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Three-dimensional network plots using colours for a fourth variable with binary mixtures of pentane and 1,4-dioxane under sub- and supercritical conditions

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SUMMARY

Three-dimensional contour plots are shown for the capacity ratio of chrysene, $k'(C)$, and the selectivity between pyrene and chrysene, $\alpha(PC)$, in mobile phases composed of pentane and 1,4-dioxane. For isocratic plots, the dependence of k' and α on pressure and temperature is shown, and for isobaric plots the dependence on temperature and mobile phase composition is demonstrated at two constant pressures and at one constant reduced pressure. Additional information is included in the plots by coloured shading of the three-dimensional surface, where the different colour bands represent the different ranges of an additional chromatographic variable. Thus, $k'(C)$ was combined with $\alpha(PC)$ or with the average resolution, R_m , of an aromatic-hydrocarbon standard mixture, the latter two chromatographic variables represented by colour. $\alpha(PC)$ was similarly combined with R_m . Such plots can help in clarifying interrelations between different physical and chromatographic parameters, which is useful for the optimization of separations.

INTRODUCTION

In supercritical fluid chromatography (SFC), changes in temperature, pressure, mobile phase flow-rate and mobile phase composition can be used to influence a chromatographic separation. The aim of these manipulations is to obtain a high resolution in combination with a short analysis time. It is therefore useful to know how capacity factors and resolution vary with changing physical parameters.

It has been observed experimentally that for chromatographic parameters, such as the capacity factor k' , the mean resolution R_m and the selectivity α , maxima may occur above the critical point of the mobile phase, depending on the pressure, temperature and mobile phase composition¹⁻³. Frequently, but not generally, a similar location of the maxima for capacity factors and resolution was found. A direct correlation of capacity factors with resolution or with selectivity in the same plot,

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comprising the two chromatographic variables on the z-axis or as colour, respectively, would help to illustrate the interrelations between the two chromatographic parameters. In this work, an example of such a direct correlation of the two chromatographic parameters is shown for isocratic or isobaric plots employing binary mobile phases composed of pentane and 1,4-dioxane. The plots demonstrate several fundamental features that are useful for the optimization of separations when varying temperature, composition and pressure.

EXPERIMENTAL

The chromatograms were measured on a previously described SFC instrument⁴ based on a commercially available high-performance liquid chromatograph. Pre-treatment of eluents and chromatographic conditions have also been described in detail elsewhere⁵. All measurements were made at constant volume flow-rate, as delivered by the pumps in the liquid state. The stainless-steel columns (25 cm x 4.6 mm I.D.) were packed with LiChrosorb Si 100 (10 μm). The capacity factor, k' , and the selectivity, α , were calculated using the following equations:

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

$$\alpha = \frac{k'_j}{k'_i} \text{ or } \frac{k'(\text{pyrene})}{k'(\text{chrysene})} \quad (2)$$

The resolution, R_m , was calculated as the arithmetic mean of the resolutions R_{ij} for the hydrocarbon pairs naphthalene-anthracene, anthracene-pyrene and pyrene-chrysene (the four aromatic hydrocarbons were used as a standard test mixture):

$$R_m = \frac{\sum R_{ij}^*}{n} \quad (3)$$

where $n = 3$ and where the resolutions of the individual peak pairs R_{ij}^* are given by⁶

$$R_{ij}^* = \frac{f_{ij}}{g_{ij}} + \frac{d_{ij}}{w'_i + w'_j} \cdot \sqrt{\ln 4} \quad (4)$$

The mean resolution R_m was chosen as a measure of the separation quality because of its simplicity and its direct connection with the basic chromatographic parameters k' , α and plate number, N . For interpolation and plotting of the three-dimensional network plots, in which a fourth variable is represented by colouring the network, a computer program (Unimap; Uniras European Software Contractors, Lyngby, Denmark and Diisseldorf, F.R.G.) was used, as described in detail elsewhere⁷.

Although for a variety of binary fluid media the critical data and their variance with composition have been determined experimentally, no experimental data have been published so far for the pair pentane-1,4-dioxane. Since a knowledge of the critical data is essential for supercritical fluid chromatography, the data were

calculated according to the method of Chueh and Prausnitz⁸. The binary interaction parameter needed for the calculation was estimated to be $k_{ij} = 0.05$, in analogy with similar values for other solvent pairs. The resulting curves are shown in Fig. 1, giving the critical temperature, T_c , and the critical pressure, p_c , as a function of the volume fraction of 1,4-dioxane in pentane. The volume fraction was chosen as a scale in order to facilitate correlation of the calculated critical data with the chromatographic results shown in the subsequent figures.

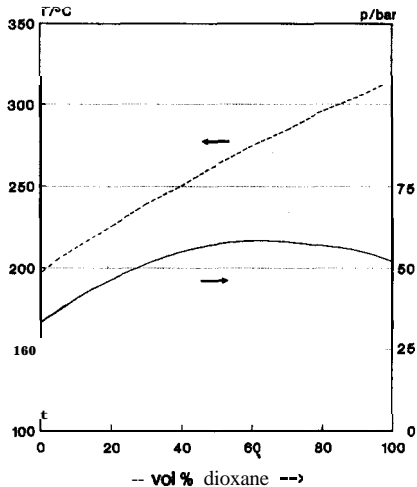


Fig. 1. Critical pressure (full line) and critical temperature (broken line) for pentane-1,4-dioxane calculated by the method of Chueh and Prausnitz⁸.

RESULTS AND DISCUSSION

A three-dimensional network plot of two chromatographic versus two physical parameters, showing the capacity factor of chrysenes, $k'(C)$, as a contour variable (z -axis), depending on pressure, p (bar) (x -axis) and temperature, T ($^{\circ}C$) (y -axis), is shown in Fig. 2. As a second z -variable, the mean resolution, R_m , is added as coloured contour bands. The mobile phase was pentane containing 10% of dioxane, for which the experimental data have been presented previously⁹. The colour scale on the left of Fig. 2 shows the actual mean resolution values corresponding to the colours used in the plot. For both the capacity factor and the resolution a maximum is found fairly close to the mobile phase critical temperature of $212.5^{\circ}C$ (cf., Fig. 1). The maximum for the mean resolution is, however, shifted by about $20^{\circ}C$ to lower temperatures compared with the maximum for the capacity factor. Going to higher pressures, the maxima for both variables form a "mountain ridge", which slopes downward strongly with higher pressures and which shifts at the same time to higher temperatures. The highest values for both parameters are shown in the region of subcritical pressure ($p_c \approx 40$ bar), where the capacity factor exceeds 70 and the mean resolution reaches values around 8. High absolute values for both parameters may be of interest for the separation of complex mixtures in which compounds with low capacity factors are combined with

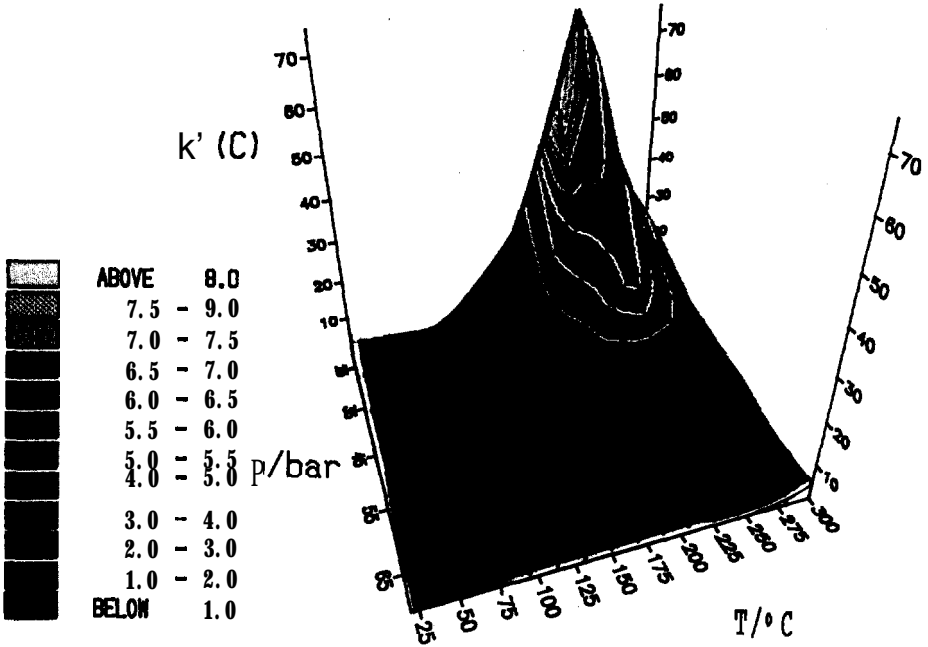


Fig. 2. Capacity factor of chrysenes, $k'(C)$, and mean resolution, R_s , as a function of column outlet pressure, p , and temperature, T , for pentane-10% (v/v) 1,4-dioxane.

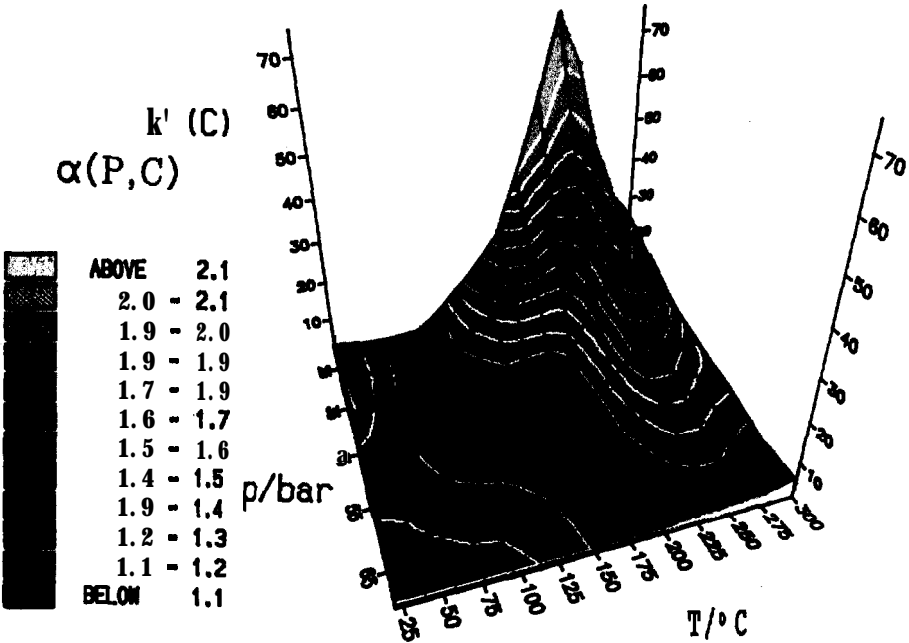


Fig. 3. Capacity factor, $k'(C)$, and selectivity, $\alpha(PC)$, as a function of column outlet pressure, p , and temperature, T , for pentane-10% (v/v), 1,4-dioxane.

compounds with much higher capacity factors. For less difficult separations, much lower resolutions will, of course, be **sufficient**. The plot demonstrates that for the test mixture used here, resolutions above 1.0 are found over a fairly wide range of capacity factors, depending on temperature and pressure of the mobile phase.

The selectivity, α , between two peaks is also useful for the characterization of chromatographic separations. Fig. 3 again shows the capacity factor, $k'(C)$, as the contour variable but, instead of R_m , the selectivity, $\alpha(PC)$, between pyrene and chrysene as the **coloured** contour bands. The general trend is the same as in the previous plot. The behaviour of k' and α differs only at low temperatures, where α is found at relatively high values (up to 1.3), as opposed to the very low values of k' .

An increase in selectivity with decrease in temperature has frequently been observed in liquid chromatography (LC) and has also been reported for the supercritical range^{10,11}. Further information can be obtained from a plot which correlates selectivity and mean resolution, as presented in Fig. 4. The combination of selectivity, $\alpha(PC)$, as the contour variable and the mean resolution, R_m , as colour information shows that in the low-temperature area a fairly high selectivity can still result in a low mean resolution; the minimum of selectivity with respect to temperature is not reflected in a **corresponding** behaviour of the mean resolution. Fig. 4 demonstrates that in the supercritical region the selectivity generally needs to be high for the resolution to exceed unity.

In contrast to the isocratic plots in Figs. 2-4 which are valid for 10% dioxane, Fig. 5 shows an isobaric plot for pentane-dioxane at 20 bar. The variables are the capacity factor, $k'(C)$ (z-axis, contour), the amount of dioxane in the mobile phase, %B (x-axis), the temperature, $T(^{\circ}C)$ (v-axis) and the mean resolution, R_m (z-axis, colour bands). For both z-variables, maxima at about the same position are observed, the general behaviour of the capacity factor and mean resolution being similar to that described before for Figs. 2-4. For the whole plot, the pentanedioxane system is below the critical pressure. As shown in Fig. 1, the critical parameters T_c and p_c vary with changing dioxane content, *i.e.*, along the %B axis in the plots. The increase of the critical temperature with increase in the content of the modifier dioxane may be explained by the observed shift of the "mountain ridge" to higher temperatures on increasing the dioxane content. Fig. 6 shows a plot for the same system at 36 bar. Here, part of the plot is in the supercritical region with respect to both temperature and pressure; the highest values for the two z-parameters are found in this supercritical area. However, when compared with Fig. 5 the absolute values of capacity factors and resolutions decrease with increasing pressure. Generally, a low pressure is advantageous for the resolution of complex mixtures of volatile and non-volatile compounds, whereas a higher pressure reduces capacity factors. With respect to the reduced capacity factors, it is observed by comparison of Figs. 5 and 6 that the decrease in capacity factor with increasing pressure is much more pronounced than the corresponding decrease in resolution. For parts of the plot in Fig. 6 the resolution still exceeds 2, *i.e.*, it may be high enough for the separation of not too complex mixtures.

Figs. 7 and 8 show plots for an estimated reduced pressure, p/p_c of 1.09 for the pentanedioxane system. This means that the pressure is above p_c for the whole area of the plots. The experiments were carried out such that the pressure was increased according to the increase in the critical pressure, p_c , with composition. However, the low-temperature parts of the plots are still subcritical with respect to temperature (*cf.*,

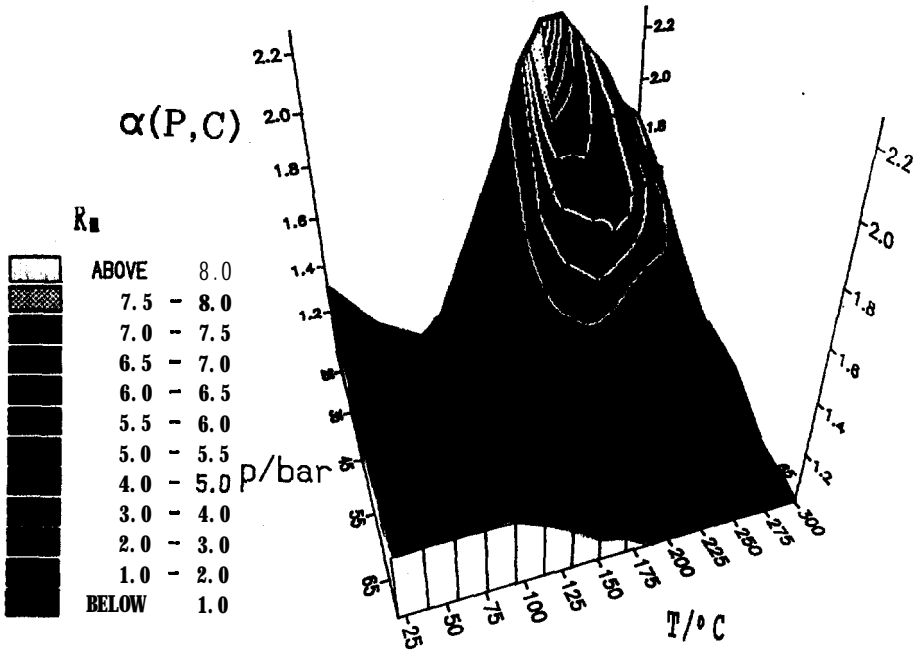


Fig. 4. Selectivity, $\alpha(PC)$, and resolution, R_m , as a function of column outlet pressure, p , and temperature, T , for pentane-10%, (v/v) 1,4-dioxane.

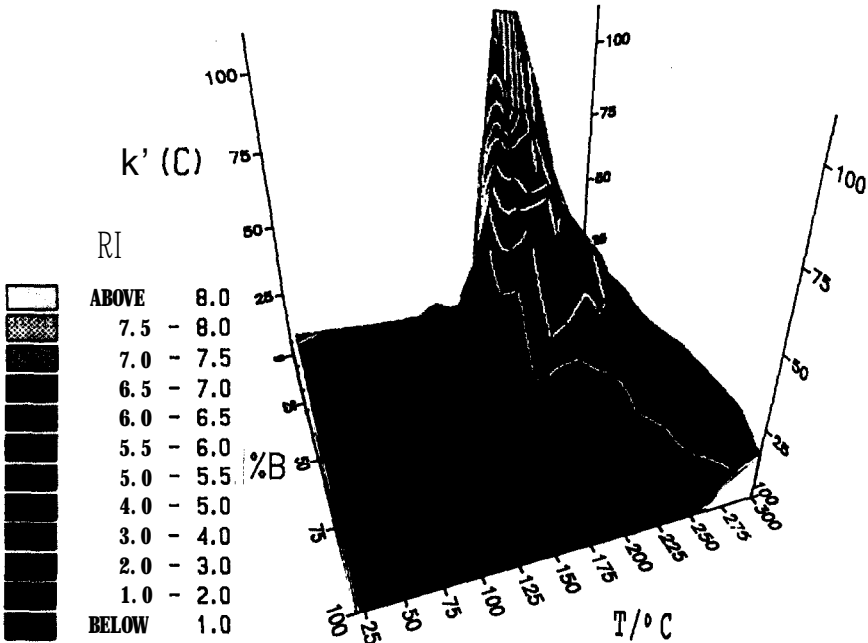


Fig. 5. Capacity factor, $k'(C)$, and resolution, R_m , as a function of mobile phase composition, $\%B$ (v/v), and temperature, T , for pentane-1,4-dioxane at a constant column outlet pressure of 20 bar.

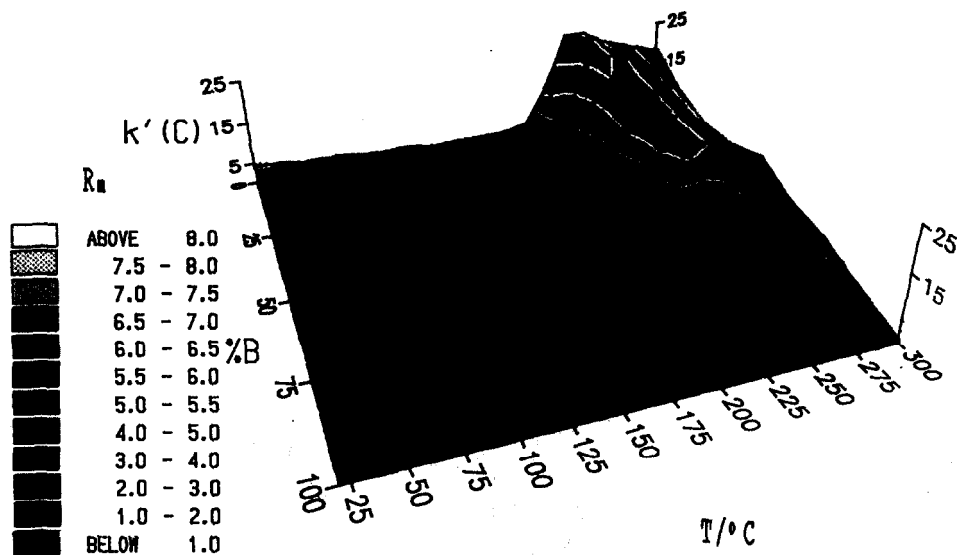


Fig. 6. Capacity factor, $k'(C)$, and resolution, R_m , as a function of mobile phase composition, %B (v/v), and temperature, T , for pentane-1,4-dioxane at a constant column outlet pressure of 36 bar.

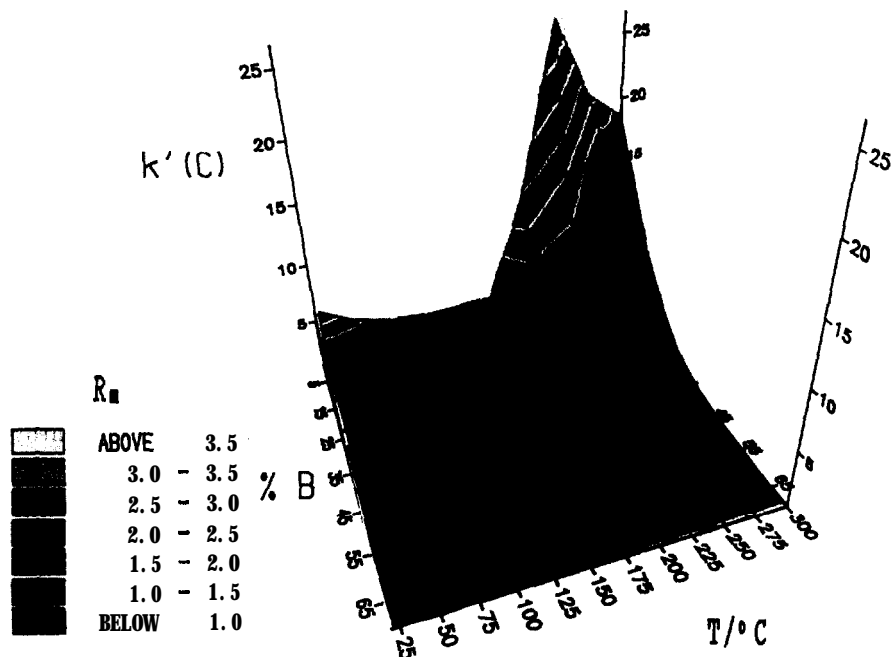


Fig. 7. Capacity factor, $k'(C)$, and resolution, R_m , as a function of mobile phase composition, %B (v/v), and temperature, T , at a constant reduced pressure of $p_r \approx 1.09$.

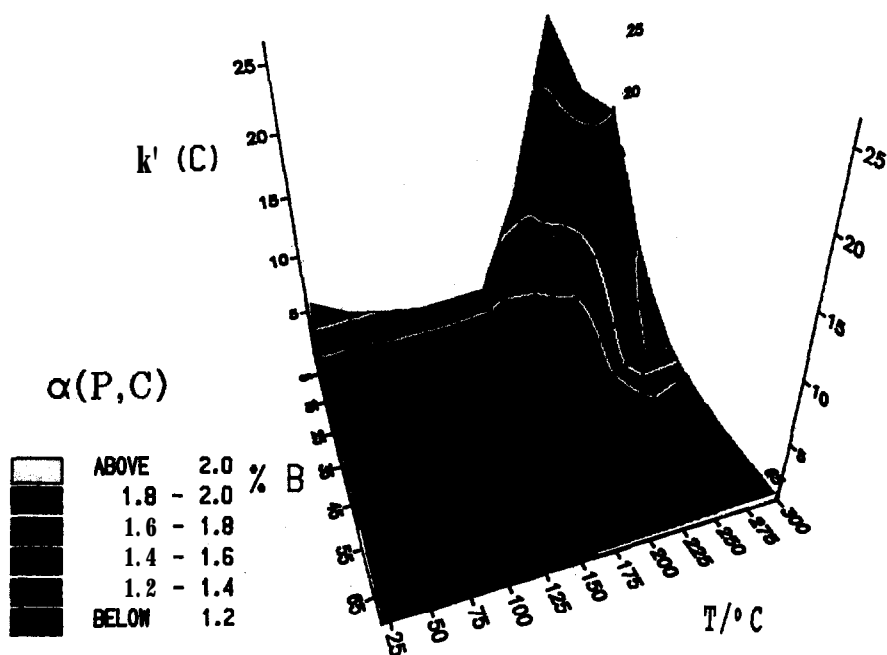


Fig. 8. Capacity factor, $k'(C)$, and selectivity, $\alpha(PC)$, as a function of mobile phase composition, %B (v/v), and temperature, T at a constant reduced pressure of $p_r \approx 1.09$.

Fig. 1). Fig. 7 shows the capacity factor as the contour variable and resolution as colour information for a composition range between 0 and 70% dioxane. Both z-variables show a nearly parallel behaviour with a maximum in the supercritical area. Fig. 8 shows the combination of capacity factor and selectivity for the same composition-temperature range. There is an area (red) with low capacity factors but still relatively high selectivities, as already found to some extent in Fig. 3. A combined plot for selectivities, $\alpha(PC)$, and resolutions, R_m , demonstrates the differences in behaviour between selectivity and resolution (not shown). Whereas the selectivity contour reveals three separate maxima, only two of these coincide with resolution maxima. In the third a-maximum, which is located at ca. 20–30% dioxane at high temperatures, selectivity values are seen that are as high as for the two other maxima, but resolution remains below unity. This is due to increasing peak widths yielding reduced plate numbers. This demonstrates that high selectivities do not necessarily lead to highly resolved peaks.

CONCLUSIONS

The coloured three-dimensional plots, in which two axes represent physical parameters such as pressure and temperature in isocratic plots and temperature and mobile phase composition in isobaric plots, are useful for providing an overview of the dependence of two chromatographic parameters chosen among k' , α and R_m from the two named physical parameters. The chromatographic parameters all pass through

maxima with changing temperature. Thereby, for both the isocratic and the isobaric plots, the maxima for k' , α and R_m tend to be in similar locations with respect to the physical parameters but they do not usually coincide. The maxima decrease in height with pressure and also with the content of dioxane in the pentanedioxane binary mobile phase used in this work. Whereas this decrease is very strong for k' , it is much less pronounced for R_m . Hence high resolutions can still be obtained with reasonably low capacity factors. The plots indicate the values for the physical parameters which give particularly favourable resolutions at a given capacity factor.

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