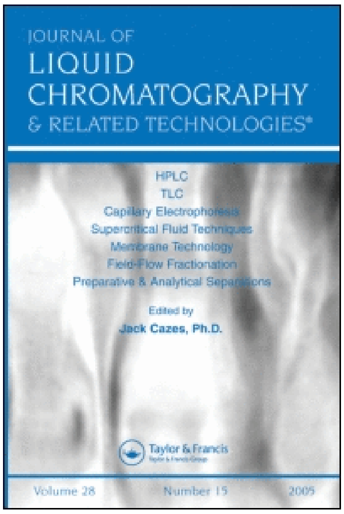

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SELECTIVITY FACTORS FOR SEVERAL PAH PAIRS ON C_{18} BONDED PHASE COLUMNS

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ABSTRACT

The selectivity factors for four pairs of polycyclic aromatic hydrocarbons (PAHs) have been found to be very different on the HC-ODS column in comparison to most other C_{18} bonded-phase columns. The selectivity factors for these PAH pairs varied slightly with different manufacturing lots of the HC-ODS material, the selectivity variations for each PAH pair being linearly correlated with those for the other pairs.

INTRODUCTION

We have previously reported (1) the separation of 15 of the 16 polycyclic aromatic hydrocarbons (PAHs) on the EPA Priority Pollutant list, using reversed-phase chromatography on an HC-ODS column. We observed that the selectivity factors for several pairs of these PAHs on the HC-ODS column were very different from those on many other C_{18} bonded-phase columns. In a recent publication comparing the retention and selectivity characteristics of eight commercial C_{18} bonded-phase materials (2), we also reported the variations in the capacity factors, k', and the selectivity factors, α, for these PAHs on different manufacturing lots of the HC-ODS material. The behavior of the selectivity factor for two of these PAHs, dibenz[a,h]anthracene (diB[a,h]A) and benzo[ghi]perylene (BPer), were of particular concern to us since these two are the only pair not quite baseline resolved in our method (1). We have subsequently found that the variations in α for this pair were correlated with the variations in α for other PAH pairs.

While examining the retention on C_{18} bonded-phase columns of PAHs other than our original set of 16, we observed that the elution pattern on the HC-ODS column sometimes differed from the patterns on several other C_{18} columns. The reversal of the elution order for 2-methylanthracene and 9-phenylanthracene was particularly surprising. We also observed some variations in the α for this pair on HC-ODS columns from different manufacturing lots. These variations correlated with those in the α for diB[a,h]A relative to BPer.

MATERIALS

We used a Perkin-Elmer Series 3 liquid chromatograph with dynamic stirrer accessory, a Rheodyne Model 7120 injection valve with 10-μL sample loop, a Perkin-Elmer Model 650-10S fluorescence detector, and a Perkin-Elmer Sigma 10 chromatography data station.

Anthracene, 2-methylanthracene, benzo[a]pyrene, and dibenz[a,h]anthracene were purchased as 100 μg/mL solutions in hexane from Chem Services (West Chester, PA). 9-Phenylanthracene was obtained in pure form from Analabs, Inc., (North Haven, CT). Dibenz[a,c]anthracene was obtained in pure form from Pfaltz and Bauer, Inc., (Stamford, CT). Benzo[e]pyrene was purchased from Aldrich Chem. Co. (Milwaukee, WI), and benzo[b]fluoranthene was purchased from Nanogens (Watsonville, CA). The structures and abbreviations for these compounds are given in Figure 1.

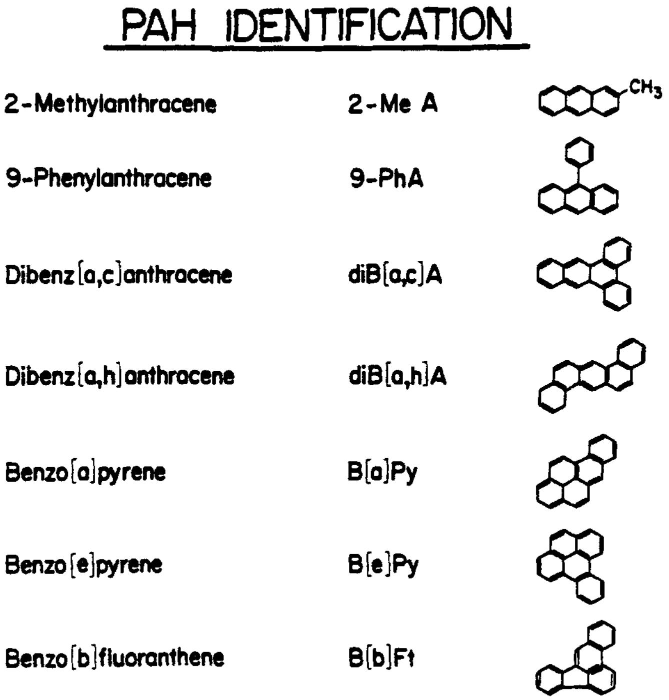

FIGURE 1. Identification and structure of the PAHs used in this study.

Acetonitrile and water used for the mobile phase were the same as used previously (1,2).

We used Perkin-Elmer HC-ODS columns packed with material from different manufacturing lots. We also used many of the same commercial C_{18} bonded-phase columns used in our earlier study (2).

All columns were run with 80% acetonitrile/water mobile phase, at room temperature. The flow rate was 0.6 mL/min for 2.6 mm I.D. columns, and the flow rate was adjusted for columns of different internal diameters to give similar linear flow velocities.

The excitation and emission wavelengths on the Model 650-10S fluorescence detector were set to 305 nm and 430 nm, respectively, with 7 nm bandpass used for each monochromator. The detector gain was set to 1/1.

RESULTS

The lot-to-lot variations in the selectivity factor, α, for diB[a,h]A relative to BPer on different lots of HC-ODS packing were correlated with the variations observed in the α values for some other PAH pairs, in particular, for benzo[e]pyrene (B[e]Py) relative to benzo[b]fluoranthene (B[b]Ft). This latter pair is usually just baseline resolved in our method (1) so variations in the α for this pair were also of interest. Figure 2 is a plot of the selectivity factor for diB[a,h]A and BPer as a function of the selectivity factor for B[e]Py and B[b]Ft on columns packed with different lots of HC-ODS material. The dotted line is the linear least squares fit of the data.

A similar plot of the α for diB[a,h]A relative to BPer as a function of the α for diB[a,h]A relative to benzo[a]pyrene (B[a]Py) on HC-ODS columns from different manufacturing lots, Figure 3, shows that the variations in the α for each of these two PAH pairs were also linearly correlated.

The separation of at least two other PAH pairs on the HC-ODS column differed from that on most other C_{18} bonded-phase columns. The k' data for anthracene and four anthracene derivatives, 2-methylanthracene (2-MeA), 9-phenylanthracene (9-PhA), diB[a,c]A, and diB[a,h]A, are plotted in Figure 4. This plot uses the graphical format that we introduced in our previous paper (2). The ordinate is the k' of one of the PAHs, and the abscissa is the k' of B[a]Py on the same column. With this format, the k' data for different compounds on a given column are ordered vertically at the k'

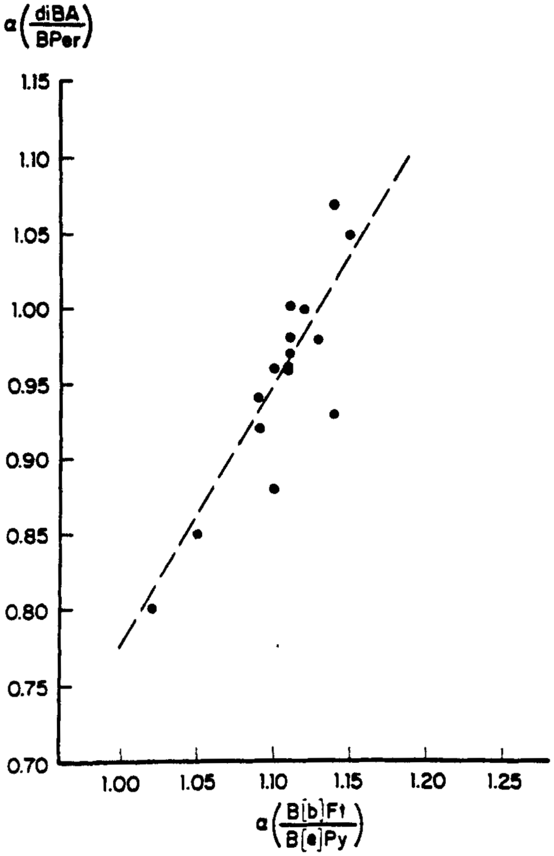

FIGURE 2. Plot of the selectivity factor for diB[a,h]A and BPer as a function of the selectivity factor for B[b]Ft and B[e]Py for different manufacturing lots of HC-ODS C_{18} silica.

for B[a]Py on that column. (The choice of B[a]Py as a reference is arbitrary). The columns are identified across the top of the figure. A dotted line in Figure 4 connects the data points for an individual PAH on the different C_{18} columns with the exception of data from the HC-ODS column.

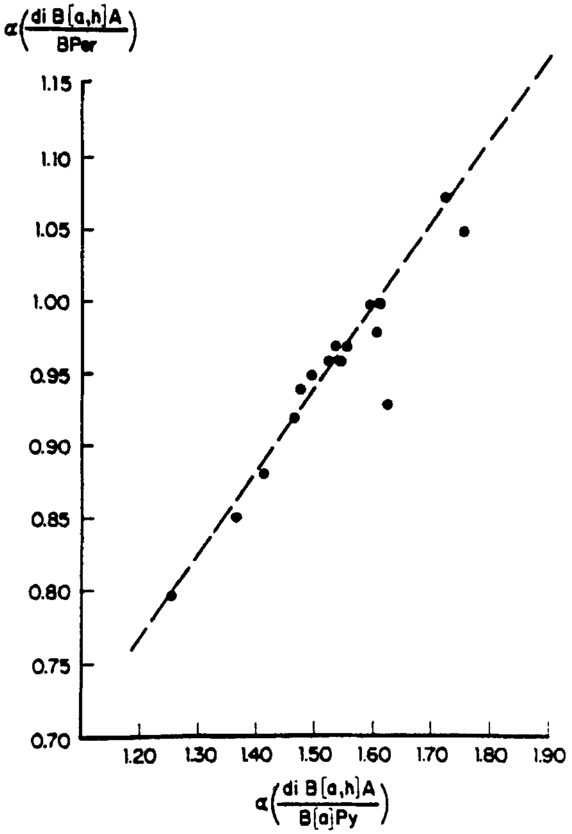

FIGURE 3. Selectivity factor for diB[a,h]A relative to BPer as a function of the selectivity factor for diB[a,h]A relative to B[a]Py for different manufacturing lots of HC-ODS material.

Figure 5 is a plot of the α for diB[a,h]A relative to its geometrical isomer, diB[a,c]A (see Figure 1) as a function of the α for diB[a,h]A relative to B[a]Py on columns from different manufacturing lots of the HC-ODS material. Figure 6 is a similar plot of the α for 2-MeA relative to 9-PhA. Selectivity data for these PAH pairs on several other C_{18} columns are also

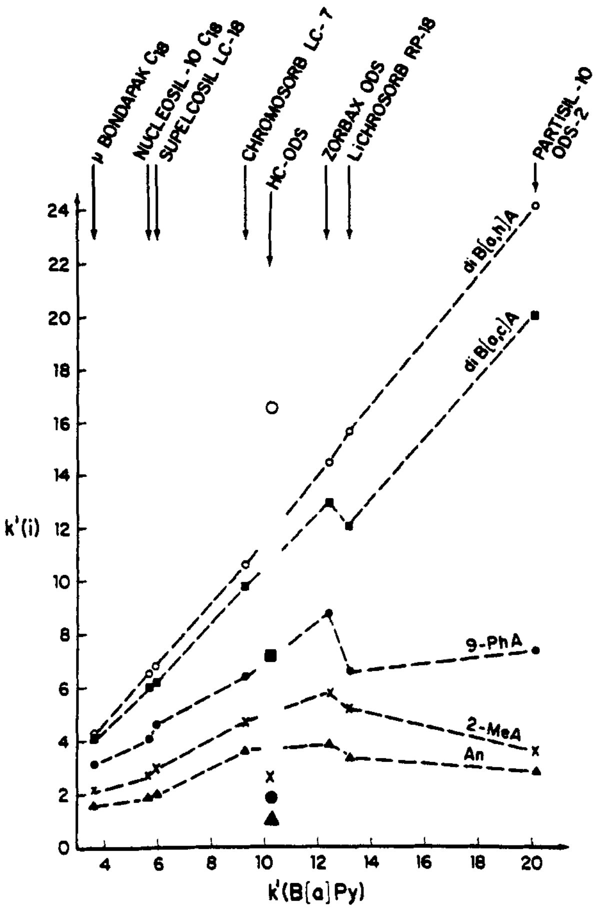

FIGURE 4. The k' values of several PAHs on several C$_{18}$ columns, plotted as a function of the k' of benzo[a]-pyrene on the different columns. The index *i* in the ordinate label refers to the PAHs identified on the right.

included in Figures 5 and 6, as indicated by the open circles with accompanying numbers corresponding to the column identification in Table I. Table I also lists the selectivity factors for three of these PAH pairs.

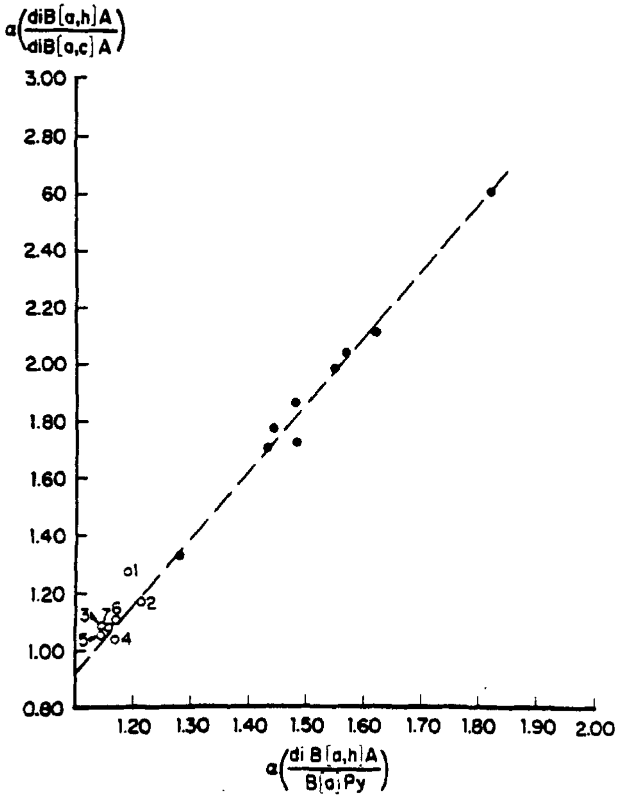

FIGURE 5. Selectivity factor for diB[a,h]A relative to diB[a,c]A as a function of the selectivity factor for diB[a,h]A relative to B[a]Py for different manufacturing lots of HC-ODS columns and for other commercial C_{18} columns. The commercial columns are identified in Table I.

DISCUSSION

In an earlier paper (2) we described the range in selectivity factors for several PAHs on different manufacturing lots of the C_{18} silica used in HC-ODS columns. We found that the selectivity factors for some PAH pairs were fairly constant, while those for

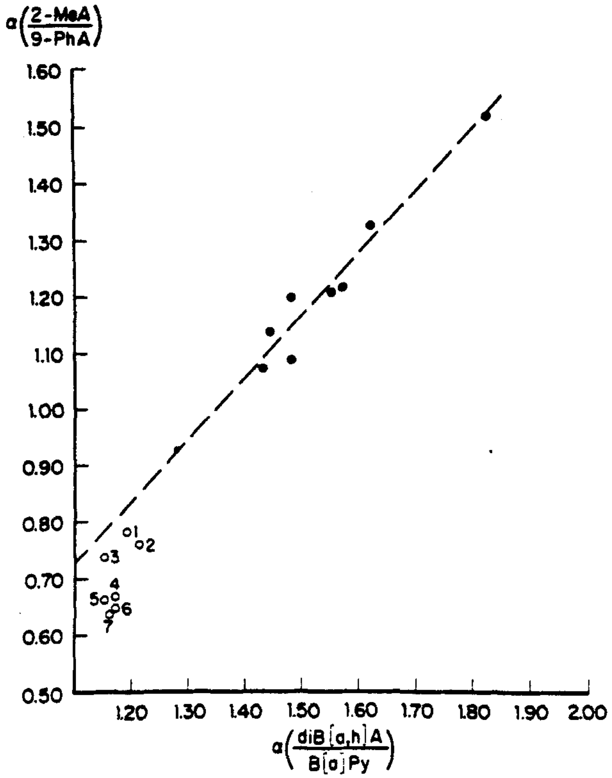

FIGURE 6. Selectivity factor for 2-MeA relative to 9-PhA as a function of the selectivity factor for diB-[a,h]A relative to B[a]Py. Column identification is the same as for Figure 5.

other pairs varied somewhat from lot to lot. We were particularly concerned about the variations in the selectivity factor for diB[a,h]A relative to BPer, since these two were usually not quite baseline resolved in our analytical method (1). With the gradient used in our analytical method, this pair eluted under conditions approaching 100% acetonitrile. Isocratic runs at 100% acetonitrile gave a value for this α of less than 1.0, i.e. BPer eluted before diB[a,h]A. As we

TABLE I

Selectivity Data for Different C_{18} Bonded-phase Columns

C_{18} Columns	$\alpha\left(\frac{\text{2-MeA}}{\text{9-PheA}}\right)$	$\alpha\left(\frac{\text{diB[a,h] A}}{\text{diB[a,c] A}}\right)$	$\alpha\left(\frac{\text{diB[a,h] A}}{\text{B[a] Py}}\right)$
HC-ODS lot #36	1.52	2.62	1.82
#34	1.33	2.12	1.62
#35	1.22	2.05	1.57
#31	1.21	1.99	1.55
#24	1.20	1.87	1.48
#25	1.14	1.78	1.44
#40	1.09	1.73	1.48
#37	1.08	1.71	1.43
#38	0.93	1.33	1.28
1. LiChrosorb RP-18	0.78	1.27	1.19
2. Partisil-10-ODS-2	0.76	1.16	1.21
3. Chromosorb LC-7	0.74	1.08	1.15
4. µ Bondapak C_{18}	0.67	1.04	1.17
5. Nucleosil-10	0.66	1.07	1.15
6. Zorbax ODS	0.65	1.10	1.17
7. Supelcosil LC-18	0.64	1.08	1.16

have already described (1,3), the selectivity factor for this pair increases with decreases in the acetonitrile content of the mobile phase. For 80% acetonitrile, our normal test conditions, α increased to near 1.0, i.e. there was no separation of these two compounds. Lower values of α at 80% acetonitrile corresponded to better separation at 100% acetonitrile and thus better separation in the analytical method.

Figure 2 demonstrates that the same subtle physical differences between HC-ODS packing material from different manufacturing lots that affected the separation of diB[a,h]A and BPer also affected the separation of another PAH pair. B[e]Py and B[b]Ft. These two compounds were usually just baseline resolved in our analytical method, and hence lot-to-lot variations in the α for these two compounds were also of interest. Because this pair eluted under conditions similar to 80% acetonitrile in our PAH method, values less than 1.05 for 80% acetonitrile as mobile phase corresponded to less than baseline resolution of these two in our PAH method. The correlation in Figure 2 between these two sets of selectivity factors meant that there was a "window" in the observed range of α values for these pairs, within which the α values were suitable for our PAH method. Loss of separation between diB[a,h]A and BPer defines the upper limit, and loss of separation between B[e]Py and B[b]Ft defines the lower limit of this window. For example, the lowest point in Figure 2 represents a column on which B[e]Py and B[b]Ft had only a resolution of 0.7. (This lot of HC-ODS material was rejected because it failed to meet other specifications.) The upper point in Figure 2 represents the opposite extreme, a column on which there was no resolution of diB[a,h]A and BPer.

Because α(diB[a,h]A/BPer) usually has a value near 1.0 for 80% acetonitrile/water as mobile phase, its measurement required that these two PAHs be injected individually, a time-consuming step. From our earlier work (2), we knew that the α for BPer relative to B[a]Py was fairly constant on the different lots of HC-ODS material (see Figure 10 in reference 2). From this observation, we expected that variations in α(diB[a,h]-A/B[a]Py) would mirror those in α(diB[a,h]A/BPer), and this was observed to be the case, as Figure 3 shows.

In the course of evaluating the retention and selectivity characteristics of the HC-ODS column for additional PAHs, we observed the reverse elution order from that predicted for two different pairs of compounds. First, we found that diB[a,c]A (see Figure 1) eluted before B[a]Py, even though diB[a,c]A is of higher molecular weight and also has fewer fused edges than B[a]-Py. Second, we were surprised to find that 9-PhA eluted before 2-MeA. We chromatographed these four PAHs on the other C_{18} columns and observed the elution orders that we originally expected. (The only exception was that diB[a,c]A did elute slightly before B[a]Py on the LiChrosorb RP-18 column.)

The k' data for four anthracene-based derivatives on the various C_{18} columns are presented in Figure 4. The k' for diB[a,c]A showed a general increase with increasing k' for B[a]Py, while the k' for diB-[a,h]A exhibited an excellent linear correlation with the k' for B[a]Py on all columns except the HC-ODS column. On the HC-ODS column, the k' for diB[a,c]A was significantly lower, while that for diB[a,h]A was significantly higher, indicating that a different retention mechanism was present. The α for diB[a,h]A relative to diB[a,c]A on HC-ODS columns from different manufacturing lots varied in the same way that the α for diB-[a,h]A relative to B[a]Py varied, Figure 5. This suggested that the α for diB[a,c]A relative to B[a]Py should be constant for the different lots of HC-ODS material. In fact, this α was not precisely constant, but did vary to a much smaller degree than the other selectivity factors that we evaluated.

Not only were the k'values for 2-MeA and 9-PhA lower on the HC-ODS column than on any of the other columns, but their elution order was reversed, with 9-PhA eluting before 2-MeA. We also observed slight differences in the selectivity factors for this pair on HC-ODS columns from different manufacturing lots.

As Figure 6 clearly shows, these variations correlated very closely with the variations in α for a pair of compounds of analytical interest. It is interesting to find that the α for these two compounds, which share the same fused-ring kernel, correlated with the α for pairs of larger, dissimilar fused-ring compounds. Because these two compounds also eluted very quickly (k'<3) under the test conditions, we now use this pair to select columns for PAH analyses in our laboratory.

While we have not identified the microscopic properties of the HC-ODS column that are responsible for its different selectivity, we have discovered several additional PAH pairs which are evidently sensitive to variations in these properties. Observations such as these will hopefully provide some insight into the retention processes on C_{18} bonded-phase columns.

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