

High retentivity and selectivity for polycyclic aromatic hydrocarbons with poly(4-vinylpyridine)-grafted silica in normal-phase high-performance liquid chromatography

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Available online 15 December 2007

Abstract

In this study, we introduce an attractive stationary phase, poly(4-vinylpyridine)-grafted silica (VP_n) for normal-phase high-performance liquid chromatography. The retention behavior of polycyclic aromatic hydrocarbons (PAHs) was investigated with VP_n column under *n*-hexane/2-propanol mixture as mobile phase. Conventional octadecylated silica, aminopropyl-bonded silica, bare silica and poly(styrene)-grafted silica columns were used as reference columns. Extremely high retention factors were observed for PAHs but not for alkylbenzenes and distinct higher selectivity towards PAHs was observed for the detailed molecular shape such as planarity and aspect ratio. The reason for these results seems to be a multiple interaction effect including an inductive interaction between the pyridyl and aromatic rings.

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Keywords: NP-HPLC; PAHs; Retention mechanism; Poly(4-vinylpyridine); Inductive interaction; Molecular polarizability

1. Introduction

Normal-phase high-performance liquid chromatography (NP-HPLC) includes stationary phases such as solid adsorbents, bonded and immobilized liquids and chiral columns operated with nonaqueous, nonpolar, or moderately polar mobile phases [1]. Notoriously bad reputations of NP-HPLC such as poor reproducibility, unpredictable retention and shorter life time of the column can be overcome using carefully dried solvents, and carefully maintained temperature with synthetic adsorbents [2–4]. Compared to the development in reversed-phase high-performance liquid chromatography (RP-HPLC), adsorbents for NP-HPLC have seldom been reported [3]. Separation of mixture of compounds having similar polarity such as structural and geometrical isomers of polycyclic aromatic hydrocarbons (PAHs) using RP-HPLC is still a challenge for the analyst [5]. On this viewpoint, NP-HPLC because of its exceptional selectivity is also the method of choice for the separation of enantiomers [3] can be the best option for their separation. So, the development

and characterisation of stationary phase suitable for NP-HPLC will be of utmost importance.

Poly(4-vinylpyridine) as a synthetic adsorbent is emerging as a new promising adsorbent for HPLC. Our group has already reported poly(4-vinylpyridine) to be useful as a novel adsorbent for RP-HPLC. It was shown to have unique molecular-shape selectivity for PAHs and positional isomers [6,7]. If the same stationary phase can also be used in NP-HPLC, a combination of RP-HPLC and NP-HPLC will expand additional possibilities in the separation process.

On the other hand, mechanism and theoretical description of analyte retention in HPLC has been the subject of many publications; different research groups and scientific schools remain in disagreement on what is the most realistic retention mechanism and what is the best theory to describe analyte retention [8]. Interpretation of solute retention in terms of molecular properties is the promising approach to understand retention mechanism at molecular level [9]. Besides this, complete understanding of retention will allow researchers to use the chromatographic column to measure physical parameters that are otherwise difficult to obtain [10]. The objective of the present work is to evaluate poly(4-vinylpyridine) as a novel organic adsorbent for the separation of PAHs in NP-HPLC. We have also tried to explore the

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retention mechanism by investigating the correlation between the retention factor and molecular properties of PAHs.

2. Experimental

2.1. Chemical and reagents

All PAHs and alkylbenzenes elutes were commercially available and used without further purification. Benzo[*a*]pyrene, dibenzo[*a,c*]anthracene, coronene and naphthacene were from Tokyo Kasei Kogyo (Tokyo, Japan). Dibenzo[*a,h*]anthracene, *cis/trans*-stilbene and chrysene were from Aldrich (Milwaukee, WI, USA). 4-Vinylpyridine monomer was purchased from Sigma–Aldrich (Steinheim, Germany) and was used after distillation. 3-Mercaptopropyltrimethoxysilane was purchased from Azmax (Chiba, Japan). YMC silica gel (120-S5, diameter 5 μm , pore size 120 \AA , specific surface area 330 $\text{cm}^2 \text{g}^{-1}$) was used as porous silica.

2.2. Columns

Poly(4-vinylpyridine) with a terminal trimethoxysilyl group was prepared according to a previously reported telomerization method [6]. The average degree of polymerization was determined by ^1H NMR spectroscopy to be 22. The polymer was readily grafted onto porous silica by mixing in toluene at the reflux temperature. The amount of the immobilized polymer was determined by elemental analysis to be 27.5% (w/w). Polymer-grafted silica, VP₂₂ (average degree of polymerization 22) was packed into a stainless-steel column (250 mm \times 4.6 mm I.D.). Poly(styrene)-grafted silica, PS₂₀ ($n=20$; amount of the immobilization 18.3%, w/w) was prepared according to a similar procedure, [6] and then packed into a stainless-steel column (250 mm \times 4.6 mm I.D.). ODS and silica columns (Inertsil ODS-3 and Inertsil silica, 250 mm \times 4.6 mm I.D., GL-Science, Tokyo, Japan) and aminopropyl-bonded silica column (Lichrospher NH₂, 250 mm \times 4.0 mm I.D., Kanto Chemicals, Tokyo, Japan) were used as reference columns for the analysis of PAHs.

2.3. Measurements

The analysis was conducted at 35 $^\circ\text{C}$ under an isocratic condition using chromatograph with a pump (JASCO PU-980), a column heater (Sugai U-620 Type 30VP) and a JASCO multi-wavelength detector (MD-910). *n*-Hexane, *n*-hexane/2-propanol and *n*-hexane/acetone were used as the mobile phases. Five microliters of each sample was injected through an injector (Reodyne Model 7725). A flow rate of 1 ml min^{-1} was maintained in all the analysis. The retention factor (k) was determined by $(t_e - t_o)/t_o$, where t_e and t_o are the retention times of a sample and deflection due to injection of *n*-dodecane, respectively. The separation factor (α) was given by the ratio of the retention factors.

2.4. Calculations

The structures of *o*-terphenyl and triphenylene were estimated by HyperChem Ver. 5.1 with molecular mechanics (until the

energy changes were below 0.001 kcal mol^{-1}) and following semi-empirical AM1 method. The dipole moments of acetone and 2-propanol were determined by HyperChem Ver. 5.1 with the same method.

3. Results and discussion

3.1. Retention behavior for alkylbenzenes and PAHs

A series of alkylbenzenes and PAHs were used to evaluate the retention mode of VP₂₂ in NP-HPLC. When *n*-hexane/2-propanol mixture (9:1) was used as mobile phase at 35 $^\circ\text{C}$, the chromatogram shown in Fig. 1 was obtained. Complete separation was not observed for alkylbenzenes but much better separation was observed for PAHs. It seems that the VP₂₂ phase is sensitive to the molecular aromaticity of elutes. The abnormality is clearer by plotting the retention factor against the number of carbon atoms, as shown in Fig. 2. The retention factor for alkylbenzenes decreased with an increase in the number of carbon atoms. This can be understood by the hydrophobic effect: hydrophobic elutes having high number of carbon atoms prefers to be in a hydrophobic mobile phase. On the other hand, the retention factor for PAHs increased with

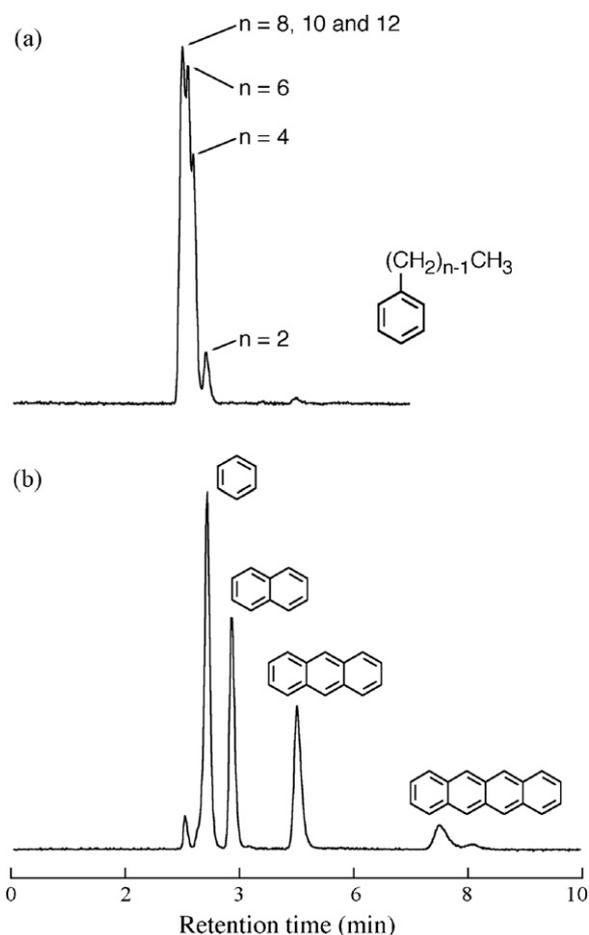


Fig. 1. Typical chromatograms for a mixture of alkylbenzenes (a) and polycyclic aromatic hydrocarbons (b) with VP₂₂. Mobile phase: *n*-hexane/2-propanol (9:1), column temperature: 35 $^\circ\text{C}$, flow rate: 1 ml min^{-1} .

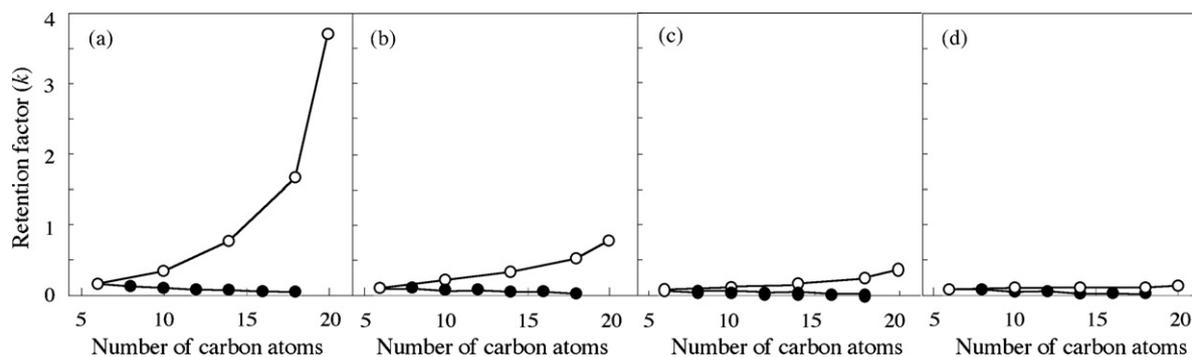


Fig. 2. Relationships between the retention factor (k) and number of carbon atoms with VP₂₂ (a), PS₂₀ (b), NH₂ (c) and silica (d). Mobile phase: *n*-hexane/2-propanol (9:1) at 35 °C. Elutes: benzene, naphthalene, anthracene, naphthacene, and benzo[*e*]pyrene (open circles); ethyl-, butyl-, hexyl-, octyl-, decyl- and dodecyl-benzenes (solid circles).

Table 1

Retention (k) and separation factors (α) for linear PAHs in VP₂₂, PS₂₀, NH₂, silica and ODS at 35 °C

PAHs	No. of double bonds	VP ₂₂		PS ₂₀		NH ₂		silica		ODS	
		k^a	α	k^a	α	k^a	α	k^a	α	k^a	α
Benzene	3	0.17	2.06	0.12	1.75	0.09	1.44	0.42	1.69	0.15	1.27
Naphthalene	5	0.35		0.21		0.13		0.71		0.19	
Anthracene	7	0.76	2.17	0.34	1.62	0.18	1.38	1.15	1.62	0.25	1.32
Naphthacene	9	1.65		0.52		0.26		1.85		0.36	

^a Mobile phases: *n*-hexane/2-propanol (9 : 1) in VP₂₂, PS₂₀ and NH₂; *n*-hexane in silica and ODS.

an increase in the number of carbon atoms. This is expected since NP-HPLC has already been reported to separate PAHs into fractions with regard to ring size [11] and aminopropylsilane-bonded silica had provided the distinct separation of PAHs based on the number of the condensed rings [12]. Interestingly, VP₂₂ showed much larger retention factors than PS₂₀, NH₂, silica and ODS, although the retention factors for alkylbenzenes in VP₂₂ were quite small similar to that in PS₂₀, NH₂, silica and ODS. This indicates that VP₂₂ provides a specific interacting site for PAHs. This property was accompanied by the selectivity enhancement as shown in Table 1. Higher separation factor ($\alpha = 2.17$) was obtained for naphthacene/anthracene pair in VP₂₂

while $\alpha = 1.53$ in PS₂₀, 1.44 in NH₂, 1.61 in silica and 1.44 in ODS.

3.2. Molecular-shape selectivity

The molecular-planarity selectivity with VP₂₂ was evaluated by using triphenylene and *o*-terphenyl as elutes. These two compounds possess the same number of carbon atoms and π -electrons, but their molecular-planarity is absolutely different as shown in Fig. 3. Therefore, the separation factor between them could be a good marker to evaluate molecular-planarity selectivity as suggested by Jinno et al. [13,14]. As shown in

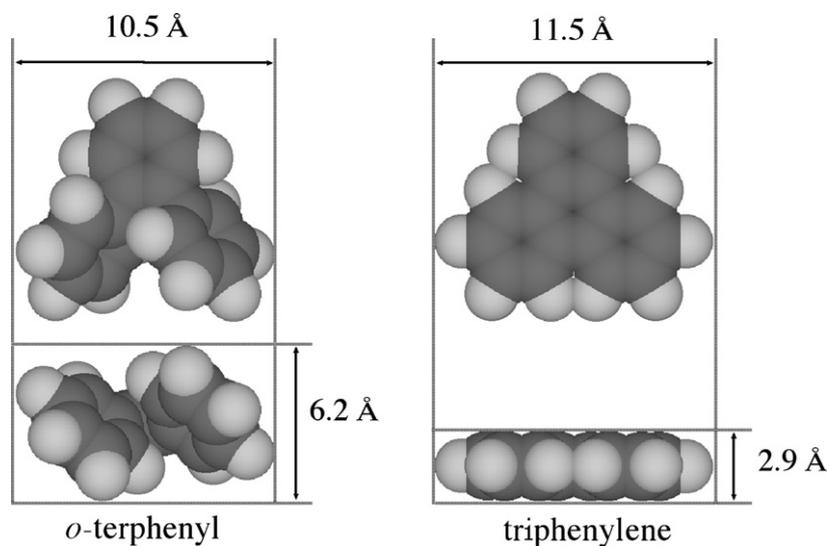


Fig. 3. CPK models of *o*-terphenyl and triphenylene estimated by HyperChem Ver. 5.1 with molecular mechanics and following semi-empirical AM1 method.

Table 2
Retention (k) and separation factors (α) for planar and non-planar PAHs in VP₂₂, PS₂₀, NH₂, silica and ODS at 35 °C

PAHs	VP ₂₂		PS ₂₀		NH ₂		silica		ODS	
	k^a	α	k^a	α	k^a	α	k^a	α	k^a	α
<i>o</i> -Terphenyl	0.26	9.85	0.23	2.57	0.12	2.50	0.09	1.44	0.11	3.18
Triphenylene	2.56		0.59		0.30		0.13		0.35	
<i>cis</i> -Stilbene	0.23	1.91	0.19	1.32	0.11	1.36	0.08	1.13	0.11	1.55
<i>trans</i> -Stilbene	0.44		0.25		0.15		0.09		0.17	
Hexahelicene	2.32	3.63	0.77	1.47	0.34	1.50	0.13	1.15	0.27	2.56
Coronene	8.42		1.13		0.51		0.15		0.69	

^a Mobile phases: *n*-hexane/2-propanol (9 : 1) in VP₂₂, PS₂₀, NH₂ and silica; *n*-hexane in ODS.

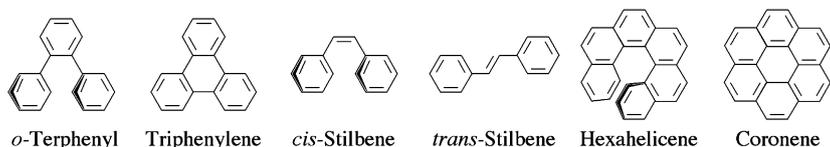


Table 2, much higher separation factor was obtained in VP₂₂ ($\alpha = 9.85$) compared with PS₂₀ ($\alpha = 2.57$), NH₂ ($\alpha = 2.50$), silica ($\alpha = 1.44$) and ODS ($\alpha = 3.18$). This is quite interesting because the molecular-planarity selectivity has been often realized by a planar and rigid organic phase having a strong π - π interaction source, such as porphyrin [15,16], phthalocyanine [17] and dicoronylene [18]. For example, $\alpha = 9.01$ for triphenylene/*o*-terphenyl was obtained in Cu(II)-phthalocyanine-bonded silica with *n*-hexane as mobile phase [17]. Furthermore, shape discrimination of PAHs has been described by the formation of donor-acceptor complex with electron-acceptor (electron deficient) phases such as tetrachlorophthalimidopropyl and tetranitrofluoreniminopropyl in NP-HPLC [19]. The authors have also reported that almost no retention of PAHs had been observed by the use of electron donor-phase such as pyrene in NP-HPLC [19]. Thus the unique selectivity is achieved in VP₂₂ despite the fact that pyridine polymer neither possesses any planar and rigid structure nor is electron-acceptor [20]. Other evidences of planarity selectivity with VP₂₂ can also be seen in the separation of *trans*-/*cis*-stilbenes and coronene/hexahelicene as planar/non-planar elutes, as shown in Table 2.

The uniqueness of VP₂₂ can also be found in the separation of terphenyl-isomers. The three terphenyl-isomers differ strongly in the extent of their non-planarity [21]. The close proximity of the two π -electron clouds of the aryl groups in *ortho*-position

provides a strong sterical hindrance that is amplified by the repulsion of the two aromatic π -electron clouds. Hence the *o*-terphenyl isomer possesses the highest deviation from planarity followed by *m*-terphenyl and *p*-terphenyl and similar was the retention order with VP₂₂ along with higher separation factor between the *p*-/*o*-terphenyls compared to the other reference columns as shown in Table 3.

Specificity of VP₂₂ was also observed for structural isomers of four-ring PAHs. All of them are planar compounds with the same numbers of carbon atoms and π -electrons. As shown in Table 4, the retention factor in VP₂₂ was higher in the order of triphenylene > chrysene > benz[*a*]anthracene > naphthacene. This order is same as that in PS₂₀, NH₂ and silica, and is in the reverse order of $\log P$, which is water/1-octanol partition coefficient [6]. Therefore, the retention order can be understood by the hydrophobic effect. On the contrary, much higher separation factors were obtained in VP₂₂ than the other columns: for example, α for triphenylene/chrysene = 1.20 in VP₂₂, 1.07 in PS₂₀, 1.07 in NH₂, 1.08 in silica and 1.00 in ODS. Higher selectivity can also be seen in the separation of five-ring PAHs as shown in Table 4. It seems that VP₂₂ prefer disk-like PAHs with a small aspect ratio (length-to-breadth ratio, L/B) to linear one. The driving force for this selectivity is discussed with an inductive interaction and polymeric effect in the next section.

Table 3
Retention (k) and separation factors (α) for terphenyl-isomers in VP₂₂, PS₂₀, NH₂, silica and ODS at 35 °C

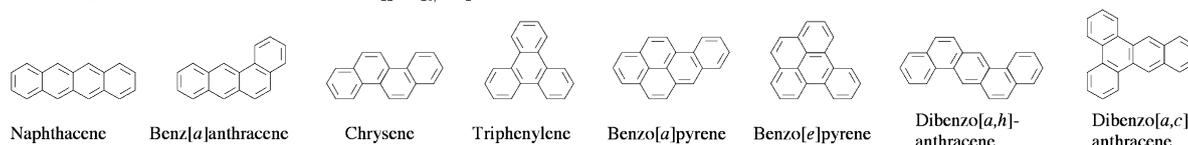
PAHs	VP ₂₂		PS ₂₀		NH ₂		silica		ODS	
	k^a	α	k^a	α	k^a	α	k^a	α	k^a	α
<i>o</i> -Terphenyl	0.26	2.15	0.23	1.35	0.12	1.25	0.09	1.00	0.11	1.55
<i>m</i> -Terphenyl	0.53		0.31		0.15		0.09		0.15	
<i>p</i> -Terphenyl	0.56		0.31		0.15		0.09		0.17	

^a Mobile phases: *n*-hexane/2-propanol (9 : 1) in VP₂₂, PS₂₀, NH₂ and silica; *n*-hexane in ODS.

Table 4
Retention (k) and separation factors (α) for four- and five-ring PAHs in VP₂₂, PS₂₀ NH₂, silica and ODS at 35 °C

PAHs	Number of double bonds	VP ₂₂		PS ₂₀		NH ₂		silica		ODS	
		k^a	α	k^a	α	k^a	α	k^a	α	k^a	α
Naphthacene	C ₁₈ H ₁₂	9	1.65	0.52	0.26	0.12	0.36				
Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂	9	1.95	0.53	0.27	0.12	0.33				
Chrysene	C ₁₈ H ₁₂	9	2.13	0.55	0.28	0.12	0.35				
Triphenylene	C ₁₈ H ₁₂	9	2.56	0.59	0.30	0.13	0.35				
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	10	3.14	0.74	0.34	0.13	0.45				
Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	10	3.68	0.79	0.38	0.13	0.45				
Dibenzo[<i>a,h</i>]anthracene	C ₂₂ H ₁₄	11	4.14	0.84	0.38	0.13	0.45				
Dibenzo[<i>a,c</i>]anthracene	C ₂₂ H ₁₄	11	5.06	0.90	0.39	0.13	0.47				

^a Mobile phases: *n*-hexane/2-propanol (9:1) in VP₂₂, PS₂₀, NH₂ and silica; *n*-hexane in ODS.



3.3. Retention mechanism

For a solute to be retained by a column, it must transfer from the mobile phase into or onto its stationary phase. In general, the solutes association with the stationary phase involves partitioning, adsorption, or their combination [22]. In normal-phase chromatography, the retention is dominantly based on an adsorption process [23]. Various interactions have been described to explain the retention and separation process in liquid chromatography. According to Reusbaet and Jinno [24], the separation of closely related compounds basically involves π – π interactions, hydrogen bond formation, dipole–dipole interactions and steric interactions (shape-fit). It has also been described that normal-phase processes are sensitive to the dipole–dipole interactions and hydrogen bond formation [25]. Previously, we reported that VP_{*n*} showed the selective retention for *o*-isomers of dinitro- and dicyanobenzenes, which possess the strong electron-withdrawing groups, in a reversed-phase mode and this selectivity was brought about through electrostatic interaction such as a dipole–dipole interaction [6]. Therefore, it can be expected that there is a dipole–dipole interaction between a pyridyl group and solute. However, PAHs used in this study are non-polar solutes, having no or very small permanent dipole moments. In such cases, the retention would be dominated by an electrostatic interaction involving a dispersive and inductive effect [26,27] and/or a quadrupolar effect [9,28].

In order to explore the cause for the higher retentivity in VP₂₂, we investigated on the correlation between retention factors and various parameters related to the properties of PAHs. The used parameters such as average molecular polarizability (MP), quadrupole moment (QM), length-to-breadth ratio (*L/B*), water/1-octanol partition coefficient ($\log P$) and electron affinity (EA), whose values for four-ring PAHs are summarized in Table 5. Table 6 shows the correlation coefficients obtained by linear regression analysis for the plots of $\log k$ against MP, QM, *L/B*, $\log P$ and EA. From the results it is clear that VP₂₂ shows the significant correlation with MP and QM, while rather high corre-

Table 5
Molecular properties, MP, QM, *L/B*, $\log P$ and EA of four-ring PAHs

PAHs	MP ^a	QM ^b	<i>L/B</i> ^c	$\log P$ ^d	EA ^e
Naphthacene	32.27	–16.87 ^f	1.89	5.71	1.04
Benz[<i>a</i>]anthracene	32.86	–16.91	1.58	5.42	0.51
Chrysene	33.06	–16.96	1.72	5.40	0.35
Triphenylene	33.51	–17.00	1.12	5.28	0.285

^a Average molecular polarizability; data taken from Ref. [27].

^b Quadrupole moment (buckingham); data taken from Ref. [30].

^c Length-to-breadth ratio; data taken from Ref. [31].

^d Partition coefficient between water and 1-octanol phases; data taken from Ref. [6].

^e Electron affinity (eV); data taken from Ref. [32].

^f Data taken from Ref. [29].

tion coefficient was obtained with MP. It has been reported that if an inductive interaction (dipole-to-induced dipole interaction) is mainly included in the solute-stationary phase interaction, the average molecular polarizability, MP of the solute would be related to its retention [33]. Therefore, we assume that an inductive interaction is included in an association between the pyridine polymers and PAHs, and this interaction is one of the sources for high selectivity toward disk-like PAHs. As support-

Table 6
Correlation coefficients obtained by linear regression analysis for the plots of $\log k$ against MP, QM, *L/B*, $\log P$ or EA

Columns	Correlation coefficients, r^2				
	MP	QM	<i>L/B</i>	$\log P$	EA
VP ₂₂ ^a	0.988	0.971	0.820	0.892	0.827
PS ₂₀ ^a	0.879	0.920	0.834	0.705	0.616
NH ₂ ^a	0.910	0.992	0.653	0.764	0.757
Silica ^a	0.742	0.817	0.783	0.534	0.441
ODS ^a	0.0682	0.00361	0.0577	0.211	0.184

^a Mobile phases: at 35 °C, *n*-hexane/2-propanol (9:1) in VP₂₂, PS₂₀ NH₂ and silica; *n*-hexane in ODS; Elutes: naphthacene, benz[*a*]anthracene, chrysene and triphenylene.

Table 7
Effect of mobile phase on separation factors (α) between triphenylene and naphthacene in VP₂₂ and PS₂₀

	$\alpha_{\text{naphthacene/triphenylene}}^a$	
	10% Acetone	10% 2-Propanol
VP ₂₂	1.36	1.55
PS ₂₀	1.13	1.13

^a Mobile phases: 35 °C, *n*-hexane/acetone (9: 1) or *n*-hexane/2-propanol (9:1).

ing this assumption, the use of acetone as an alternative mobile phase to 2-propanol decreased the selectivity in VP₂₂, although no such decrease was observed in PS₂₀ (Table 7). Since acetone is more polar than 2-propanol (dipole moment: 2.75 in acetone; 1.61 in 2-propanol), the acetone molecule would work as an inhibitor for the inductive interaction between VP₂₂ and PAHs but not for π – π interaction between PS₂₀ and PAHs.

The conformational effect of the polymer chain should be discussed because an unexpected increase of selectivity has often been observed in a polymeric organic phase [34]. Earlier, we reported that a multiple interaction is more effective for linear PAHs such as naphthacene than triphenylene when π – π interaction sources are one-dimensionally aligned in the ordered polymer-grafted silica [14,35]. On the other hand, it is obvious that VP₂₂ has no driving force to form any ordered structure. In addition, the nitrogen atoms in VP₂₂ can interact with the residual silanol groups on the silica surface through hydrogen bonding [6], and thus the mobility of the polymer chains must be reduced. Therefore, it is estimated that VP₂₂ provides disordered adsorption sites leading to a multiple interaction preferably for disk-like PAHs such as triphenylene and coronene.

These understandings lead us to the following estimations for a retention mechanism in VP₂₂: (1) an inductive interaction is included in an association between the pyridine polymers and PAHs. (2) This interaction must be derived from the nitrogen atom in a pyridine ring because it is strongly polarized (point charge: –0.142). Nitrogen atom having negative point charge can induce dipole in PAHs, and thus a dipole-to-induced dipole interaction is developed between a pyridine ring and PAHs. (3) The pyridine rings must be in disordered state because VP_n has no driving force to form any ordered structure. As a result, (4) disk-like PAHs such as triphenylene and coronene provide more effective interaction area with randomly placed pyridine rings, than linear ones such as naphthacene.

4. Conclusions

We have demonstrated unique separation behaviors of poly(4-vinylpyridine)-grafted silica in NP-HPLC: extremely high retentivity and selectivity for planar and disk-like PAHs. Through the correlation study between the retention factor and various physico-chemical parameters of PAHs, it is estimated that the high selectivity for disk-like PAHs is derived from multiple interactions including an inductive interaction. The mixed

mode retention mechanism exhibited by VP_n column offers the potential for the development of novel separations that are not currently achievable by more conventional reversed-phase or normal-phase columns.

Acknowledgments

This research was partially supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- [1] J.G. Dorsey, W.T. Cooper, B.A. Siles, J.P. Foley, H.G. Barth, *Anal. Chem.* 70 (1998) 592R.
- [2] P. Jandera, *J. Chromatogr. A* 965 (2002) 239.
- [3] M. Petro, F. Svec, J.M.J. Frechet, *Anal. Chem.* 69 (1997) 3131.
- [4] T. Adachi, E. Isobe, *J. Chromatogr. A* 989 (2003) 19.
- [5] L.C. Sander, M. Pursch, S.A. Wise, *Anal. Chem.* 71 (1999) 4821.
- [6] H. Ihara, M. Fukui, T. Mimaki, A. Shundo, W. Dong, M. Derakhshan, T. Sakurai, M. Takafuji, S. Nagaoka, *Anal. Chim. Acta* 548 (2005) 51.
- [7] H. Ihara, W. Dong, T. Mimaki, M. Nishihara, T. Sakurai, M. Takafuji, S. Nagaoka, *J. Liq. Chromatogr. Rel. Technol.* 26 (2003) 2473.
- [8] Y.V. Kazakevich, *J. Chromatogr. A* 1126 (2006) 232.
- [9] Q.-H. Wan, L. Ramaley, R. Guy, *Chromatographia* 46 (1997) 495.
- [10] J.G. Dorsey, W.T. Cooper, *Anal. Chem.* 66 (1994) 857A.
- [11] C.E. Ostman, A.L. Colmsjo, *Chromatographia* 25 (1988) 25.
- [12] S.A. Wise, S.N. Chesler, H.S. Hertz, L.R. Hilpert, W.E. May, *Anal. Chem.* 49 (1977) 2306.
- [13] K. Jinno, C. Okumura, M. Taniguchi, Y.-L. Chen, *Chromatographia* 44 (1997) 613.
- [14] A. Shundo, T. Sakurai, M. Takafuji, S. Nagaoka, H. Ihara, *J. Chromatogr. A* 1073 (2005) 169.
- [15] C.E. Kibbey, M.E. Meyerhoff, *J. Chromatogr. A* 641 (1993) 49.
- [16] J. Xiao, M.E. Meyerhoff, *J. Chromatogr. A* 715 (1995) 19.
- [17] H. Akizawa, Y. Kitamura, M. Yamane, A. Iwado, J. Oda, M. Mifune, N. Motohashi, J. Haginaka, Y. Saito, *Chem. Pharm. Bull.* 52 (2004) 41.
- [18] K. Jinno, S. Shimura, J.C. Fetzer, W.R. Biggs, *Polycyclic Aromatic Compounds* 1 (1990) 151.
- [19] L.C. Sander, R.M. Parris, S.A. Wise, P. Garrigues, *Anal. Chem.* 63 (1991) 2589.
- [20] S. Kempf, H.W. Rotter, S.N. Magonov, W. Gronski, H.-J. Cantow, *Polym. Bull.* 24 (1990) 325.
- [21] J. Horak, W. Lindner, *J. Chromatogr. A* 1043 (2004) 177.
- [22] K.B. Sentell, J.G. Dorsey, *Anal. Chem.* 61 (1989) 930.
- [23] H. Kazoka, *J. Chromatogr. A* 942 (2002) 1.
- [24] J.L.E. Reubsat, K. Jinno, *Trends Anal. Chem.* 17 (1998) 157.
- [25] M. Waksmundzka-Hajnos, A. Petruczynik, A. Hawryl, *J. Chromatogr. A* 919 (2001) 39.
- [26] K. Jinno, K. Kawasaki, *Chromatographia* 18 (1984) 499.
- [27] H. Lamparczyk, *Chromatographia* 20 (1985) 283.
- [28] Q.-H. Wan, L. Ramaley, R. Guy, *Chromatographia* 48 (1998) 523.
- [29] G.L. Heard, R.J. Boyd, *J. Phys. Chem. A* 101 (1997) 5374.
- [30] K.M. Ng, N.L. Ma, C.W. Tsang, *Rapid Commun. Mass Spectrom.* 12 (1998) 1679.
- [31] K. Jinno, K. Kawasaki, *Chromatographia* 17 (1983) 445.
- [32] A. Modelli, L. Mussoni, *Chem. Phys.* 332 (2007) 367.
- [33] K. Jinno, M. Saito, T. Hondo, M. Senda, *Chromatographia* 21 (1986) 219.
- [34] L.C. Sander, S.A. Wise, *Anal. Chem.* 56 (1984) 504.
- [35] H. Ihara, Y. Goto, T. Sakurai, M. Takafuji, T. Sagawa, S. Nagaoka, *Chem. Lett.* (2001) 1252.