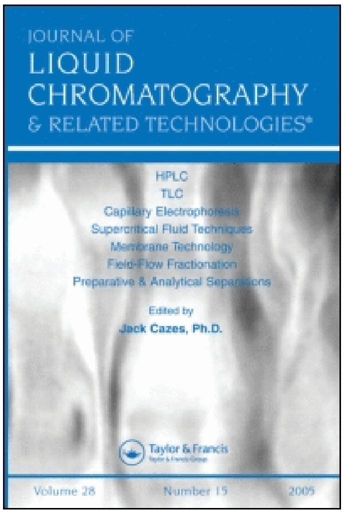

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RETENTION BEHAVIORS OF POLYCYCLIC AROMATIC HYDROCARBONS ON COMB-SHAPED POLYMER IMMOBILIZED-SILICA IN RPLC

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ABSTRACT

The comb-shaped polymer (ODA_{18}) was prepared by telomerization of octadecyl acrylate with 3-mercapto-propyltrimethoxysilane and immobilized onto porous silica gels. The DSC thermograms of both ODA_{18} and Sil-ODA_{18} showed a crystalline-to-isotropic phase transition. The polymer-immobilized silica (Sil-ODA_{18}) showed a selective retention towards polycyclic aromatic hydrocarbons (PAHs). The enhanced selectivity was observed in the crystalline region. The relatively bulky solute molecules were retained preferentially in the non-crystalline region and exhibited a *k*'-jump at around the phase transition temperature in the temperature dependent plot. The increase in retention factor with increasing temperature arises from the gradual increase in solute-stationary phase contact volume. We assume that the enhancement of retention factor in the crystalline region towards slender and planar PAHs arises from the incorporation with the ordered side chains or the alignment with the ordered carbonyl groups for π-π interaction. The selectivity of ODS and of Sil-ODA$_{18}$ at the isotropic state towards PAHs was found to be similar.

INTRODUCTION

Liquid crystals as stationary phases in gas chromatography (GC) are widely used because of their unique selectivity for solute retention. The use of liquid crystals as stationary phases was brought into GC in 1963. Kelker et al. first reported the applications of liquid crystals.[1] After that, numerous applications have been developed to solve complex separations. Witkiewicz et al. quoted hundreds of references to describe the use of liquid crystals as stationary phases in GC.[2] The reason of their wide use in GC is that they have strong shape discriminating abilities. Janini and co-workers, first observed the relationship of shape for isomeric PAHs with the retention data measured on liquid-crystalline phases for gas chromatographic separation.[3-5] They observed that the retention of isomeric PAHs increased with increasing the length to the width of solute molecules. Liquid crystals as stationary phases in high-performance liquid chromatography (HPLC) are not used much. Compared to GC, very few work has been reported.[6-11] There are some limitations in using liquid crystals as stationary phases in HPLC. Liquid crystals, coated on solid supports or capillary walls, are used as stationary phases for GC. Because of low volatility, columns coated with liquid crystals have a useful lifetime. On the other hand, only chemically bonded liquid crystals could be used as stationary phases for HPLC because coated liquid crystals would result in rapid loss due to solubility in the mobile phase or to removal at high column pressure. Several studies have shown that liquid crystals, or structurally similar compounds bonded to the solid support, may retain or develop liquid-crystalline properties.[12-13] The other possibility, is that liquid crystals may lose their properties after bonding to the solid support because of restrictions on their movements. Further research is, therefore, needed to introduce liquid crystals in HPLC.

Liquid crystalline polymers, containing a flexible spacer between the main chain and the mesogenic group, have greater abilities to form mesophase than polymers lacking a spacer, while other factors remain the same.[14] X-ray crystallographic studies, showed a series of side-chain liquid crystalline polymers to be smectic, and the rod-like substituents were preferentially aligned in one direction to form a comb-shaped structure.[15] Both enthalpically and entropically, block-like PAHs would prefer to align themselves with the oriented stationary phase.[16] The more rod-like the solute isomer, the more readily it can be accommodated into the well-ordered domains.[13]

One of the great interests of our research, is preparation of highly-ordered silica-supported polymers and finding their applications as stationary phases for HPLC. Hence, we have prepared a highly-oriented, comb-shaped polymer (ODA_{18}), poly(octadecyl acrylate), by telomerization of octadecyl acrylate with 3-mercaptopropyltrimethoxysilane, with a trimethoxysilyl group at one end of the terminal group.[17-20] The polymer is readily immobilized onto porous silica gels through the reactive terminal group. It undergoes a crystalline-to-isotropic phase transition which includes a nematic liquid crystalline state. The crystalline-to-isotropic phase transition is accompanied by the change in the orientation order of the immobilized phase. Hence, the selectivity greatly depends upon the orientation state of Sil-ODA_{18}. The selectivity for geometric isomers was found to be enhanced by the participation of δ^+-electrons of carbonyl groups of Sil-ODA_n.[20] A new parameter "*f*" has been introduced from our laboratory for evaluation of π-π interaction.[21-22] For further evaluation of the selectivity controlling factors of Sil-ODA_{18}, we are now presenting the retention behaviors of PAHs and their derivatives with the change in the orientation order of the immobilized phase.

EXPERIMENTAL

Materials

Silica-supported polymer (Sil-ODA_{18}) was prepared, characterized, and packed into a stainless steel column (150 × 4.6 mm) as reported previously.[20] A YMC (5 μm, 120 Å, 295 m^2 g^{-1}) silica gel was used for immobilization of the polymer. For comparison, an ODS (Inertsil) column was purchased from G. L. Sciences Inc., Tokyo, Japan.

Chemicals

All samples were purchased from Sigma-Aldrich (Tokyo, Japan) or Fluka Chemika-Biochemika (Tokyo, Japan), and HPLC grade methanol or THF from Wako Pure Chemicals (Tokyo, Japan).

Measurements

The chromatography was performed using methanol or methanol-water as the mobile phases, at the flow-rate of 1 or 0.8 mL min^{-1}. The chromatography system consisted of a type 880 PU pump and a type MD-910 uv-vis photodiode array detector or a type 930 intelligent RI detector, both obtained from Jasco (Tokyo, Japan), a Rheodyne 7125 injection valve (Rheodyne, Cotati, CA, USA), a type U-620 column oven (Sugai, Tokyo, Japan), and a type C-R6A data processor (Shimadzu, Tokyo, Japan). Volumes of five microliter of the samples dissolved in methanol or THF were injected. The retention factor (k') was determined by the equation $(t_e - t_o)/t_o$, where t_e and t_o are the retention time of solutes and the void volume mark, respectively. The retention time of D_20 or a deflection mark, due to injection, was used as the void volume mark t_O.

RESULTS AND DISCUSSION

Phase Transition of Sil-ODA$_{18}$

Both ODA$_{18}$ and Sil-ODA$_{18}$ showed an endothermic crystalline-to-isotropic phase transition in the DSC measurement. The peak top temperature (T_{c2}) in methanol-water (80:20) dispersion was detected at 47°C for ODA$_{18}$, and at 40°C with a shoulder from 30°C for Sil-ODA$_{18}$. Sil-ODA$_{18}$ was in the crystalline state at temperature below 30°C. Crystalline-to-liquid crystalline and liquid crystalline-to-isotropic states were detected between 30-40°C and 40-46°C, respectively. The phase became isotropic at temperature above 46°C. The decrease in phase transition temperature of ODA$_{18}$ after immobilization, indicates that interfacial constraints influence the orientation order of ODA$_{18}$. Phase characterization has been discussed in more details, in our previous report.[20]

Comparison of Retention of PAHs with ODS and Sil-ODA$_{18}$ Supports

The retention factor (k') of PAHs on ODS (Inertsil) and Sil-ODA$_{18}$ phases was measured at 25°C and 55°C using methanol-water (85:15) as the mobile phase, and plotted against the partition coefficient (log P) values. The log P values are not the actual water/octanol partition coefficient values. These values were determined from the calibration curve of log k' vs. log $P°$(octanol/water) for alkylbenzenes (methyl-, ethyl-, butyl-, hexyl-, octyl,- and decylbenzene). The k' values of alkylbenzenes were measured on ODS (Inertsil, monomer type) at 25°C using methanol-water (85:15). The correlation coefficient of this curve was 0.9999. For comparing the retention behaviors of PAHs on ODS and Sil-ODA$_{18}$, the same log P values were put in all the log k' vs. log P plots. The log k' values of PAHs measured on ODS at 25°C and 55°C showed good linearity with the log P values (Figure 1-a). On the other hand, some deviations were observed towards four- and higher than four-membered ring solute molecules, when the log k' values measured on Sil-ODA$_{18}$ at 25°C were plotted against the log P values (Figure 1-b). A good linearity was, however, obtained with Sil-ODA$_{18}$ (R = 0.9986) at 55°C (Figure 1-c). This deviation cannot be explained only by the partitioning effect. It might be due to the selective incorporation of solute molecules with the oriented structure.

Classification of PAHs

In the plot of k' vs. temperature, small-size PAHs (up to four-membered) on Sil-ODA$_{18}$ showed a distinct k'-jump at around the phase transition temper-

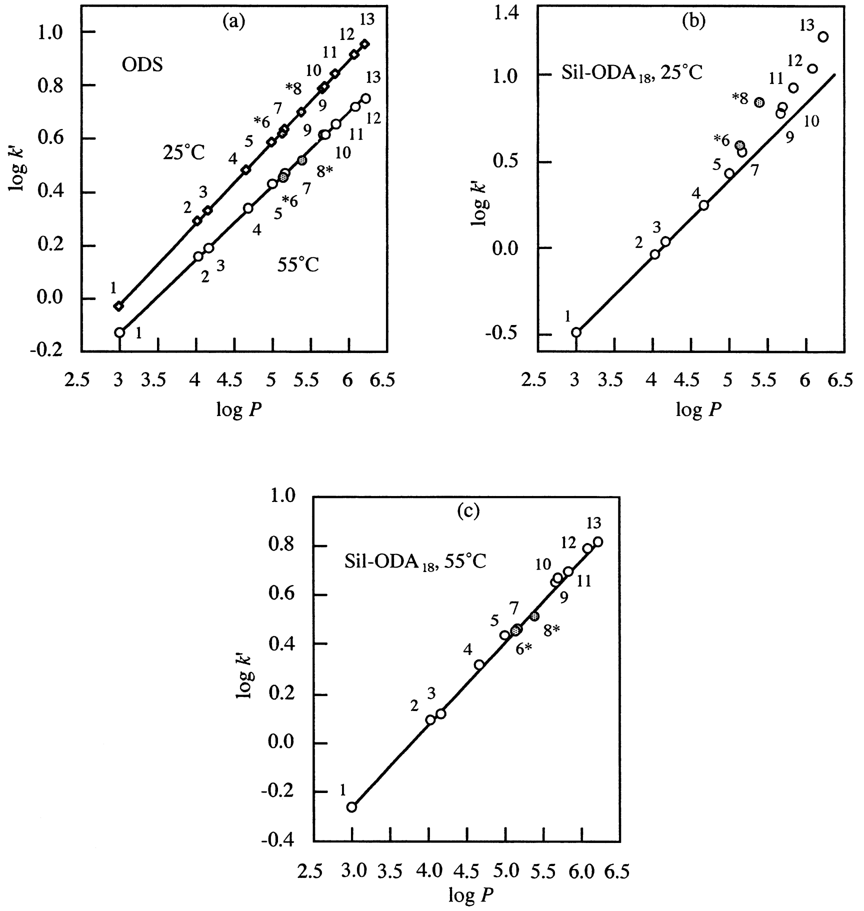

Figure 1. Relationship between log *k*' and log *P* at 25°C and 55°C for PAHs on ODS and Sil-ODA$_{18}$ columns. Solute molecules: naphthalene (1), phenanthrene (2), anthracene (3), pyrene (4), triphenylene (5), chrysene (6), benz(a)anthracene (7), naphthacene (8), benzo(e)pyrene (9), perylene (10), benzo(a)pyrene (11), dibenz(a,c)anthracene (12), dibenz(a,h)anthracene (13). Mobile phase: methanol-water (85:15). Flow-rate 1 mL min^{-1}.

ature (Figure 2-a). On the other hand, large-size molecules (five-membered) benzo(a)pyrene, dibenz(a,c)anthracene, dibenz(a,h)anthracene, pentacene, etc., showed a decrease in retention with increasing temperature (Figure 2-b,c). Some exceptions were, however, observed with the intermediate molecules, i.e., four- and five-membered ring molecules (Figure 2-d). Naphthacene is a four-membered ring molecule but behaved like a large-size molecule, i.e., a decrease

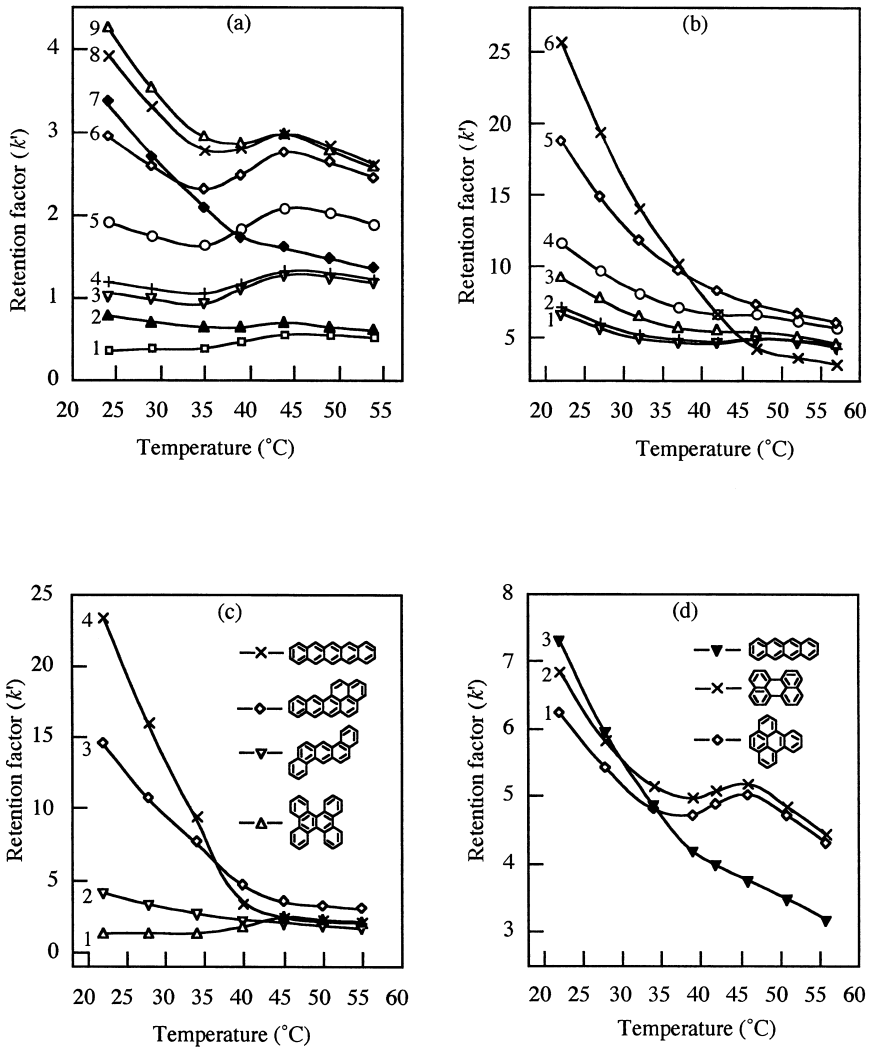

Figure 2. Retention behaviors of PAHs and quinones on Sil-ODA$_{18}$. Up to four-membered ring solutes (a): naphthalene (1), anthraquinone (2), phenanthrene (3), anthracene (4), pyrene (5), triphenylene (6), 5,12-naphthacenequinone (7), benz(a)anthracene (8), chrysene (9); five-membered ring solutes (b): benzo(e)pyrene (1), perylene (2), benzo(a)pyrene (3), dibenz(a,c)anthracene (4), dibenz(a,h)anthracene (5), 6,13-pentacenequinone (6); five- and six-membered solutes (c): dibenzo(g,p)chrysene (1), deibenz(a,h)anthracene (2), naphtho(2,3-a)pyrene (3), pentacene (4); and intermediate (4- and 5-membered ring) solutes (d): benzo(e)pyrene (1), perylene (2) and naphthacene (3). Mobile phase: methanol-water (85:15) for (a), (b), (d), and methanol for (c). Flow-rate: 1 mL min^{-1}.

in retention with increasing temperature. On the other hand, benzo(e)pyrene and perylene with five rings showed a *k*'-jump. In contrast, PAHs did not show such a *k*'-jump when measured on an ODS (Inertsil) column.

Elution Order of PAHs and Quinones on Sil-ODA$_{18}$ and ODS columns

The elution order of PAHs and quinones varies between ODS (Inertsil) and Sil-ODA$_{18}$ columns at 25°C temperature. We found the elution order on ODS: naphthalene < anthraquinone < phenanthrene < anthracene < 5,12-naphthacenequinone* < pyrene < triphenylene < chrysene* < benz(a)anthracene < naphthacene* < 6,13-pentacenequinone* < benzo(e)pyrene < perylene < benzo(a)pyrene < dibenz(a,c)anthracene < dibenz(a,h)anthracene < pentacene* < naphtho(2,3-a)pyrene; and on Sil-ODA$_{18}$: naphthalene < anthraquinone < phenanthrene < anthracene < pyrene < triphenylene < 5,12-naphthacenequinone* < benz(a)anthracene < chrysene* < benzo(e)pyrene < perylene < naphthacene* < benzo(a)pyrene < dibenz(a,c)anthracene < dibenz(a,h)anthracene < 6,13-pentacenequinone* < naphtho(2,3-a)pyrene < pentacene* (Figures 1,2,3). 6,13-Pentacenequinone* eluted after benzo(e)pyrene, perylene, benzo(a)pyrene, dibenz(a,c)anthracene and dibenz(a,h)anthracene on Sil-ODA$_{18}$ at the crystalline state, whereas it eluted first on ODS. Naphthacene* eluted after benzo(e)pyrene and perylene on Sil-ODA$_{18}$, even though naphthacene is a four-membered ring molecule, and 5,12-naphthacenequinone* after pyrene and triphenylene, whereas they eluted earlier on ODS. Similarly, pentacene eluted after naphtho(2,3-a)pyrene on Sil-ODA$_{18}$. On the other hand, it eluted prior to naphtho(2,3-a)pyrene on ODS (not shown in figure). Typical chromatograms for PAHs on Sil-ODA$_{18}$ and on ODS are shown in Figure 3. We assume, that this kind of unusual elution order with Sil-ODA$_{18}$, arises from the selective retention of PAHs on Sil-ODA$_{18}$ in the crystalline region. The results have also revealed that the elution order on ODS at 25°C and 55°C, and on Sil-ODA$_{18}$ at 55°C is identical. Therefore, shape discriminating abilities of Sil-ODA$_{18}$ at the isotropic state, and of ODS, could be assumed similar.

Shape Parameter (*L/B*) and Retention Behaviors of PAHs on Sil-ODA$_{18}$

The retention behaviors of solutes depend upon slenderness, i.e., length/breadth (*L/B*) ratio. The *L/B* is defined as the ratio of length to breadth dimensions of a box drawn about the molecule, such, that the maximum *L/B* value is produced. The *L/B* ratios of naphthacene, chrysene, benz(a)anthracene, and triphenylene are 1.89, 1.72, 1.58, and 1.12, respectively. The most slender naphthacene showed a decrease in *k*' with increasing temperature, whereas, the others showed a *k*'-jump at around T_C (Figure 2-a,d). The *L/B* ratios of disk-like benzo(e)pyrene (1.12) and perylene (1.27) are much smaller than benzo(a)pyrene (1.50) and dibenz(a,h)anthracene (1.79). Consequently,

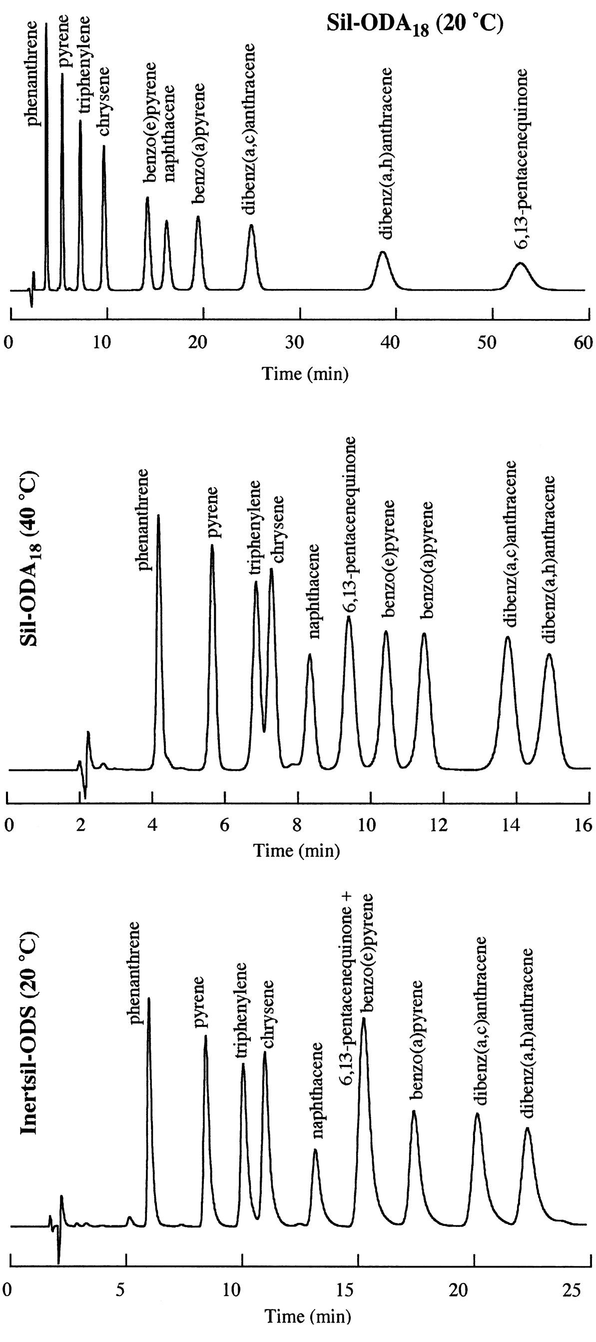

Figure 3. Typical chromatograms for PAHs on Sil-ODA$_{18}$ and ODS stationary phases. Mobile phase: methanol-water (85:15). Flow-rate: 1 mL min^{-1}.

benzo(e)pyrene and perylene showed a *k*'-jump (Figure 2-b,d). On the other hand, although the *L/B* ratios of perylene and dibenz(a,c)anthracene are almost the same, i.e., 1.27 and 1.24, respectively, they behaved unlike at around T_C We have also observed, that six-membered ring molecules, naphtho(2,3-a)pyrene and benzo(ghi)perylene, and seven-membered ring, coronene, did not exhibit such a jump. It appears that size is likely the factor that influences the retention in the non-crystalline region. Six-membered ring dibenzo(g,p)chrysene, however, exhibited a *k*'-jump (Figure 2-c). Therefore, size is not the only determining factor to show a *k*'-jump. The *L/B* values were obtained from reference 23.

Retention-Jump of Solutes on Sil-ODA$_{18}$ at Around T_C

Molecular theory of chromatographic selectivity enhancement for block-like solutes in anisotropic stationary phases derived by Yan and Martire, shows that the contact areas of solutes with the isotropic phases are much larger than with the anisotropic phases.[24] Therefore, the contact volumes of non-planar solutes with the isotropic phases would be larger than the corresponding planar solutes. The effect of solute-stationary phase contact volume on *k*'-jump is understood from the comparison of *k*'-jump between planar and non-planar solutes. For example, *k*'-jump from 35°C to 45°C for cyclohexane and *trans*-decalin was found to be 5 and 8 times higher than benzene and naphthalene, respectively (Figure 4). The *k*'-jump of benzene, 1,4-cyclohexadine, cyclohex-

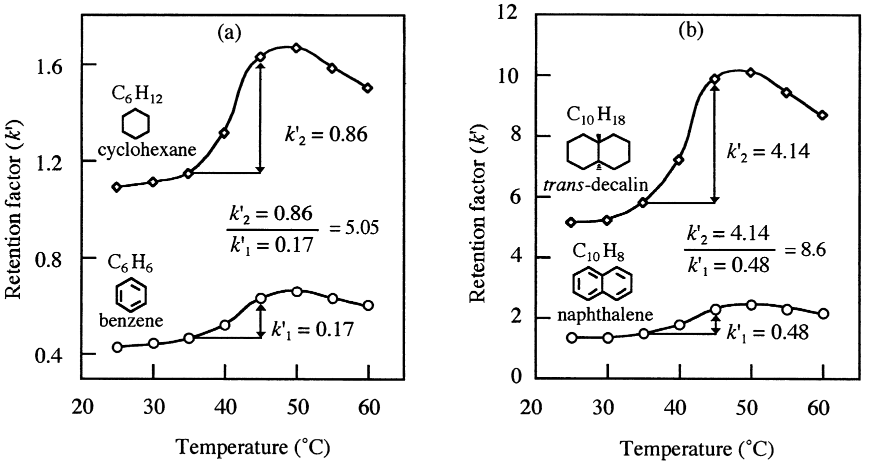

Figure 4. Comparison of *k*'-jump between planar and non-planar solutes on Sil-ODA$_{18}$. Mobile phase: methanol-water (70:30). Flow-rate 0.8 mL min^{-1}.

ene, and cyclohexane, or naphthalene, 1,4-dihydronaphthalene, 1,2,3,4-tetrahydronaphthalene, and *trans*-decalin on Sil-ODA$_{18}$ further supports the effect of solute non-planarity on retention. The *k*'-jump increased with increasing non-planarity (Table 1). These results are, thus, suggesting that molecular planarity influences the retention of solutes at around the phase transition temperature.

The PAHs with small *L/B* ratios often possess sterically crowded regions, also called "bay-regions", which make the molecules to be less planar resulted from the hindrance of approximate hydrogen and/or carbon atoms.[25-26] The strain that creates a twist in the molecule is characterized by the dihedral angle between affected atoms. The "dihedral angle of distortion" was characterized by Garrigues and co-workers.[25] The distortion angle is defined as the dihedral angle between the aromatic rings opposite to each other (i.e., not adjacent rings) in the bay-region. Dibenzo(g,p)chrysene has four bay-regions, and both perylene and benzo(e)pyrene have two. This could be the reason to show an exceptional retention behavior at around T_C (Figure 2-c,d). On the other hand, both dibenz(a,c)anthracene and triphenylene have three bay-regions, but only triphenylene showed a *k*'-jump. Similarly, dibenz(a,h)anthracene did not show such a jump, whereas benz(a)anthracene showed with a fewer bay-regions (Figure 2-a,b). Size factor is also understood from the retention behaviors of naphthalene, anthracene, naphthacene, and pentacene. They do not have any bay-region. Consequently, naphthacene and pentacene did not exhibit any increase in retention with increasing temperature (Figure 2-c,d). In contrast, naphthalene and anthracene showed a distinct *k*'-jump (Figure 2-a). Therefore, whether PAHs would exhibit a *k*'-jump depends upon the molecular size and shape (particularly *L/B* ratio), planarity and slenderness. Thus, we assume that (i) relatively small-size solutes are able to incorporate with the non-crystalline region more readily than the large-size solutes, (ii) non-planar solutes are retained preferentially with the flexible non-crystalline region, and slender and planar solutes with the ordered region.

Table 1

Retention-Jump of Cyclic Planar and Non-Planar Soluteson Sil-ODA$_{18}$*

Solutes	*k*'- Jump (45°C-30°C)	Solutes	*k*'-Jump (45°C-30°C)
Benzene	0.13	Naphthalene	0.36
1,4-Cyclohexadine	0.25	1,4-Dihydronaphthalene	0.51
Cyclohexene	0.41	1,2,3,4-Tetrahydronaphthalene	0.73
Cyclohexane	0.65	*trans*-Decalin	3.25

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* Mobile phase: Methanol-Water (75:25). Flow-rate: 1 mL min^{-1}.

Cross-Over Phenomena due to Change in Orientation Order of Sil-ODA$_{18}$

The cross-over in the temperature dependent plots between slender pentacene, naphthacene, 6,13-pentacenequinone, or 5,12-naphthacenequinone, and relatively bulky PAHs, was observed because of the unusual enhancement of the retention factor towards slender solute molecules at the crystalline state (Figure 2, 3). We assume that this enhancement was resulted from, either by the π-π interaction, or the selective incorporation of solute molecules with the ordered side chains. In both situations, retention enhancement in the crystalline region would be more pronounced towards slender isomeric PAHs because of the length factor.

Carbonyl groups of octadecyl acrylate moieties of Sil-ODA$_{18}$ exist on the same plane in the ordered structure. Therefore, solute molecules have to align themselves parallel to the ordered carbonyl groups, rather than to incorporate with the ordered side chains to reach the maximum number of π-electrons for the effective π-π interaction. Carbonyl groups, however, gradually distort from the plane with decreasing phase organization, and hence, the π-π interaction diminishes on transition from crystalline to isotropic state. A cross-over of pentacene, naphthacene, 6,13-pentacenequinone, or 5,12-naphthacenequinone, thus, occurred with that PAH whose enhancement of the retention factor due to π-π interaction was relatively small, but relatively large because of the partitioning driving force.

If the solutes, however, are aligned preferentially with the slots (stretched side chains) than with the ordered carbonyl groups, solute-stationary phase contact area has to be taken into consideration. The entropy loss for a more rod-like solute to interact with the aligned nematic liquid-crystalline phase is more than compensated by its enthalpy gain, making it soluble than a less rod-like solute molecule.[5] In other words, planar and slender solutes are readily accommodated with the ordered phase than bulky solutes. Consequently, slender and planar solutes have greater contact areas than the corresponding non-planar bulky solutes. The enhancement of the retention factor for pentacene, naphthacene, 6,13-pentacenequinone, or 5,12-naphthacenequinone, in the crystalline region, was thus, resulted from the large solute-stationary phase contact area and a close interaction. To explain the *k*'-jump, we have shown that the contact volumes of non-planar solutes with the isotropic phase are larger than planar solutes. Therefore, on transition from the ordered crystalline state to the less ordered isotropic state, the decreasing rate of the retention factor would be more distinctive for the rod-like planar and slender solute than the corresponding bulky solute. Pentacene, naphthacene, 6,13-pentacenequinone, or 5,12-naphthacenequinone, thus, crossed over that bulky PAH molecule whose contact volume was relatively small with the ordered phase, but relatively large with the isotropic phase (Figure 2, 3).

The results, thus, indicate that solute-stationary phase contact volume greatly influences the selectivity and the retention behavior of PAHs with Sil-ODA_{18}, and which is dependent upon the orientation order of the immobilized phase. Whether the alignment of solute molecules with the ordered carbonyl groups, or the incorporation with the ordered side chains of Sil-ODA_{18} would be the predominating factor for the enhancement of the retention factor of PAHs at the crystalline state, is the subject of our subsequent issue.

CONCLUSION

The retention of PAHs on Sil-ODA_{18} depends upon the planarity and slenderness of solute molecules. Relatively bulky solutes are retained preferentially with the flexible non-crystalline region, whereas planar and slender solutes with the more ordered region.

The *k*'-jump at around the phase transition temperature arises from the increased solute-stationary phase contact volume on transition from crystalline to isotropic state.

The retention of PAHs on Sil-ODA_{18} in the crystalline region is highly selective, and the shape discriminating abilities of this column are much better than that of an ODS (monomeric type) column. The selectivity of Sil-ODA_{18} in the non-crystalline region and of ODS is, however, almost identical.

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