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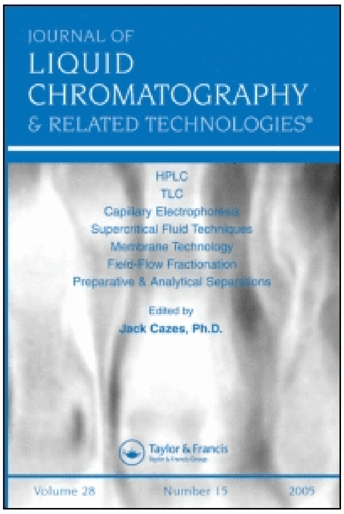

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JOURNAL OF LIQUID CHROMATOGRAPHY, 10(8&9), 1917-1947 (1987)

COMPARISON OF ELUENTS IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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Summary

The chromatographic behavior of a number of low boiling eluents has been compared in supercritical fluid chromatography (SFC) with packed columns. Unmodified silica gel has been used as the stationary phase and a test mixture of polycyclic aromatic hydrocarbons (PAH's) as the substrate. Carbon dioxide, nitrous oxide, trifluoromethane, chlorotrifluoromethane, n-pentane, n-butane, i-butane, propane, ethane, diethylether, and dimethylether have been investigated as mobile phases.

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Of the mobile phases CO_2, N_2O, C_2H_6, CHF_3, and $CClF_3$, which all possess low critical temperatures, comparisons were made at the same pressure and at similar reduced pressure. Poor transport properties were observed for $CClF_3$, exemplified by extremely high capacity ratios for the PAH's. Of the remaining four mobile phases, at the same pressure, the highest capacity ratios were found for C_2H_6, followed by CO_2, N_2O and CHF_3. The highest resolution was obtained with C_2H_6, followed by CHF_3, N_2O, and CO_2. At similar reduced pressure, C_2H_6 showed again the highest capacity ratios, while CHF_3, CO_2, and N_2O had lower values. The resolution showed a similar order.

For a given mobile phase, capacity ratio and resolution were correlated. To a first approximation, a higher capacity ratio leads to higher resolution. This correlation differs, however, for different eluents. For instance, among all mobile phases, the highest resolutions at a given k' were found for CHF_3.

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Introduction

For HPLC the choice of a suitable mobile phase is of greatest importance. Because this may be expected for supercritical fluid chromatography (SFC), a comparative study has been undertaken for a series of mobile phases

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which are suitable for SFC. Some of these phases, like CO_2 and pentane, have frequently been used in SFC, while others, like ethane and CHF_3, have not or only rarely been used. The choice of a mobile phase depends in large measure on the solubility power of the mobile phase for the substrate to be analysed. The common rule that "like dissolves like" is valid also for supercritical fluids if not only the molecular structure, but also the density of the supercritical fluid is considered. Therefore, the solubility parameter, δ , of Hildebrandt and Scott <1>, as extended by Giddings to supercritical fluids <2,3>, considers not only the critical pressure, p_c, as a molecular constant, but also the reduced density, ρ_r, as a variable of state

$$1) \qquad \delta\ (gas) = (3\ p_c)^{0,5} \cdot \frac{\rho\ (gas)}{\rho_c} = (3\ p_c)^{0,5} \cdot \rho_r$$

According to this simple equation, fluids of high p_c and ρ_r should lead to a high δ. With a higher δ the solubility power for more polar substrates usually increases. However, the solubility parameter concept does not account for specific interactions between fluid and substrate, e.g. for specific hydrogen bonding. Modification of Eq. 1 has been suggested <2,3> and the δ have also been calculated considering a thermodynamic equation of state <4,5>. Again, specific interactions have not been considered.

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Besides solubility, the selection of a supercritical mobile phase clearly depends on the critical temperature, T_c. The T_c should not be higher than the thermal stability of the substrate permits. On the other hand, it is convenient to choose an eluent whose T_c is above ambient temperature. In this case the mobile phase can be pumped and metered as a liquid which, at the same pressure, possesses a lower compressibility than the supercritical gas. Moreover, the δ and the solubility power tend to decrease with decreasing T_c.

Mobile phases having a T_c not far above ambient possess the advantage of allowing low operating temperatures for SFC. They also allow admixing of a second component of higher T_c to the mobile phase, without raising the T_c of the resulting eluent to excessive levels. The second component is usually added for its higher solubility power. CO_2 with T_c = 31.3 °C has often been used because of its low price, noninflammability and nontoxicity. Its good dissolution properties for nonpolar to moderately polar substrates is indicated by a relatively high p_c of 78.5 bar. N_2O possesses similar critical data, but due to its small permanent dipole moment it may be capable of specific interactions. Fluorocarbons having a T_c shortly above room temperature are CHF_3 and $CClF_3$. Both are noninflammable and of low toxicity, but are more expensive in chromatographic purity and may have harmful effects on the ozone layer of the upper atmosphere. In the homologous series of the alkanes, it is only C_2H_6 which has a low T_c above room temperature.

The results obtained with the five eluents of low T_c are presented in this work, together with results on mobile phases of higher T_c studied earlier, i.e. alkanes <6,7> and linear ethers <8>. The earlier work on alkanes and ethers has given capacity ratios, k', and resolutions, R, in dependence of temperature, T, and column outlet pressure p_e <6-9>. As an outstanding feature, the k' and R exhibited temperature dependent maxima above T_c. It is of interest now whether the five mobile phases of low T_c will show a similar behavior.

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Experimental

The apparatus and the column have been described previously <8>. All chromatographic runs were performed on columns (25 x 0.46 cm) packed with unmodified silica gel and a test mixture of the polycyclic aromatic hydrocarbons naphthalene, anthracene, pyrene and chrysene (PAH's) as the substrate. Purities and sources of mobile phases and substrates are given in Table I. For all runs the flow rate was 1 ml/min, measured at the pumps in the liquid state and checked volumetrically at the column outlet.

Table I: Mobile phases and substrates

pentane	technical product	dried over sodium, distilled
butane	Linde AG, Höllriegelskreuth, F.R.G.	99.5 %
i-butane	Linde AG	99.5 %
propane	Linde AG	99.5 %
ethane	Messer-Griesheim, Hermülheim, F.R.G.	99.5 %
diethyl ether	technical product	dried over sodium distilled
dimethyl ether	Merck AG, Darmstadt F.R.G	99 %, 0.3 % methanol
CO_2	Messer-Griesheim	99.995 %
N_2O	Messer-Griesheim	99.8 %
CHF_3	Messer-Griesheim	99.8 %
$CClF_3$	Messer-Griesheim	99.8 %
heptane	technical product	dried over sodium, distilled
naphthalene, anthracene, pyrene, chrysene		recrystallized

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Capacity ratios, k', and resolutions, R, were calculated as described earlier <10>:

$$2) \qquad k' = \frac{t_r - t_o}{t_o}$$

$$3) \qquad R_{ij} = \frac{f_{ij}}{g_{ij}} + \frac{d_{ij}}{w'_i + w'_j} \cdot \sqrt{\ln 4}$$

4) $$R_m = \frac{\sum_{1}^{n} R_{ij}}{n}$$

t_r = retention time

t_o = dead time

R_{ij} = resolution between neighboring peaks i and j

f_{ij} = depth of valley between neighboring peaks, as measured by starting from the average peak height

g_{ij} = average peak height

d_{ij} = baseline distance between tangent on peaks

w' = peak width at half height

R_m = mean resolution

n = total number of pairs of neighboring peaks (here: n = 3)

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Results and discussion

The critical data and the boiling points of all mobile phases are collected in Table II. The low boiling temperatures of CO_2, N_2O, C_2H_6, CHF_3, and $CClF_3$ and the prepressurization of the mobile phase by helium in the storage tank require considerable working pressure to prevent gas formation at ambient temperature in the apparatus, e.g. in the detector. This is particularly true for C_2H_6 and $CClF_3$ which require a rather high minimum column outlet pressure p_e. The temperature and the pressure ranges for the chromatographic runs are listed in Table III.

Table II: Critical data and boiling points of eluents

eluent	critical temperature T_c/°C	critical pressure p_c/bar	critical density ρ/g cm^{-3}	boiling temperature T_b/°C
n-pentane	196.5	33.7	0.237	36.1
n-butane	152.0	38.0	0.228	- 0.5
i-butane	135.0	36.5	0.221	-11.7
propane	96.7	42.5	0.217	-42.1
ethane	32.3	48.8	0.203	-88.7
diethyl ether	192.6	35.6	0.265	34.6
dimethyl ether	126.9	52.6	0.271	-24.8
CO_2	31.3	73.8	0.468	-78.5 (s)*
N_2O	36.4	72.7	0.435	-88.5
CHF_3	25.6	48.4	0.516	-82.1
$CClF_3$	28.9	39.2	0.579	-81.5

(s)* = sublimation

Comparison between different mobile phases may be conducted in different ways. Generally applicable is a comparison at the same reduced free volume <11> since this comparison is independent of the molecular weight of the eluents. Related is a comparison at equal reduced density, because the reduced density and free volume are both relative densities. Using simply the same density is less informative, an exception being homologous series, because

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Table III: Experimental temperature and pressure ranges

eluent	temperature/ °C	pressure/bar
pentane	20 - 280	6, 20, 36, 70
butane	20 - 280	39, 70
i-butane	20 - 280	37, 70
propane	20 - 280	43, 70
ethane	20 - 250	180, 210, 250
diethyl ether	20 - 280	6, 38, 70
dimethyl ether	20 - 280	56, 70
CO_2	20 - 250	120, 150, 180, 210, 250
N_2O	20 - 230	120, 180, 250
CHF_3	20 - 200	150, 200
$CClF_3$	100 - 200	250, 300

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then the same density represents approximately the same free volume <12>. For practical reasons, a comparison at equal pressure and temperature or at the same reduced pressure and temperature is useful. Comparison at the same capacity ratio, k', has also been used in SFC <13> and leads to a comparison by way of a chromatographic parameter.

The behavior of k' versus temperature at p_e = const. for the two fluorinated hydrocarbons CHF_3 and $CClF_3$ is presented in Figs. 1 and 2, respectively. The CHF_3 shows

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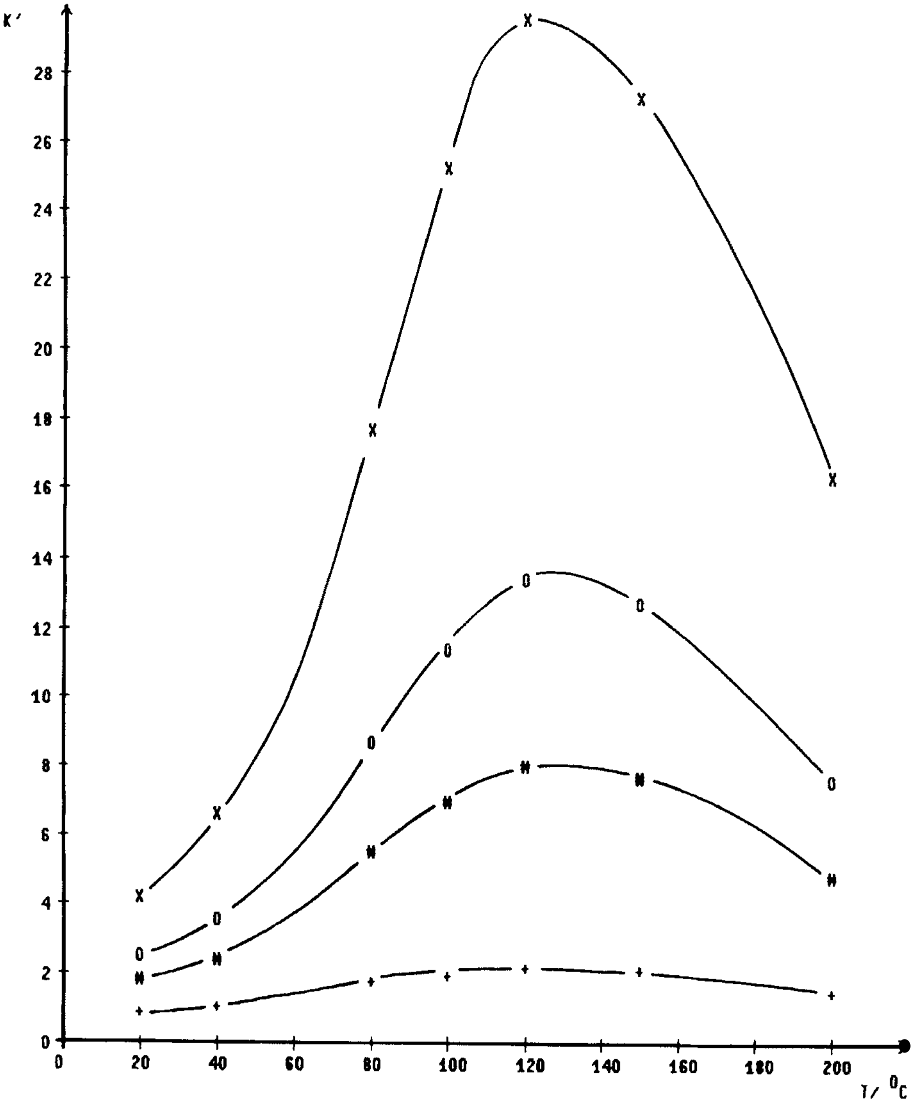

Fig. 1 Dependence of capacity ratios, k', on column temperature, T. Eluent: CHF_3 (Freon 23). Column end pressure, p_e: 150 bar. Substrates: (+) naphthalene, (#) anthracene, (O) pyrene, (X) chrysene (PAH's).

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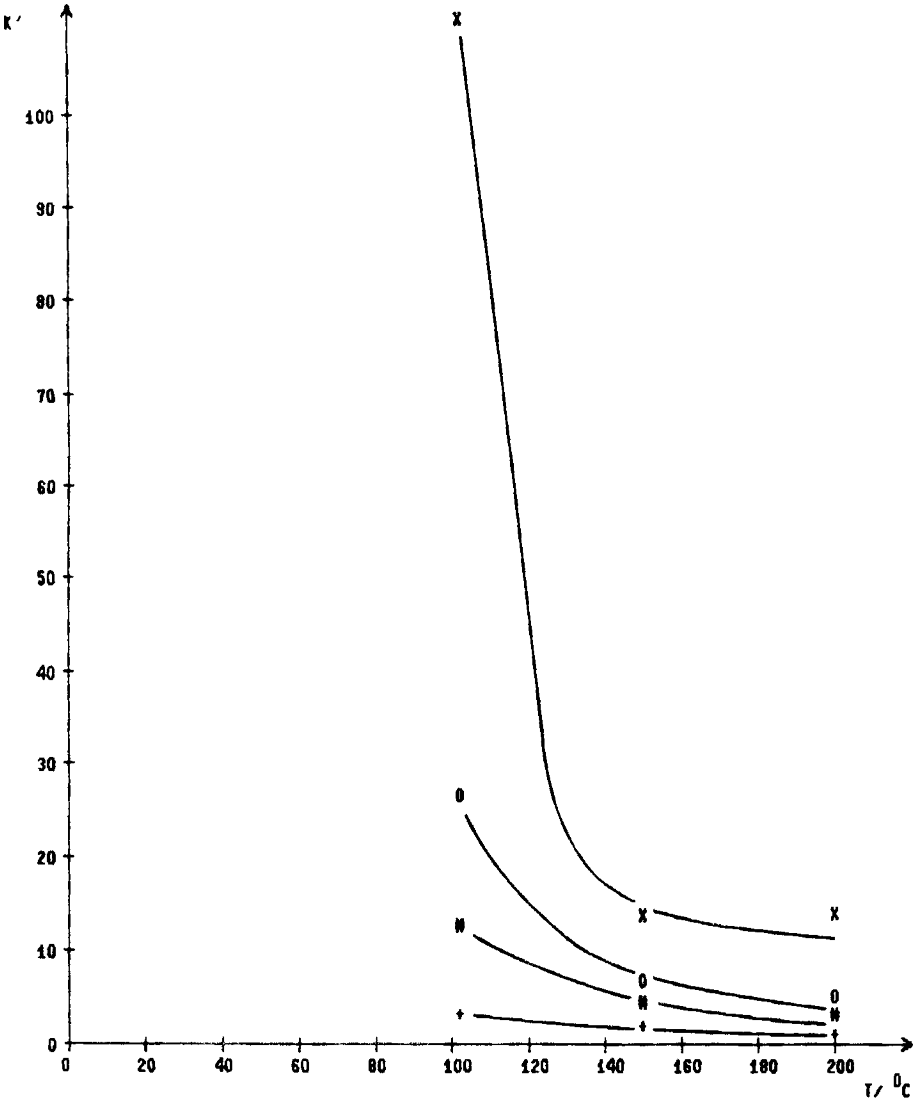

Fig. 2 Dependence of capacity ratios, k', on column temperature, T. Eluent: $CClF_3$ (Freon 13). p_e: 250 bar. Substrates as in Fig. 1.

a strong maximum of k' for the four PAH's in analogy to the maxima found for eluents of higher T_c, i. e. alkanes <6,7> and ethers <8>. For $CClF_3$ very high k' were indicated at temperatures between T_c and 100 °C, values which could not be determined because of very slow elution. The very high k' are found despite of an increase in pressure from p_e = 150 bar for CHF_3 to p_e = 250 bar for $CClF_3$. Therefore, the elution power and probably also the dissolution ability of $CClF_3$ is much smaller than for CHF_3 and too small to yield measurable k'. As a consequence, the $CClF_3$ is not included further in the comparisons between mobile phases.

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The T_c of CO_2, N_2O, C_2H_6, and CHF_3 are all between 25 and 37 °C. Nevertheless, there exist large differences in k' at the same p_e. For chrysene as the substrate, the k'(c) (c = chrysene) versus T curves of different p_e are shown in Figs. 3 - 5. The highest k' are found for C_2H_6, followed by CO_2, N_2O, and CHF_3. The outstanding feature of the isobaric curves in Figs. 3 - 5 is a more or less well developed maximum. The temperature at which the maximum occurs and the pressure dependence of this temperature is different for different eluents. For instance, the k' maximum for C_2H_6 is located at about 100 °C at a pressure of 180 bar (Fig. 3). This is significantly below the temperature of the maximum for N_2O or CO_2 which both lie at approximately 120 °C. At

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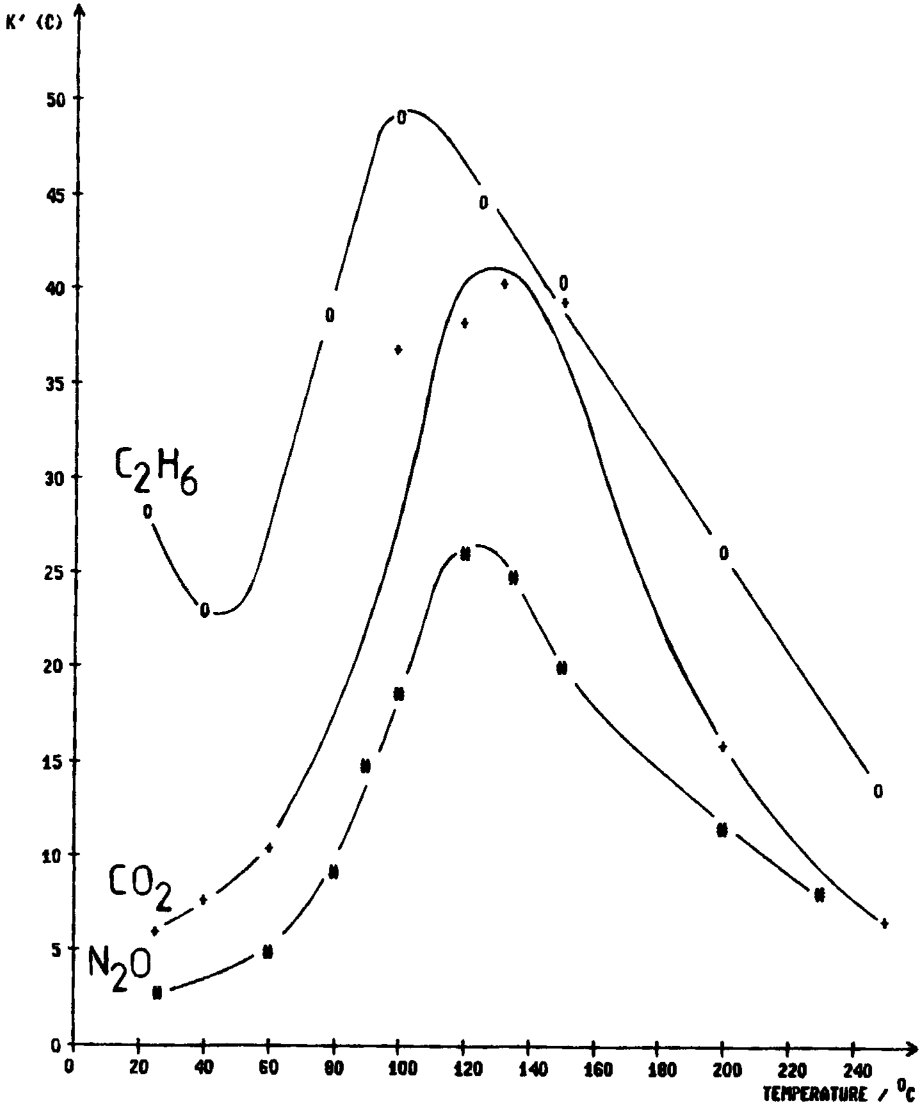

Fig. 3 Dependence of the capacity ratios of chrysene, k'(C), on column temperature, T. Eluents: (+) CO_2, (#) N_2O, (O) C_2H_6. p_e: 180 bar.

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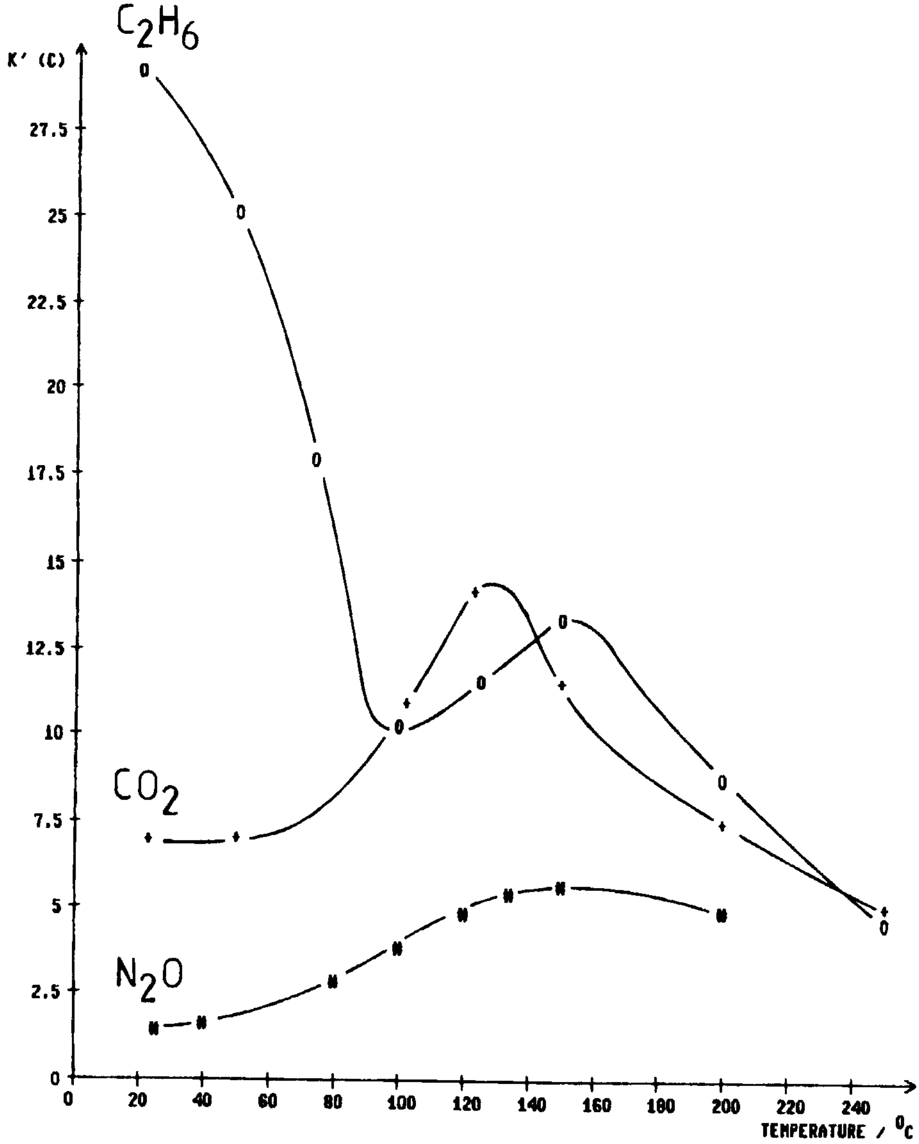

Fig. 4 Dependence of the capacity ratios of chrysene, k'(C), on column temperature, T. Eluents: (+) CO_2, (#) N_2O, (O) C_2H_6. p_e: 250 bar.

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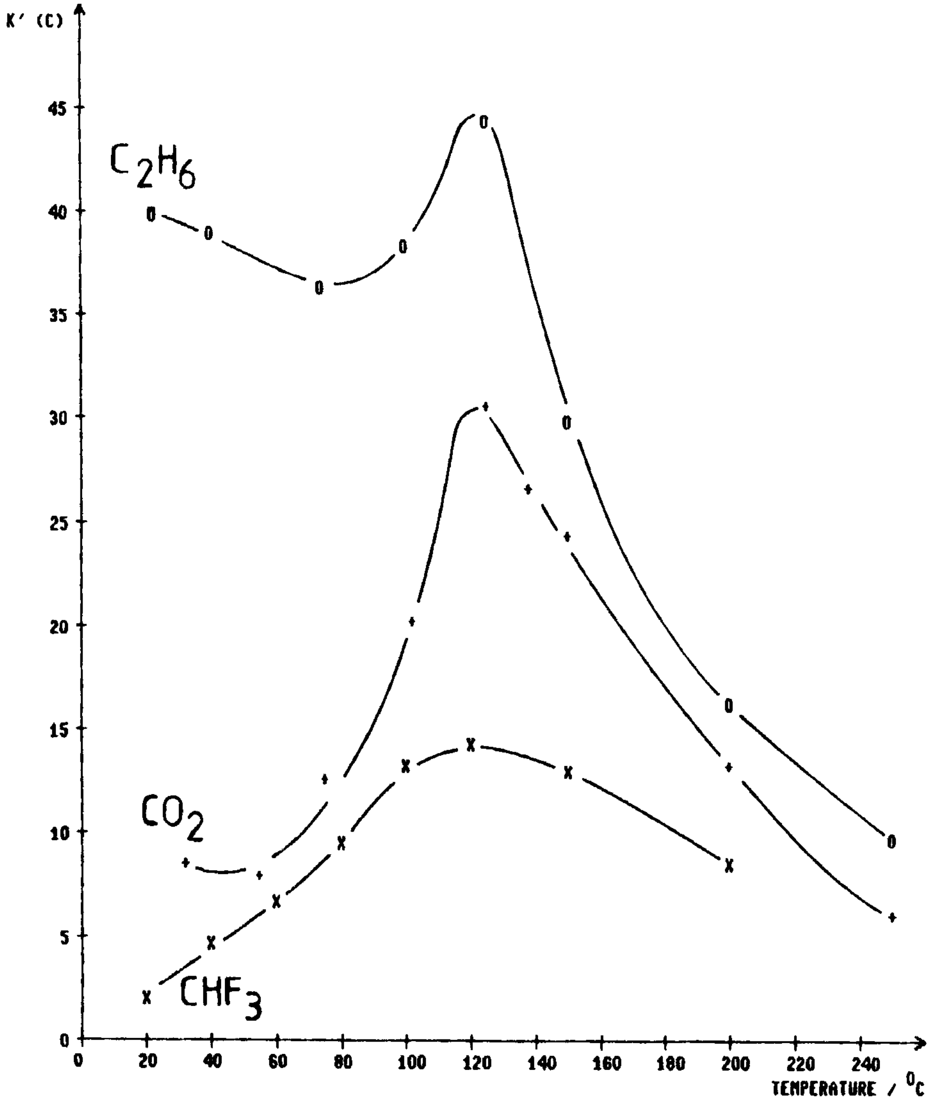

Fig. 5 Dependence of the capacity ratios of chrysene, k'(C), on column temperature, T. Eluents: (+) CO_2, (O) C_2H_6, (X) CHF_3. p_e: 210 bar for CO_2 and C_2H_6, 200 bar for CHF_3.

250 bar, however, the C_2H_6 and N_2O maxima are situated both at about 160 °C, while that for CO_2 has hardly moved (Fig. 4). At an intermediate pressure of 210 bar, the maxima of C_2H_6 and CO_2 are seen at the same temperature of 120 °C. Besides the dependence of location of the maximum on pressure, there is a dependence of area and height of the maximum on this variable. A higher pressure reduces both area and height (cf. Figs 3 and 4). This type of pressure dependence of area and height of the k' maxima has also been found before <6,7>.

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The mean resolution R_m, obtained for the four mobile phases, is given in Figs. 6 - 8. The chromatographic conditions are the same as for Figs. 3 - 5. Accordingly, C_2H_6 yields not only the highest k', but also the highest R_m. In Table IV the eluents have been put in approximate order of increasing k' and R_m. The order at equal p_e is for k' and R_m not the same since CO_2 and CHF_3 have changed places. Therefore, a high R_m at p_e=const. is not necessarily obtained at the expense of a higher k', i. e. higher analysis time. The temperature of the R_m maximum is found close to that of the k' maximum, the largest differences between the two being found for C_2H_6 in Figs. 3 - 8. Like the k' maxima, the maxima for R_m move to higher temperatures and become smaller in area and height with rising pressure. Also noteworthy is, that C_2H_6 exhibits very high k' and R_m, both in the

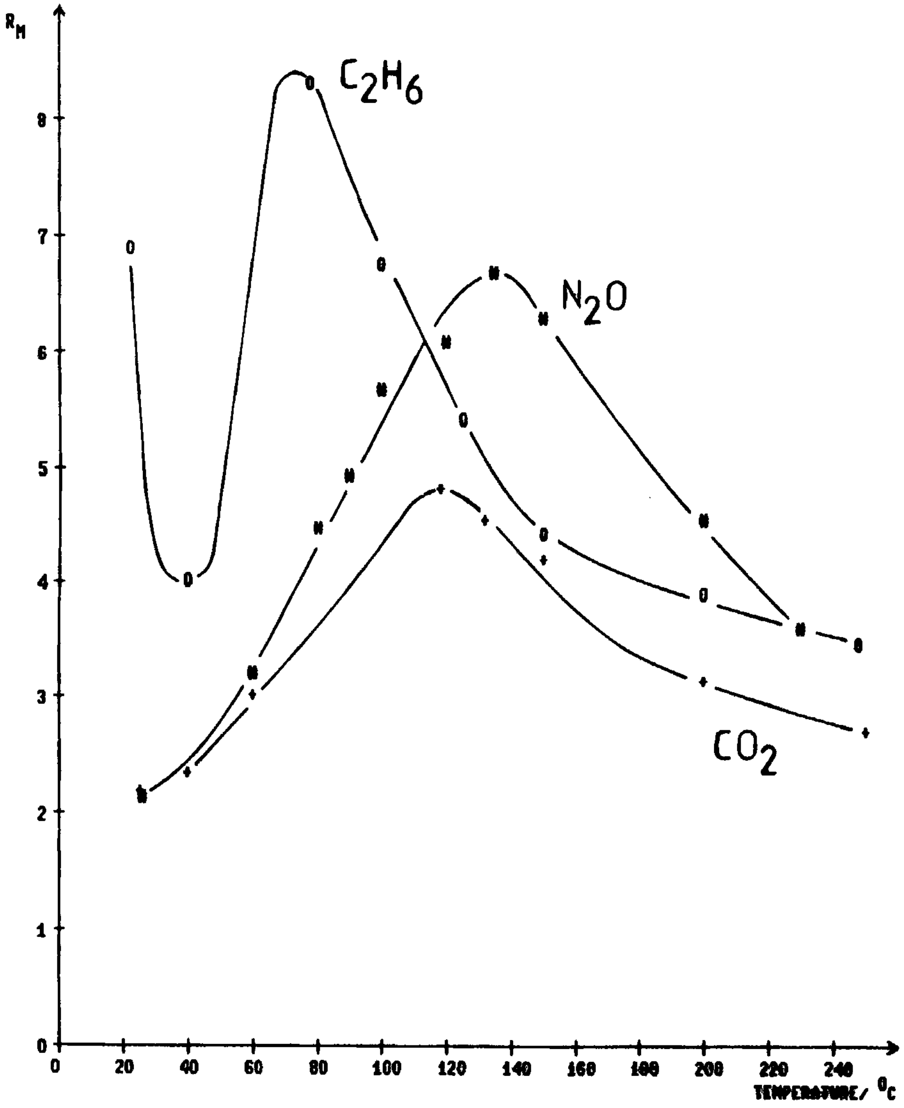

Fig. 6 Dependence of the mean resolution between the four PAH's, R_m, on column temperature, T. Eluents: (+) CO_2, (#) N_2O, (O) C_2H_6. p_e: 180 bar.

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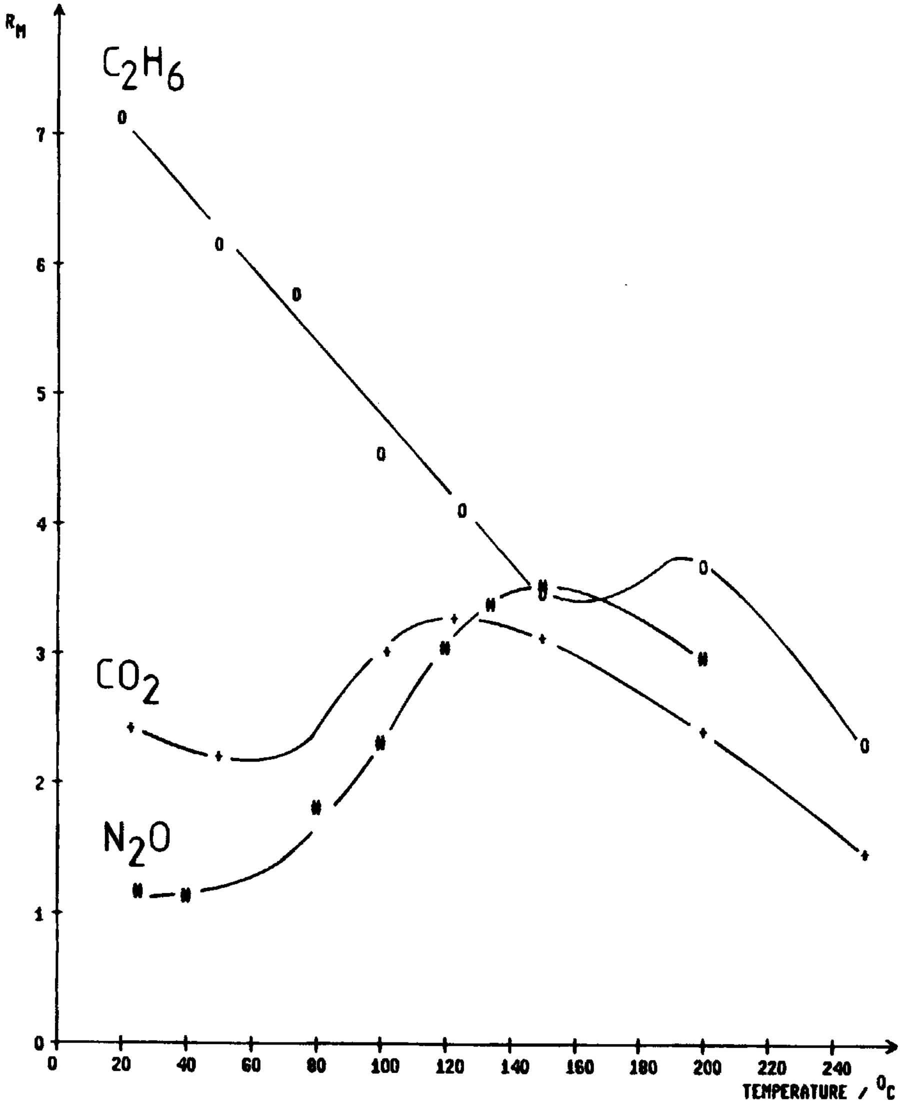

Fig. 7 Dependence of the mean resolution between the four PAH's, R_m, on column temperature, T. Eluents: (+) CO_2, (#) N_2O, (O) C_2H_6. p_e: 250 bar.

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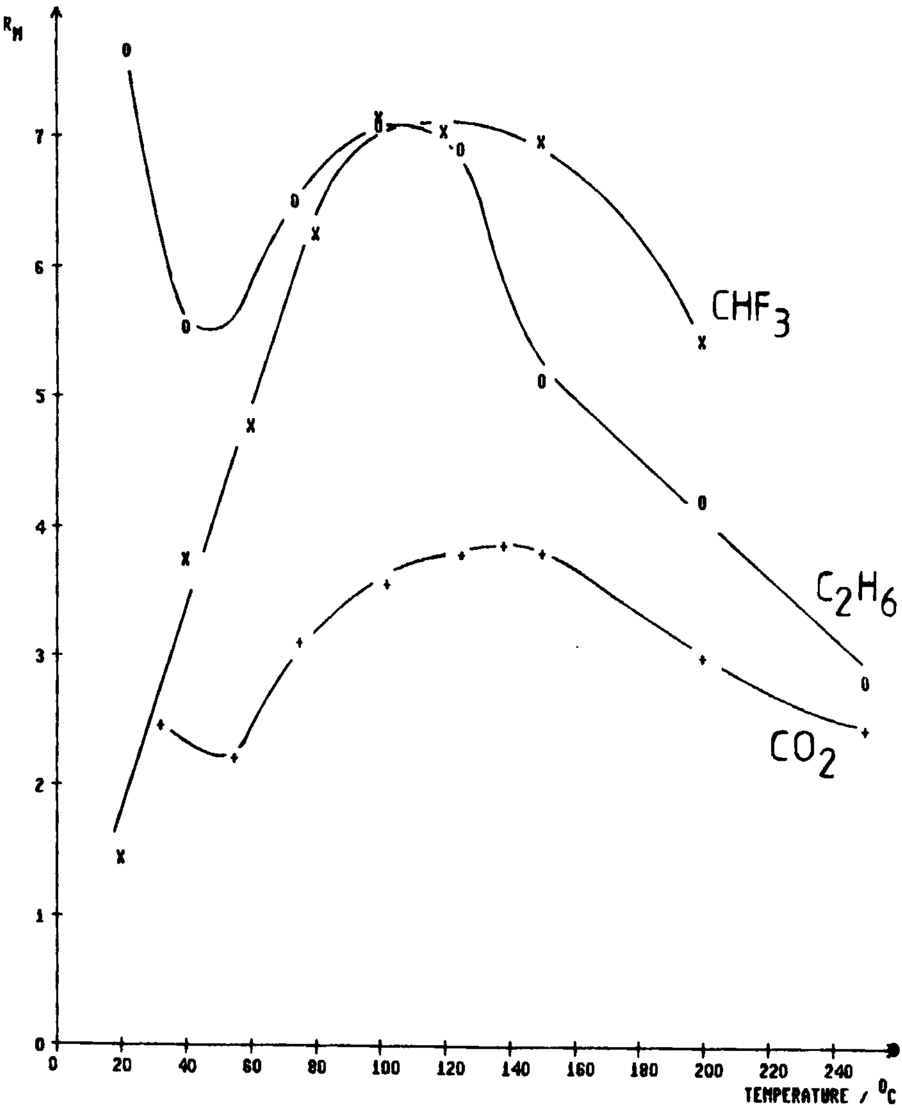

Fig. 8 Dependence of the mean resolution between the four PAH's, R_m, on column temperature, T. Eluents: (+) CO_2, (0) C_2H_6, (X) CHF_3. p_e: 210 bar.

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Table IV: Comparison of k' and R for eluents of low T_c. Comparisons carried out at equal pressure, p_e, at equal reduced pressure p_r, or at equal capacity ratio, k'.

equal p_e	k' :	CHF_3	$<$	N_2O	$<$	CO_2	$<$	C_2H_6
	R_m :	CO_2	$<$	N_2O	$<$	CHF_3	$\approx$	C_2H_6
equal p_r	k' :	N_2O	$<$	CO_2	$\approx$	CHF_3	$<$	C_2H_6
	R_m :	CO_2	$\approx$	N_2O	$<$	CHF_3	$\approx$	C_2H_6
equal k'	R(NA) :	$n\text{-}C_5H_{12} \approx C_4H_{10}O < CO_2 < N_2O < CHF_3$						

supercritical and in the liquid region. At higher pressures, the k' and R_m observed for C_2H_6 near T_c are even larger than those at the maximum in the supercritical region.

Conducting the comparison between different mobile phases at equal reduced pressures, p_r, is expected to lead to results which are different from those at the same pressure, p_e. The critical pressures of CO_2 and N_2O are much larger than for C_2H_6 and CHF_3. Therefore, a comparison at equal p_r for CO_2 and N_2O on one hand, and C_2H_6 and CHF_3 on the other, is equivalent to a comparison at a higher p_e for the first two eluents to a lower p_e for the last two eluents. In Figs. 9 and 10 such

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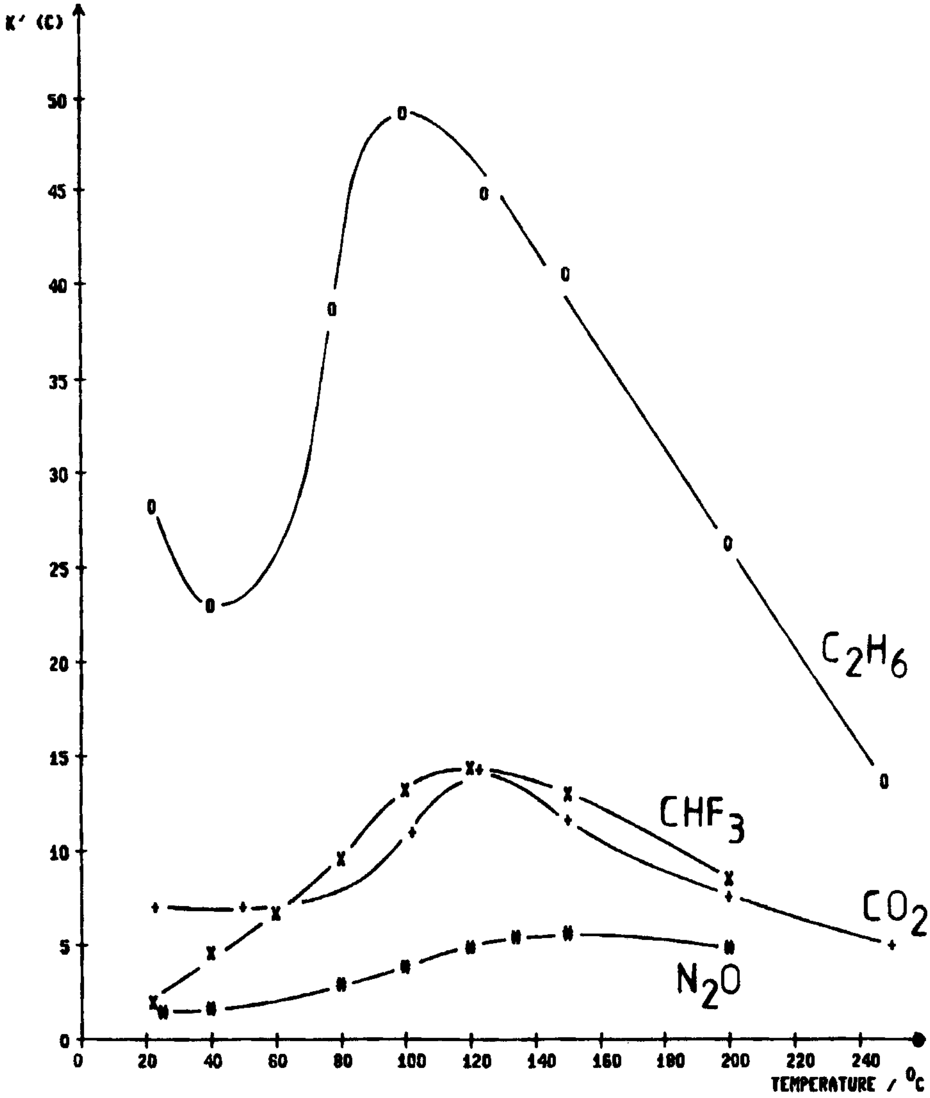

Fig. 9 Dependence of the capacity ratios of chrysene, k'(C), on column temperature, T at similar reduced pressures, p_r. Eluents and pressures:

(+) CO_2, p_e = 250 bar, p_r = 3.39;

(#) N_2O, p_e = 250 bar, p_r = 3.44;

(O) C_2H_6, p_e = 180 bar, p_r = 3.71;

(x) CHF_3, p_e = 200 bar, p_r = 4.13.

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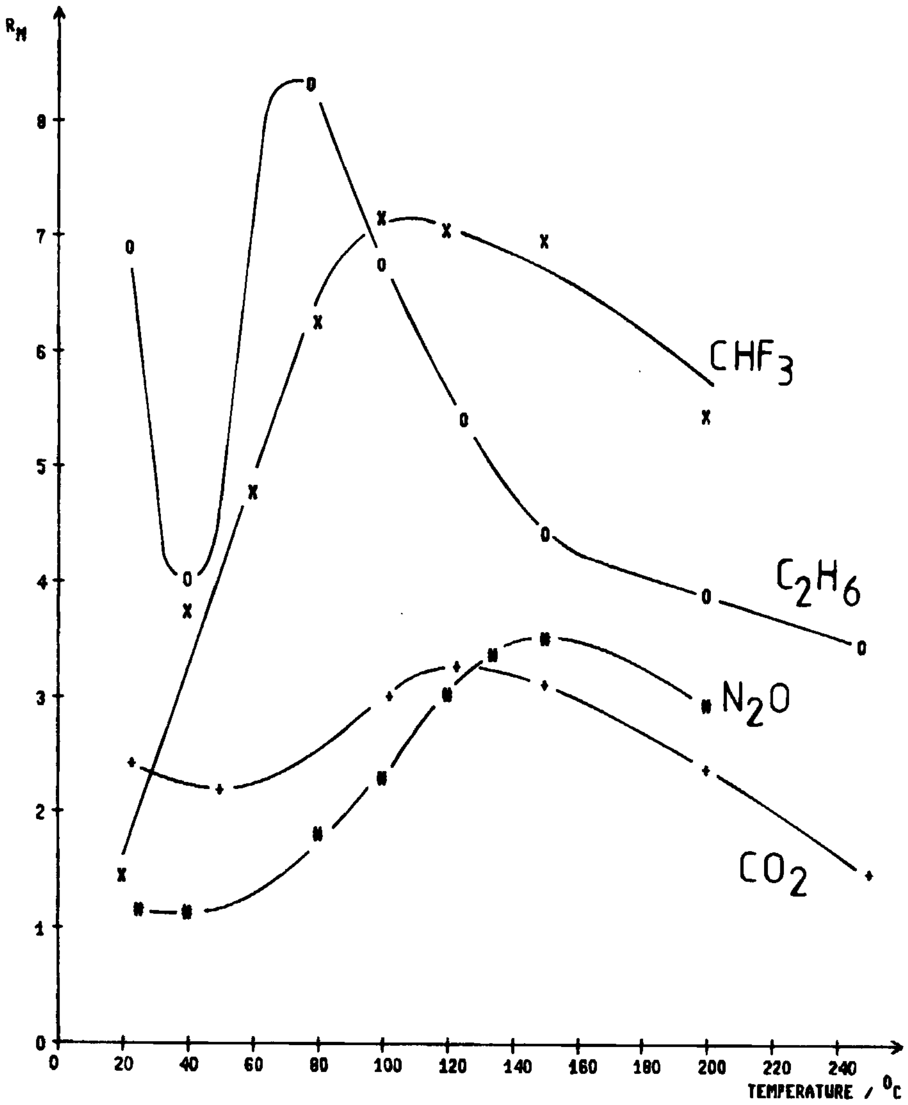

Fig. 10 Dependence of the mean resolution between the four PAH's, R_m, on column temperature, T, at similar reduced pressures, p_r. Eluents and pressures: (+) CO_2, p_e = 250 bar, p_r = 3.39; (#) N_2O, p_e = 250 bar, p_r = 3.44; (O) C_2H_6, p_e = 180 bar, p_r = 3.71; (X) CHF_3, p_e = 200 bar, p_r = 4.13.

a comparison is seen for k' and R_m. CO_2 and N_2O (p_r (CO_2) = 3.39; p_r (N_2O) = 3.44) show about the same area under the R_m-curve and the same height of the maxima (Fig. 10), but these features are smaller for the k'-curves of N_2O versus CO_2 (Fig. 9). C_2H_6 and CHF_3 (p_r (C_2H_6) = 3.71; p_r (CHF_3) = 4.13) exhibit also about the same area and height for R_m, but C_2H_6 has a decidedly higher k'. Because the t_o are similar for C_2H_6 and CHF_3, analysis time is in favor of CHF_3 at comparable resolution. Comparing now CO_2 and N_2O on one hand to C_2H_6 and CHF_3 on the other, it is to be admitted that the p_r for the latter are significantly higher. However, the differences between the two pairs of eluents are so large as to make the smaller k' and R_m for CO_2 and N_2O certain. The k' and R_m will become even smaller when the p_r would be increased to meet the p_r of C_2H_6 and CHF_3. Also, according to Eq. 1, the eluents CO_2 and N_2O give higher solubility parameters than C_2H_6 and CHF_3 at conditions of comparable p_r because the p_c of the former two phases is higher than those of the latter.

A comparison between mobile phases at the same k' is per definition a comparison at the same relative elution time, i. e. at the same ratio of the times the substrate spends in the stationary and in the mobile phase. Equal k' does, however, not necessarily mean equal retention times, t_r,

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because the same capacity ratio for different mobile phases is obtained by different t_o. This arises because for different p - T pairs the liquid volume feed rate was kept constant. Nevertheless, k' gives also an indication of analysis time.

Prior to comparison between different mobile phases at the same k', it is important to know whether there exists a correlation between R_m and k' already for a single mobile phase. The data for CO_2 at different p_e - T pairs are given for Fig. 11 as an example, whereby only runs at supercritical conditions are included. A coarse but definite correlation becomes apparent between the resolution of naphthalene and anthracene, R(NA), and the capacity ratio of anthracene, k'(A). The band, defining the range of scatter is at lower k' relatively narrow and of high slope whereas at higher k' wider and of lower slope. In the k' range between 0 and 10, which is the range of greatest practical importance, a small increase in k' will be accompanied by a large increase in R.

Because a correlation might exist between R and k' also for other single mobile phases, the R(NA) versus k'(A) data are plotted in Fig. 12 for the five alkanes n-pentane, n-butane, i-butane, propane, and ethane. Although the scatter for a given alkane is considerable and the scattering ranges overlap each other, correlations of the

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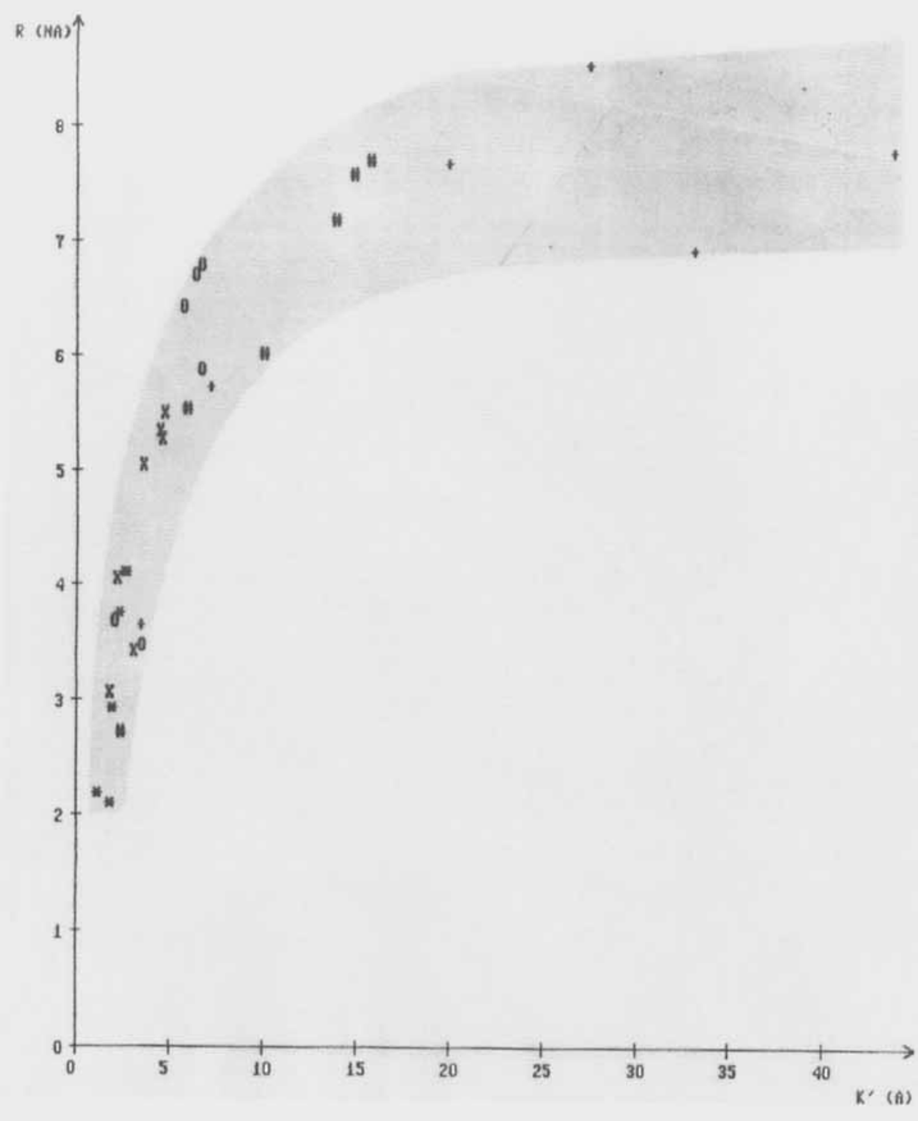

Fig. 11 Dependence of the resolution between naphthalene and anthracene, R(NA), on the capacity ratio of anthracene, k'(A). Eluent: CO_2. p_e: (+) 120 bar, (#) 150 bar, (O) 180 bar, (X) 210 bar, (*) 250 bar (ρ_r = 1.63 - 3.39). Different temperatures as shown in Table III.

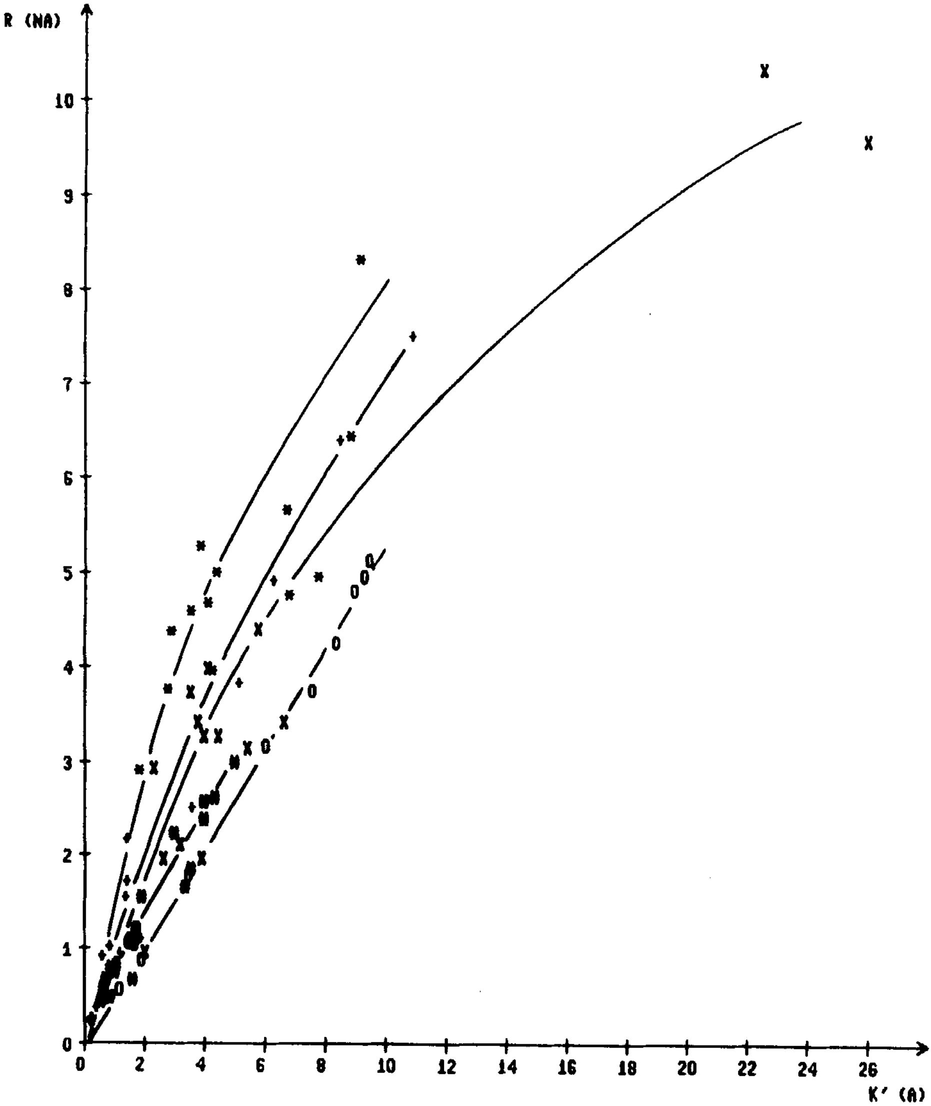

Fig. 12 Dependence of the resolution between naphthalene and anthracene, R(NA), on the capacity ratio of anthracene, k'(A). Eluents: (+) pentane, (#) butane, (O) i-butane, (X) propane, (*) ethane. Different p_e and T.

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individual alkanes apparently not only exist but the correlations also seem to differ from each other to a significant extent. In Fig. 13 this type of comparison is extended to mobile phases which do not belong to the same homologous series or the same class of compounds. Here, the differences between the curves are larger than in Fig. 12, particularly at higher k'. Larger differences in the performance of the eluents in terms of resolution and analysis times is therefore observed. Thus the CHF_3 combines high resolution with high analysis speed, particularly at higher k', while this is less the case for N_2O, CO_2, pentane, or diethylether.

In Fig. 14 the resolution of all peak pairs, R_m, is plotted versus k' of the most retained solute, chrysene, instead of only the resolution between naphthalene and anthracene, R(NA). In this way additional experimental data at higher k' are included in the comparison between different mobiles phases. Obviously, the differences of the mobile phases in Fig. 14 are basically the same as in Fig. 13.

The present study has been carried out to provide practical guide lines for the selection of mobile phases in SFC. Because the study has been carried out solely with unmodified silica gel and a test mixture of polycyclic aromatic hydrocarbons, the comparisons described should be extended to other stationary phases and other substrates.

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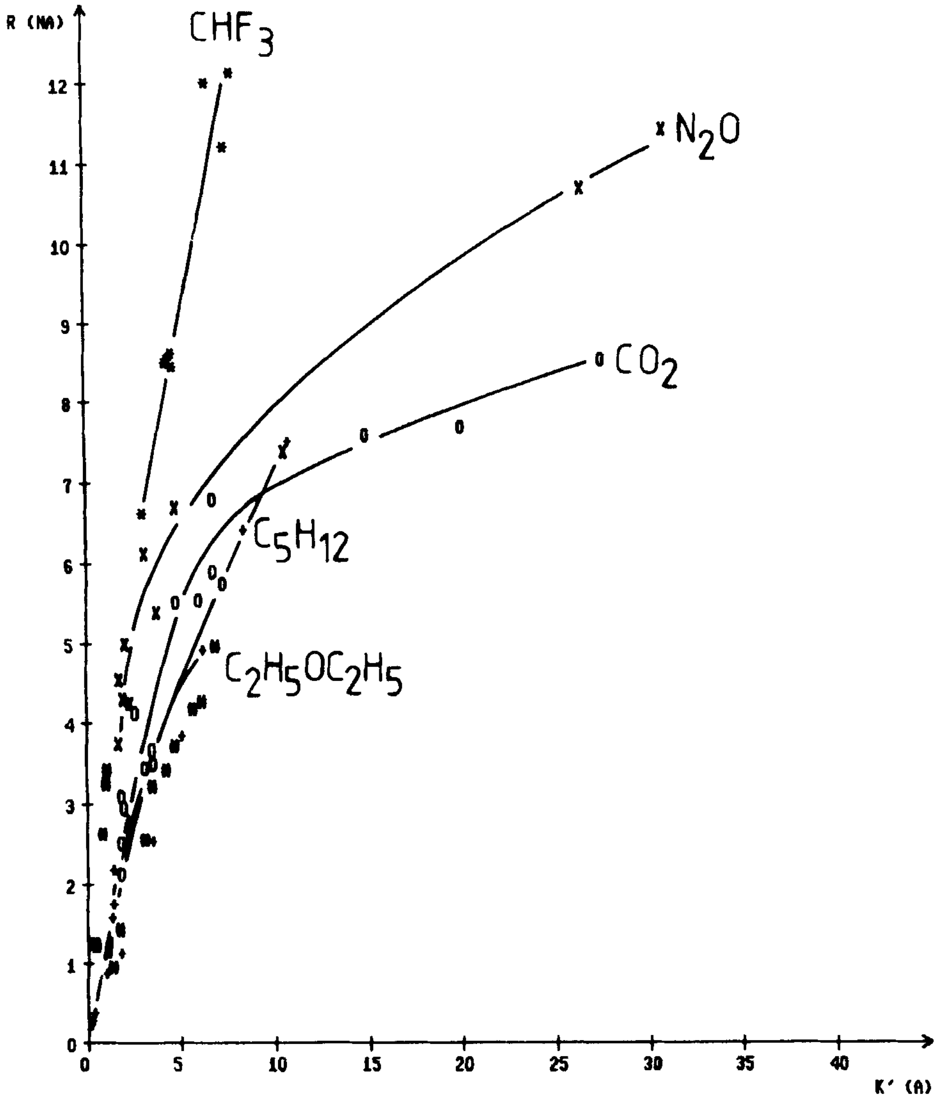

Fig. 13 Dependence of the resolution between naphthalene and anthracene, R(NA), on the capacity ratio of anthracene, k'(A). Eluents: (+) pentane, (#) diethylether, (O) CO_2, (X) N_2O, (*) CHF_3. Different p_e and T.

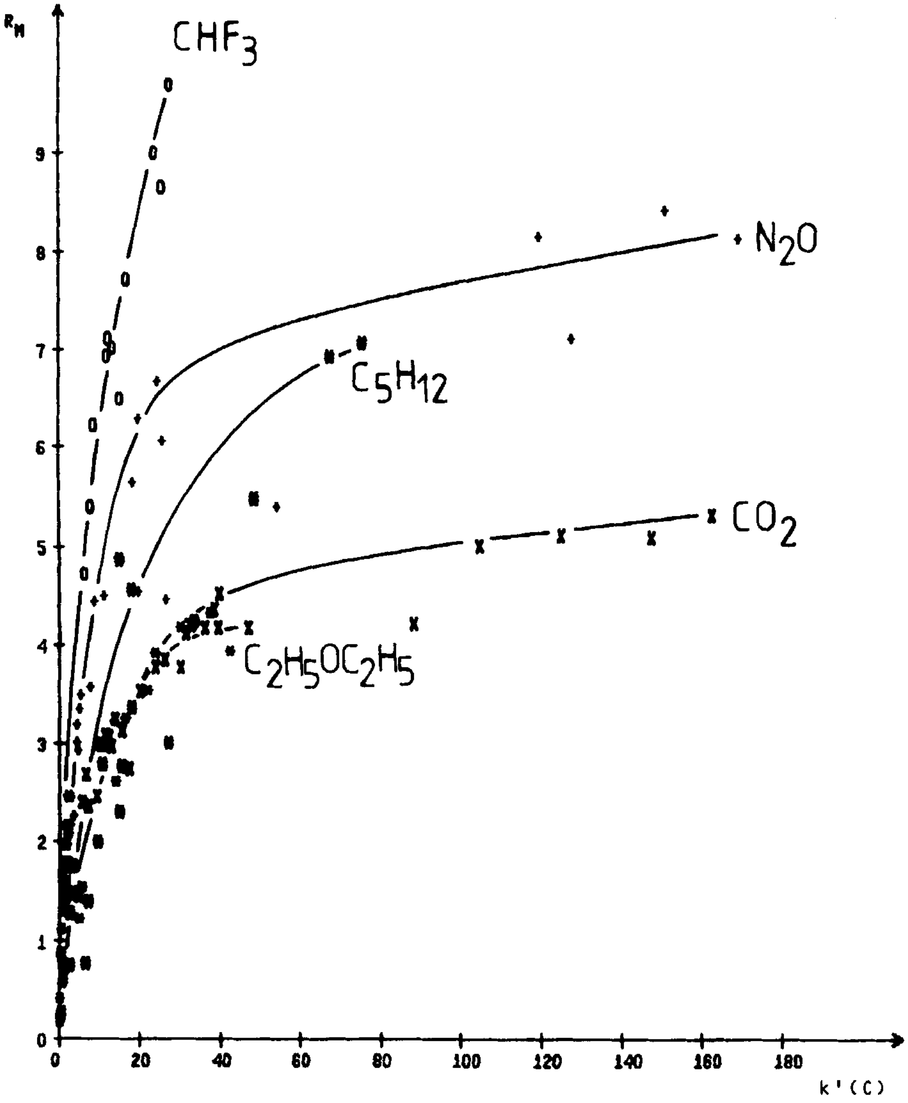

Fig. 14 Dependence of the resolution between all PAH's, R_m, on the capacity ratio of chrysene k'(C). Eluents: (#) pentane, (*) diethylether, (X) CO_2, (+) N_2O, (O) CHF_3. Different p_e and T.

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