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COMPARISON OF CARBON DIOXIDE AND PENTANE AS ELUENTS IN SUPERCRITICAL FLUID CHROMATOGRAPHY AS BASED ON THE FREE VOLUME

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SUMMARY

In supercritical-fluid chromatography, the capacity factors, k' , were found to increase with increasing free volume in carbon dioxide or pentane as mobile phase, and the same occurs for the selectivities, α . At the same free volume, a direct comparison between chemically different fluids is possible. The k' values for pyrene and chrysene as substrates are much larger in carbon dioxide than in pentane at the same free volume. This is to a large extent due to a lower solubility in carbon dioxide. The α values are also larger in carbon dioxide than in pentane.

INTRODUCTION

For supercritical-fluid chromatography (SFC), a considerable number of different mobile phases, either singly or as a mixture, have been introduced. Among the mobile phases most often employed are carbon dioxide and pentane. The choice of a fluid and its temperature, pressure and flow-rate depends on the specific separation problem. A minimum requirement is a solubility sufficient for transport, and retention by the stationary phase. The choice of a fluid is facilitated, if prior comparisons between fluids have already been carried out. Such comparisons have previously been reported under isobaric^{1,2} and isodense^{3,4} conditions.

The free volume is an important parameter governing the intermolecular forces responsible for solubility. Thus the intermolecular forces which depend on the chemical nature of the mobile phase are considered as a function of the free volume. The free volume may be defined, for instance, as the volume which exceeds that required for a close packing of the molecules in the crystalline state. Alternatively, it may be defined as the volume remaining after deduction of the volume occupied at a specified high pressure, which leaves essentially no free volume. In the first instance, the temperature of the reference state is much below the temperature of the chromatography, in the second the temperature may be chosen to be the same. Here the first reference state is selected, with the additional qualification that the volume of the crystalline state refers to the melting temperature, *i.e.*, to a thermodynamic transition of first order. For the second reference state, experimental data on the specific volume or

density at sufficiently high pressures are rather scarce. It should be noted that the free volume defined in either of these ways is not the same as the volume which is freely accessible to a substrate, because the size, shape and conformational mobility of a substrate molecule is not the same as that of a mobile phase molecule, nor are they the same for different substrates. Nevertheless the free volume derived by the use of the first reference state can be used as an approximate measure of the free volume accessible to the substrates. Therefore, it may be useful for studying the relationship of the free volume to chromatographic parameters such as the capacity factor, k' , and the selectivity, α , in addition to comparisons between different mobile phases in the state of identical free volume. In this work, the supercritical fluids pentane, carbon dioxide and, in a few experiments, propane are studied.

EXPERIMENTAL

The apparatus and columns were described previously⁵. Propane (99.5%; Linde, Höllriegelskreuth, F.R.G.) and carbon dioxide (99.995%; Messer Griesheim, Hürth, F.R.G.) were used without further purification. Pentane was dried over sodium, distilled, filtered and degassed. For measuring dead times, heptane served as an inert substrate. The two substrates pyrene and chrysene were recrystallized several times. Unmodified silica, LiChrosorb Si 60, 10 μm (Merck, Darmstadt, F.R.G.), was used as the stationary phase.

Capacity factors, k' , and selectivities, α , were calculated from retention times, t_R , and dead times, t_0 , in the usual manner:

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

$$\alpha = \frac{k'_2}{k'_1} = \frac{t_{R,2} - t_0}{t_{R,1} - t_0} \quad (2)$$

RESULTS AND DISCUSSION

It is reasonable to perform the comparison of the SFC properties of different mobile phases at the same value of their reduced variables, *i.e.*, p_r , T_r or ρ_r . Accordingly, the free volume is also defined as a reduced variable, the reduced free volume, f_r . The specific reference volume, V_0 , of by definition $f_r = 0$, was taken as the specific volume of the crystalline state at the melting temperature and atmospheric pressure. Thus it may be written:

$$f_r = \frac{V_{p,T} - V_0}{V_0} = \frac{V_{p,T}}{V_0} - 1 \quad (3)$$

Herein, $V_{p,T}$ is the specific volume at the pressure, p , and temperature, T , of the chromatographic experiment. Eqn. 3 may also be expressed in terms of the densities, ρ :

$$f_r = \frac{\rho_0}{\rho_{p,T}} - 1 \quad (4)$$

Obviously, a comparison on the basis of free volume is formally similar to one based on the reduced density, ρ_r

$$\rho_r = \rho_{p,T}/\rho_c \quad (5)$$

with ρ_c being the critical density. However, the critical state possesses considerable free volume and the dissolution ability, the viscosity and the diffusion coefficients have therefore not reached their extrema. A comparison of different mobile phases, simply at the same $\rho_{p,T}$, *i.e.*, under isodense conditions, introduces different molecular weights which are incidental to the dissolution power. However, for close members of an homologous series, a comparison between isodense states will, to a first approximation, correspond to one between equal free volumes. In this work, the comparison between pentane and carbon dioxide is based on equal free volumes.

The ρ_0 values and the points of fusion, F_p , of the reference state for the mobile phases pentane, propane and carbon dioxide are shown in Table I. The f_r values were calculated by recording the temperature and the pressure for a specific chromatogram, calculating or interpolating the corresponding densities using density tables⁸ or plots⁹ and, finally, substituting the resulting densities into eqn. 4.

TABLE I
REFERENCE STATE DATA^{6,7} FOR CALCULATING THE FREE VOLUME

Mobile phase	F_p (°C)	ρ_0 (g cm ⁻³)
Pentane	-129.8	0.76
Propane	-189.8	0.75
Carbon dioxide	- 78.1 (subl.)	1.56

In Figs. 1-3, the k' and α of pentane and carbon dioxide are seen as a function of f_r at a reduced temperature, $T_r = 1.01$, just above the critical temperature, T_c . Figs. 4-6 show similar data, but at $T_r = 1.22$. For all chromatographic experiments, pyrene and chrysene have been used as substrates and unmodified silica as the stationary phase. The scatter of the experimental points for pentane is due in part to experiments with different columns at different times and gives an indication of the reproducibility.

The slightly bent k' curves at $T_r = 1.01$ for pyrene and chrysene in Figs. 1 and 2, respectively, show k' for pyrene to be lower than those for chrysene, as expected because of the smaller molecular size of pyrene. At all f_r , pentane has much lower k' values than carbon dioxide since supercritical pentane is a better solvent for both substrates than carbon dioxide.

The lower k' for pentane as against carbon dioxide indicates the higher dissolution power of pentane, provided the competitive adsorption of pentane *versus*

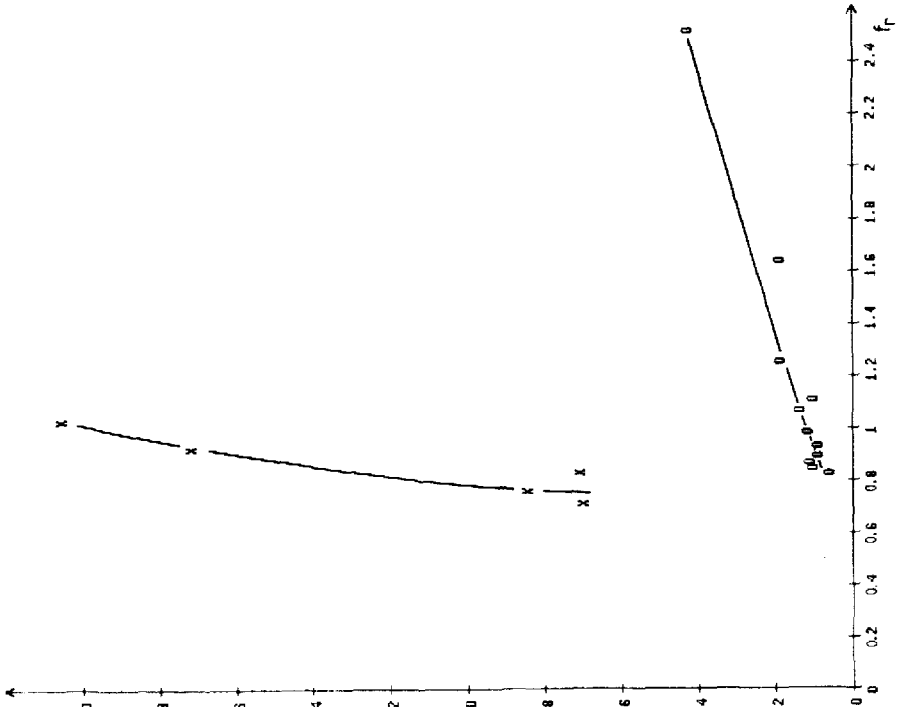


Fig. 1. Dependence of the capacity factors k' of pyrene on the free volume, f_r , at $T_r = 1.01$. Eluents: *n*-pentane (0); carbon dioxide (x).

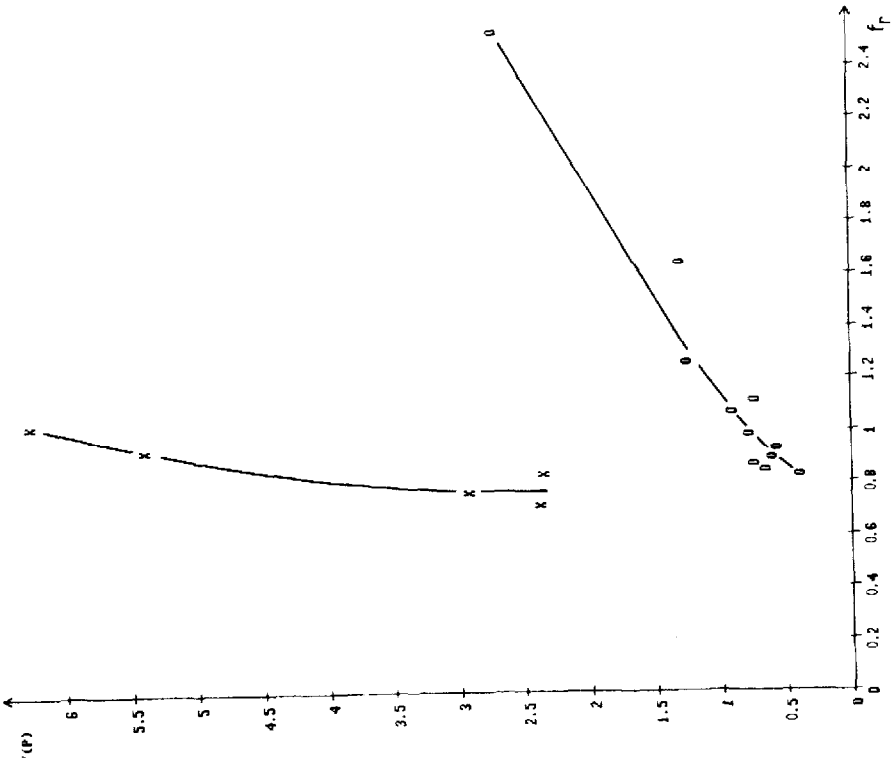


Fig. 2. Dependence of the capacity factors k' of chrysenes on f_r at $T_r = 1.01$. Symbols as in Fig. 1.

substrate on silica gel is not much less than that of carbon dioxide. The lower slope of k' for pentane shows the intermolecular interactions to be less dependent on f_r than for carbon dioxide, probably because pentane is a larger, more flexible molecule with more sites for interactions. Moreover, the slope is lower for pyrene than for chrysene in the same mobile phase.

In Fig. 3, the selectivity, α , between pyrene and chrysene is plotted. In pentane, α does not change much with f_r , but it does so in carbon dioxide. For the latter fluid, it increases with increasing f_r , *i.e.*, with decreasing density.

Figs. 4 and 5 show that the behaviour of k' at $T_r = 1.22$, is similar to that in Figs. 1 and 2. At this reduced temperature for pentane, k' is a linear function of f_r within the accuracy of measurement. Again, the k' values and their slopes are much higher for carbon dioxide than for pentane. However, at the same f_r , the k' values are lower at $T_r = 1.22$ than at $T_r = 1.01$, since the solubility may be expected to

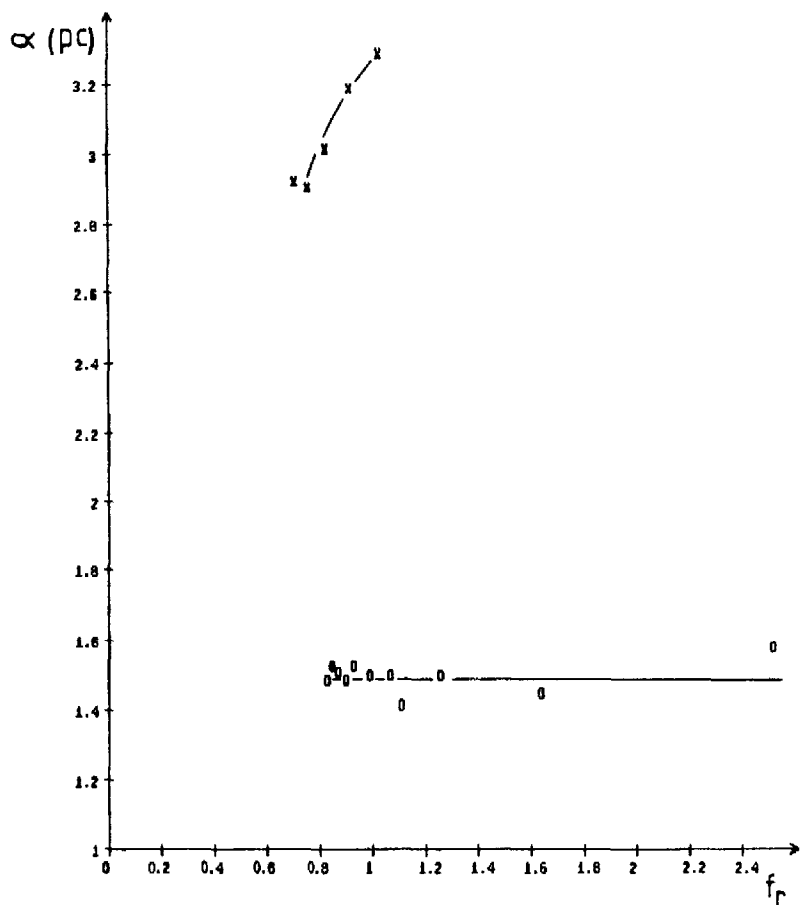


Fig. 3. Dependence of the selectivity, α , between pyrene and chrysene on f_r at $T_r = 1.01$. Symbols as in Fig. 1.

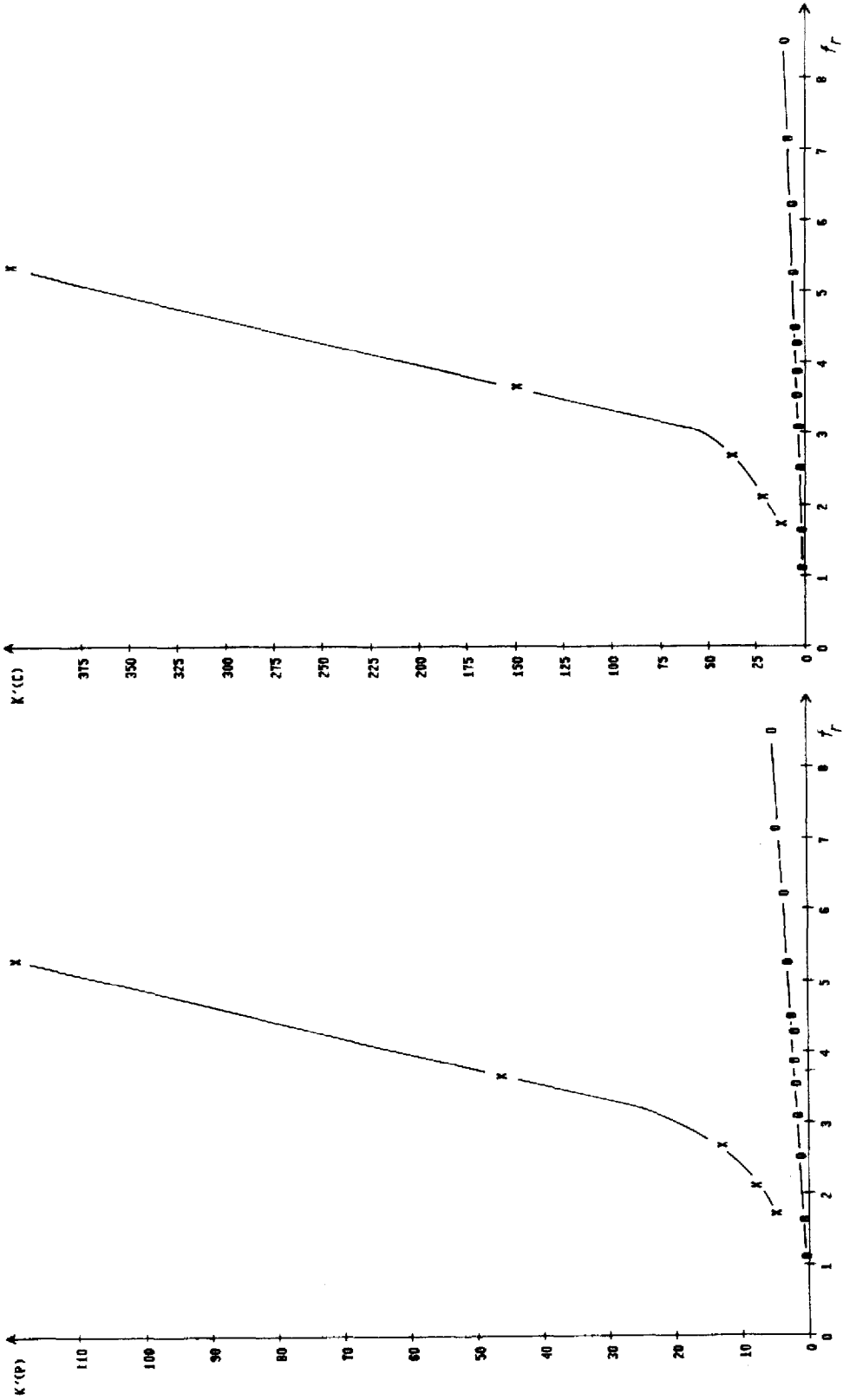


Fig. 4. Dependence of the capacity factors, k , of pyrene on f_r at $T_r = 1.22$. Symbols as in Fig. 1.

Fig. 5. Dependence of the capacity factors, k' , of chrysenes on f_r at $T_r = 1.22$. Symbols as in Fig. 1.

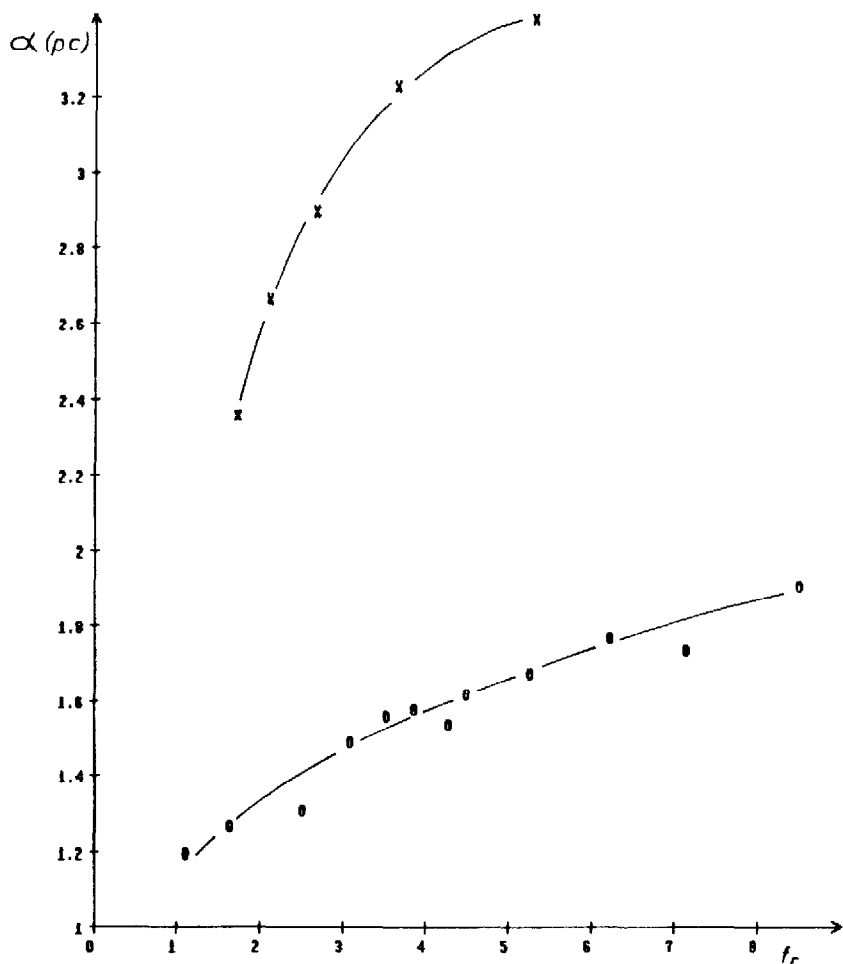


Fig. 6. Dependence of the selectivity, α , between pyrene and chrysene on f_r at $T_r = 1.22$. Symbols as in Fig. 1.

increase and adsorption to decrease at higher temperatures. Also, the slope is lower at $T_r = 1.22$ for pentane, that is, the k' values are less sensitive to f_r at higher temperatures. The values of α at $T_r = 1.22$ in Fig. 6 are also similar to those at $T_r = 1.01$ in Fig. 3, in as much as carbon dioxide shows increasing α with increasing f_r . Pentane now shows the same behaviour as carbon dioxide and is no longer independent of f_r as in Fig. 3. There appears to be a levelling-off effect at high f_r for both carbon dioxide and pentane. This is possibly connected to the decrease in the dissolution power of the mobile phase, the vapour pressure of the substrate becoming more, and finally alone, responsible for α . Some additional data, obtained with propane, indicated values of k' and α located between those of pentane and carbon dioxide. On the whole, however, it can be said that selectivity increases with increasing free volume, a tendency which may also be expected for other fluids.

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