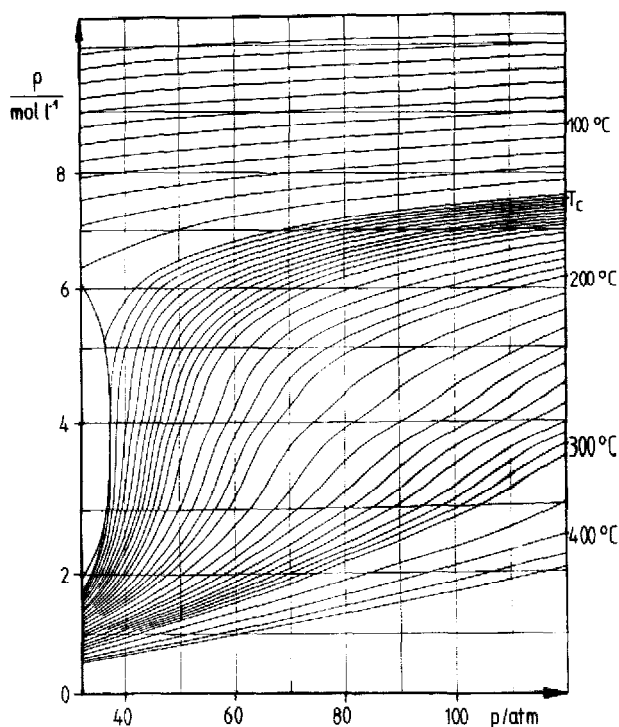


Fig. 1. Temperature and pressure dependence of the density for *n*-butane.

TABLE II

APPLIED TEMPERATURE AND PRESSURE RANGES

<i>Eluent</i>	<i>T</i> (°C)	<i>T<sub>r</sub></i>	<i>p<sub>e</sub></i> * (bar)	<i>p<sub>r</sub></i> **	<i>p<sub>i</sub></i> *** (bar)
<i>n</i> -Pentane	20–280	0.10–1.42	6	0.18	17
			20	0.60	34
			36	1.07	46
			70	2.08	80
<i>n</i> -Butane	20–280	0.13–1.84	39	1.03	48
			70	1.87	80
Isobutane	20–280	0.15–2.07	37	1.01	47
			70	1.92	80
Propane	20–280	0.21–2.89	43	1.02	51
			70	1.65	80

\* Pressures measured at column exit (column end pressures).

\*\* Reduced pressures (calculated from *p<sub>e</sub>* values).

\*\*\* Pressures measured at column inlet.

*p<sub>e</sub>* < *p<sub>c</sub>* (for *n*-pentane), *i.e.*, *p<sub>e</sub>* = 6 and 20 bar, the transition is from the liquid to the subcritical gaseous state. At *p<sub>e</sub>* > *p<sub>c</sub>* the transition is from the liquid to the supercritical gaseous state. The phase transitions are reflected as a drop in *V<sub>0</sub>* in the plot of dead volumes, *V<sub>0</sub>*, versus temperature (Fig. 2). The largest decrease in dead volumes was found at the lowest pressure, owing to a phase transition from the liquid to the subcritical gaseous state. The temperature where the decrease occurs increases

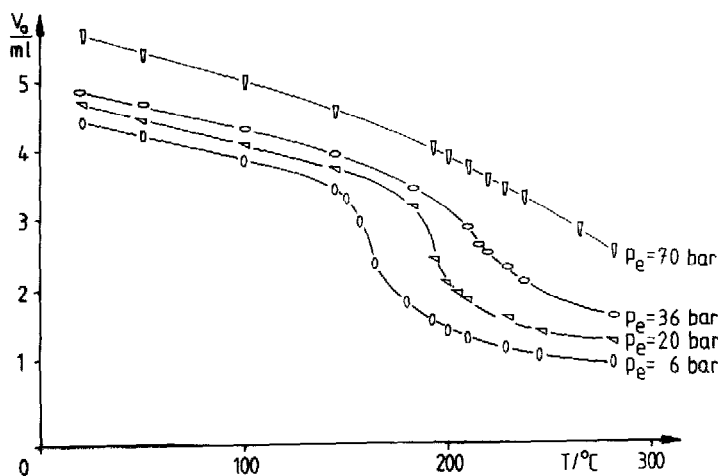


Fig. 2. Dead volumes,  $V_0$ , versus temperature for *n*-pentane as the mobile phase at different pressures  $p_e$ . Volume flow-rate: 1 ml/min.

with increasing pressure. The dead volumes were measured simultaneously with each chromatographic run by using *n*-pentane as a sample solvent or by separate injections of *n*-heptane.

Measurements of retention ( $k'$ ) and resolution ( $R_i$ ) were made by increasing the temperature from ambient to 280°C from chromatogram to chromatogram while the pressure was kept constant. The  $k'(T)$  isobars thus obtained for *n*-pentane, *n*-butane, isobutane and propane at different pressures are shown in Figs. 3–6. All the curves show similar behaviour. On increasing the temperature from ambient, *i.e.*, in the liquid state (HPLC), the  $k'$  values decrease and reach a minimum, thus reflecting increased substrate solubility at higher temperatures. After having passed the boiling temperature of the eluent (at pressures below critical) or the critical temperature (at pressures above critical), the  $k'$  values increase significantly or even greatly. This increase is more pronounced the lower the pressure, the lower the alkane and the

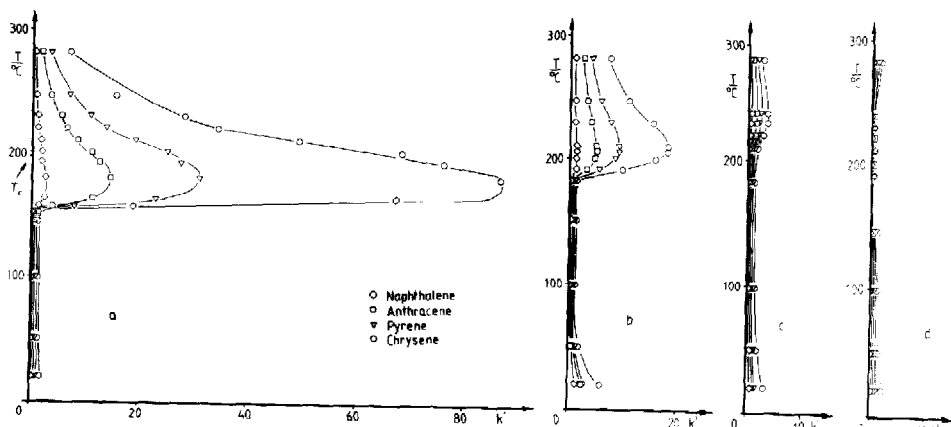


Fig. 3. Temperature versus capacity ratios,  $k'$ , for *n*-pentane as the mobile phase at different constant  $p_e$  values (isobars). Pressures: (a)  $p_e = 6$  bar (reduced pressure  $p_r = 0.18$ ); (b)  $p_e = 20$  bar ( $p_r = 0.60$ ); (c)  $p_e = 36$  bar ( $p_r = 1.07$ ); (d)  $p_e = 70$  bar ( $p_r = 2.08$ ). Substrate: naphthalene-anthracene pyrene-chrysene mixture (PAHs). Volume flow-rate: 1 ml/min.

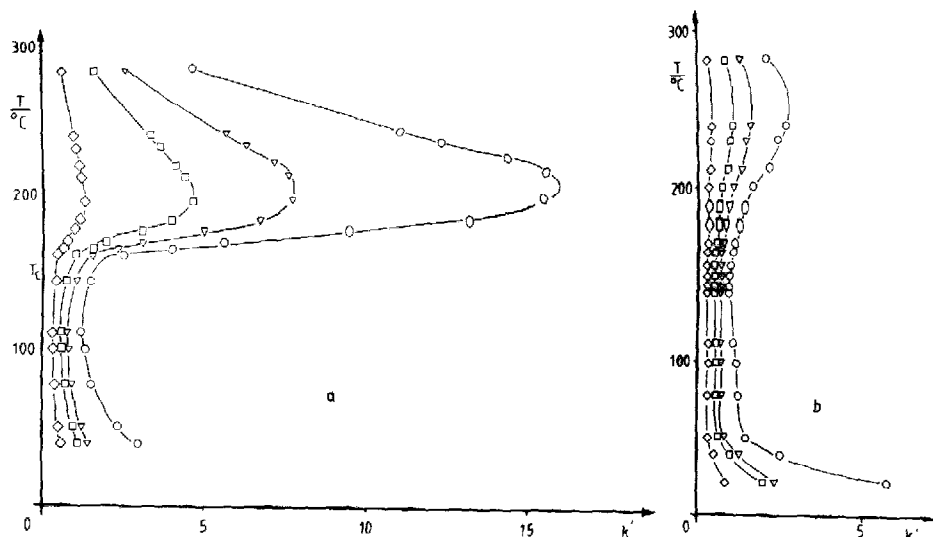


Fig. 4. Temperature versus capacity ratios,  $k'$ , in *n*-butane at different constant  $p_e$  values: (a)  $p_e = 39$  bar ( $p_r = 1.03$ ); (b)  $p_e = 70$  bar ( $p_r = 1.87$ ). Substrate: PAHs. Volume flow-rate: 1 ml/min. Symbols as in Fig. 3.

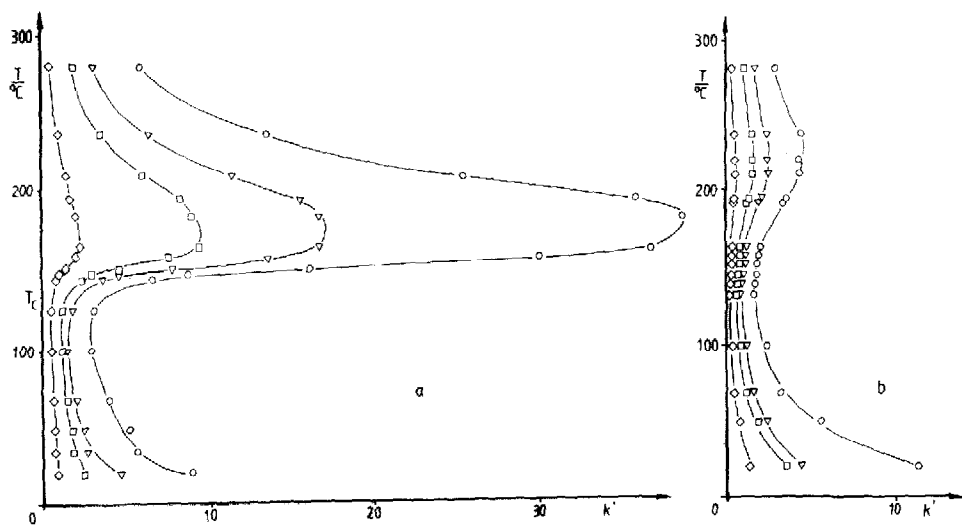


Fig. 5. Temperature versus capacity ratios,  $k'$ , in isobutane at different constant  $p_e$  values: (a)  $p_e = 37$  bar ( $p_r = 1.01$ ); (b)  $p_e = 70$  bar ( $p_r = 1.92$ ). Substrate: PAHs. Volume flow-rate: 1 ml/min. Symbols as in Fig. 3.

higher the molecular weight of the substrate. All curves pass through a distinct maximum, except that for *n*-pentane at  $p_e = 70$  bar, where the pressure is particularly high. They then decrease to values comparable again to those at low temperature.

This behaviour under sub- or supercritical gaseous conditions corresponds exactly to data obtained with dimethyl and diethyl ether as eluents<sup>12</sup>. As explained there, it is caused by two opposing effects: first, by a decrease in the eluent density and, thereby, the substrate solubility on increasing the temperature at constant  $p_e$ , and second, by the opposing effect of an increase in the vapour pressure of the substrate and an increase in solubility. The second effect overcompensates the first

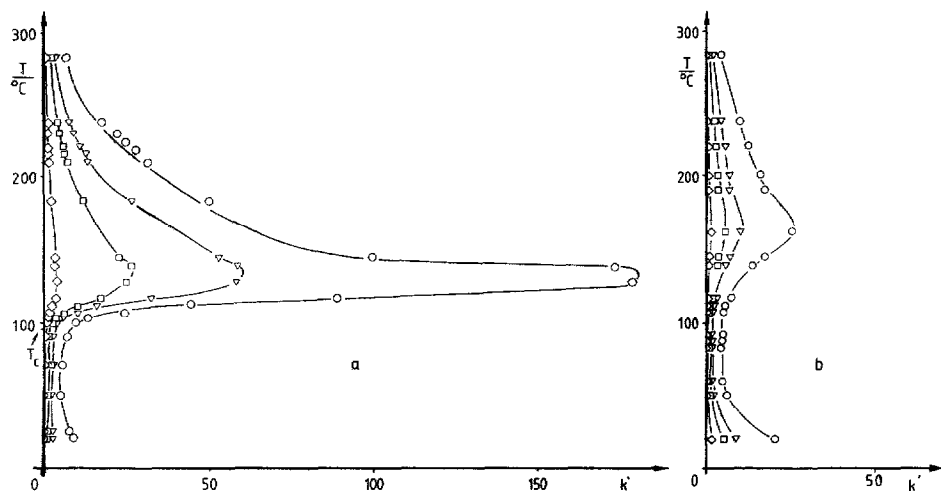


Fig. 6. Temperature versus capacity ratios,  $k'$ , in propane at different constant  $p_e$  values: (a)  $p_e = 43$  bar ( $p_r = 1.02$ ); (b)  $p_e = 70$  bar ( $p_r = 1.65$ ). Symbols as in Fig. 3.

when the temperature is increased beyond a certain level. At high pressures, the density decrease is too small for the first effect to become important and, therefore, the  $k'$  values do not reach a maximum.

The strong increase in the  $k'$  values of the different mobile phases and of the different PAHs is also reflected in the behaviour of the resolution,  $R_i$ , and the average resolution,  $\bar{R}$ . Figs. 7-10 demonstrate the changes of  $\bar{R}$  for the four alkanes on increasing the temperature at constant  $p_e$ . For the series of chromatograms with *n*-pentane temperature ranges existed where the resolution was so small that the peak

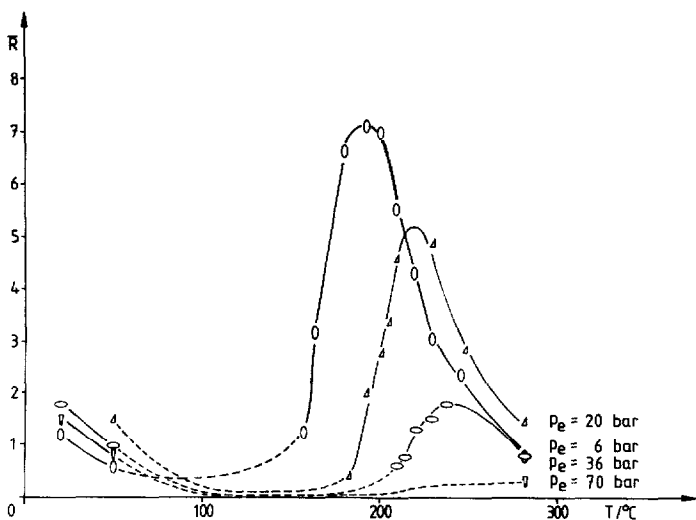


Fig. 7. Average resolution,  $\bar{R}$ , of PAHs versus temperature in *n*-pentane at different pressures,  $p_e$ . Volume flow-rate: 1 ml/min.

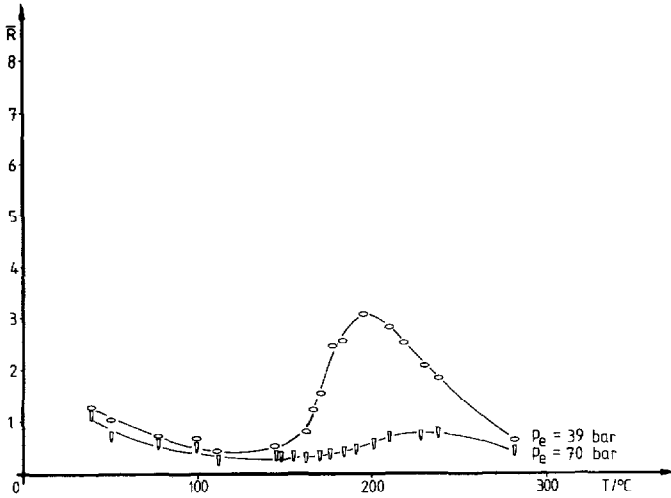


Fig. 8. Average resolution,  $\bar{R}$ , of PAHs versus temperature in *n*-butane at different pressures,  $p_e$ . Volume flow-rate: 1 ml/min.

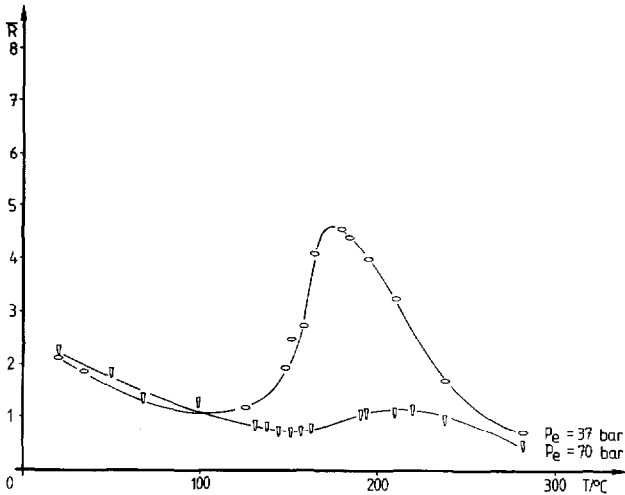


Fig. 9. Average resolution,  $\bar{R}$ , of PAHs versus temperature in isobutane at different pressures,  $p_e$ . Volume flow-rate: 1 ml/min.

widths at half-height,  $w'$ , could not be determined. This is indicated by dashed lines in Fig. 7. The  $\bar{R}$  values also pass through maxima whose positions depend on the type of eluent and on pressure. Owing to the decreasing molecular size and, therefore, the lower critical temperature, the maxima are located at lower temperatures in the order *n*-pentane > *n*-butane > isobutane > propane both at the same reduced and at the same absolute column pressure. The maxima are also found to be more pronounced the lower is the alkane.



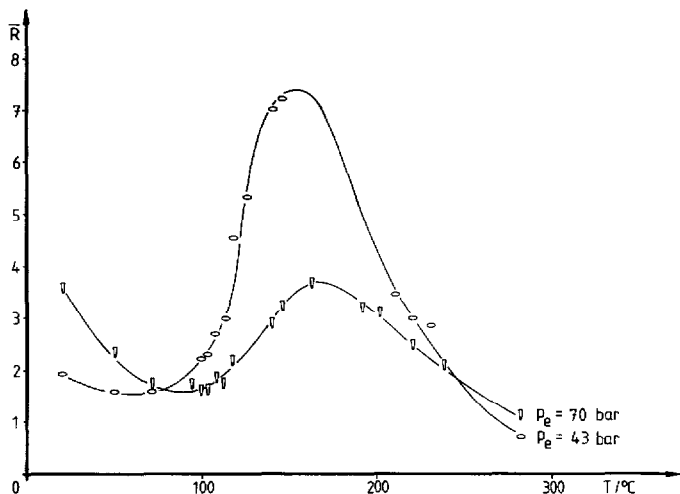


Fig. 10. Average resolution,  $\bar{R}$ , of PAHs versus temperature in propane at different pressures,  $p_e$ . Volume flow-rate: 1 ml/min.

The effect of pressure is a definite decrease in resolution with increasing pressure down to an unsatisfactory resolution ( $\bar{R} < 1$ ).

The equation for the resolution,  $R_i$ , in its frequently used form contains three variable factors:

$$R_i = \frac{1}{4} \cdot \frac{\alpha - 1}{\alpha} \cdot \frac{k'_m}{1 + k'_m} \sqrt{n_{m+1}} \quad (6)$$

This equation is valid for a pair of neighbouring peaks assuming equal peak widths. It consists of an  $\alpha$  term and a  $k'$  term, both of which are dependent only on retention behaviour. The third term, containing the plate number,  $n$ , is a measure of peak spreading. To obtain a statement valid for the whole chromatogram, the factors were calculated separately for each pair of peaks and averaged. In Fig. 11 the temperature-dependent changes of the three factors are compared with the behaviour of the average resolution,  $\bar{R}$ , for propane at a column end pressure,  $p_e$ , of 43 bar. Obviously, the change in  $n$  is mostly responsible for the change in resolution with temperature. The  $\alpha$  and  $k'$  terms also show maxima, but less pronounced. In particular, a strong decrease after having passed the maximum is found only for the  $\sqrt{n}$  values, whereas the  $(\alpha - 1)/\alpha$  and  $k'/(1 + k')$  values remain high. The maximum of  $\sqrt{n}$  is shifted to higher temperatures compared with the  $k'/(1 + k')$  values. An increase in the retention times first leads to strong peak broadening. Not until the retention times decrease again does the resolution increase. It should be noted, however, that  $\bar{R}$  is obtained from averaged  $R_i$  but not from averaging the factors themselves as is done in these comparisons.

The same conclusions can be drawn from Fig. 12, where all three factors are plotted versus  $\bar{R}$ . Because eqn. 6 is the equation of a straight line where each of the

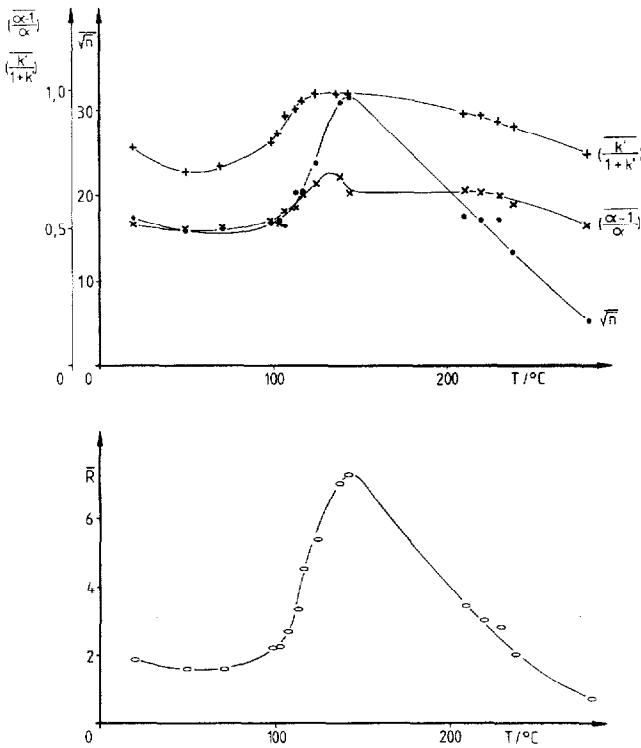


Fig. 11. Dependence of  $(\alpha - 1)/\alpha$ ,  $k'/(1 + k')$ ,  $\sqrt{n}$  and  $\bar{R}$  on temperature for propane as the mobile phase at  $p_e = 43$  bar. Volume flow-rate: 1 ml/min.

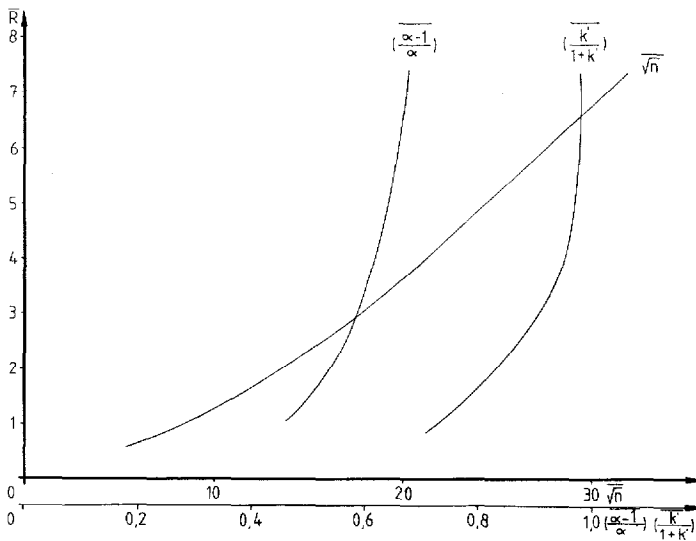


Fig. 12. Average resolution,  $\bar{R}$ , versus  $(\alpha - 1)/\alpha$ ,  $k'/(1 + k')$  and  $\sqrt{n}$  for propane as the mobile phase at  $p_e = 43$  bar. Volume flow-rate: 1 ml/min.

factors can be formally considered as the variable parameter, correlation in linear regression could be a measure of the influence of the individual factors on resolution.

The correlation coefficient was found to be 0.83 for  $(\alpha - 1)/\alpha$  versus  $\bar{R}$ , 0.82 for  $k'/(1 + k')$  versus  $\bar{R}$  and 0.94 for  $\sqrt{n}$  versus  $\bar{R}$ . Hence the variation in plate number has the greatest influence on resolution.

In general,  $\bar{R}$  values at a given pressure are similar at very low and at very high temperatures, but vary greatly around the boiling and critical temperatures. With all eluents the resolution decreases with increasing pressure, *i.e.*, maxima become less expressed and finally vanish, as can be seen from the resolution plot for *n*-pentane at  $p_e = 70$  bar (Fig. 7). Additionally, the maxima are shifted to higher temperatures with increasing pressure.

Some further information could be obtained by varying the column end pressure while the column temperature was kept constant. Fig. 13 shows a plot of average resolution,  $\bar{R}$ , versus column end pressure,  $p_e$ , at four temperatures, obtained with *n*-pentane. At low temperature (50°C), the highest resolution was observed at  $p_e = 20$  bar. At 192°C, slightly below the critical temperature of *n*-pentane ( $T_c = 196.6^\circ\text{C}$ ), the highest  $\bar{R}$  was at 6 bar, whereas at 248 and 282°C the highest  $\bar{R}$  values were found at 20 bar again (*cf.*, Fig. 7).

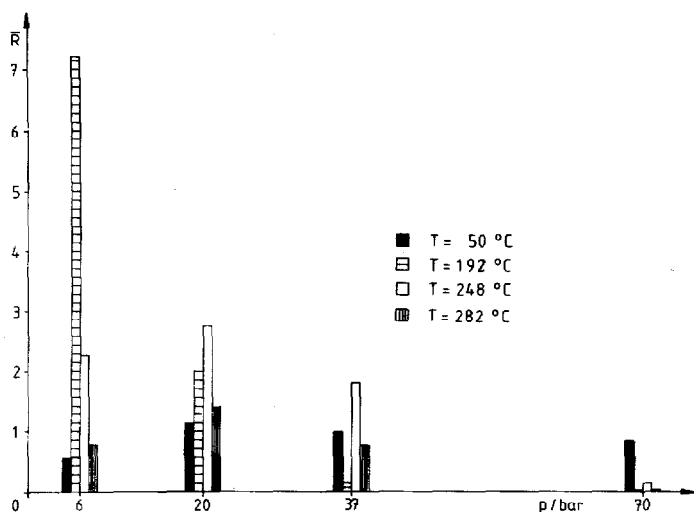


Fig. 13. Average resolution,  $\bar{R}$ , versus column end pressure,  $p_e$ , for *n*-pentane as the mobile phase at four temperatures. Volume flow-rate: 1 ml/min.

Another parameter in addition to temperature and pressure that can be varied easily is the flow-rate, which also has a great influence on separation behaviour. In SFC, the eluents have lower densities and viscosities than in HPLC, which make higher linear velocities, shorter analysis times and narrower peaks possible. Some workers have already demonstrated these advantages by examining the dependence of the effective plate height,  $H$ , on the linear velocity,  $u$ , by Van Deemter plots<sup>3,15,16,25</sup>.  $H$  reaches smaller values over a wider range of linear velocity in SFC.

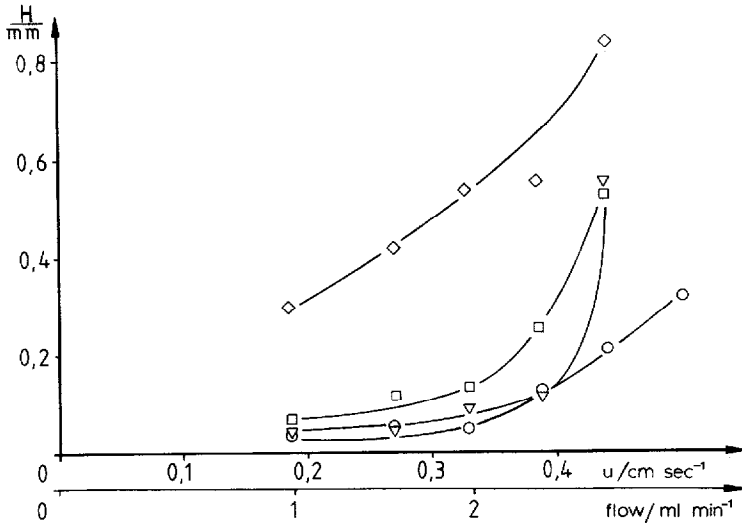


Fig. 14. Dependence of effective plate height,  $H$ , on linear velocity,  $u$ , and volume flow-rate for PAHs in  $n$ -pentane at  $T = 234^{\circ}\text{C}$  and  $p_e = 37$  bar. Symbols as in Fig. 3.

In this work,  $n$ -pentane under operating conditions that provided the best resolution in the supercritical gaseous state ( $p_e = 37$  bar;  $T = 234^{\circ}\text{C}$ ) was used. Fig. 14 shows that  $H$  is very different for the four PAHs naphthalene, anthracene, pyrene and chrysene. The higher the molecular weight of the substrate, the smaller are the  $H$  values.

Although the strong increase in effective plate heights first starts at a linear velocity of about 0.4 cm/sec (Fig. 14), the flow-rate for the best resolution,  $\bar{R}$ , for our system was lower. The decrease in  $\bar{R}$  is almost linear with increasing flow-rate, as shown in Fig. 15. At a flow-rate of 1 ml/min, corresponding to a linear velocity

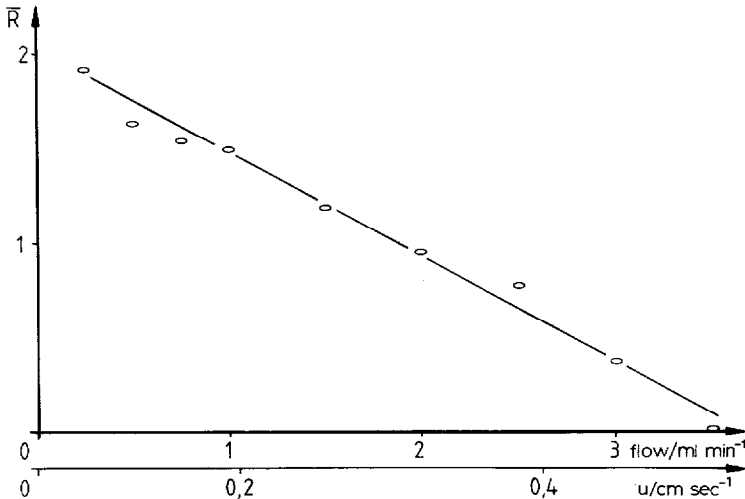


Fig. 15. Average resolution,  $\bar{R}$ , versus volume flow-rate and linear velocity,  $u$ , for PAHs in  $n$ -pentane at  $T = 234^{\circ}\text{C}$  and  $p_e = 37$  bar.

of 0.2 cm/sec, the average resolution reaches 1.5, a reasonable compromise between good resolution and short analysis times.

In Fig. 16,  $k'$  is plotted as a measure of analysis time *versus* volume flow-rate and linear velocity. On raising the flow-rate,  $k'$  first decreases. On exceeding a flow-rate of 3 ml/min ( $u \approx 0.5$  cm/sec), the decrease is replaced by a slight increase, possibly caused by a transition from laminar to turbulent flow<sup>12,15</sup>.

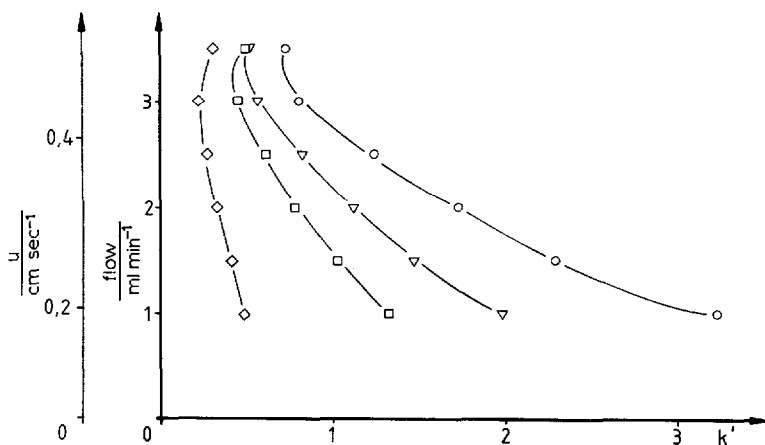


Fig. 16. Dependence of capacity ratios,  $k'$ , on volume flow-rate and linear velocity,  $u$ , for PAHs in  $n$ -pentane at  $T = 234^\circ\text{C}$  and  $p_e = 37$  bar. Symbols as in Fig. 3.

In conclusion, the existence of an optimum temperature to obtain maximum capacity ratios and maximum resolutions could be confirmed when using  $n$ -alkanes as sub- or supercritical eluents. While the resolution depends on retention, expressed by the capacity ratio,  $k'$ , and also on relative retention,  $\alpha$ , and peak width, the latter given by the plate number,  $n$ , the greatest influence on resolution is due to  $n$ . Higher flow-rates and higher pressures decrease the resolution. At the same  $p_r$ , the alkanes of lower  $T_c$  and higher  $p_c$  lead to higher resolution.

Under the present conditions, SFC is superior to HPLC with respect to resolution. Very good separations of the test mixture were possible only when passing from the liquid to the subcritical or supercritical gaseous state. For  $n$ -pentane, at least, gas chromatography at pressures below  $p_c$  is apparently best for obtaining the highest resolutions. However, compounds with poor solubility or low vapour pressure may require eluents of higher density, *i.e.*, chromatography in the supercritical gaseous state.

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