

Investigation of π - π and ion-dipole interactions on 1-allyl-3-butylimidazolium ionic liquid-modified silica stationary phase in reversed-phase liquid chromatography

Hongdeng Qiu,^{a,b} Makoto Takafuji,^a Xia Liu,^b Shengxiang Jiang,^b Hirotaka Ihara^{a,*}

^a*Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan*

^b*Lanzhou Institute of Chemical Physics, Chinese Academy of Science, No. 18 Tianshui Zhonglu, Lanzhou 730000, China*

* Corresponding author. Tel.: +81 96 342 3661; fax: +81 96 342 3662.

E-mail address: ihara@kumamoto-u.ac.jp (H. Ihara).

Abstract

1-Allyl-3-butylimidazolium bromide ionic liquid [AyBIm]Br was prepared and used for the modification of mercaptopropyl-functionalized silica through surface radical chain-transfer addition. The obtained ionic liquid-modified silica (SiImBr) was characterized by elemental analysis, infrared spectroscopy, NMR spectroscopy, and thermogravimetric analysis. The selective retention behaviours of polycyclic aromatic hydrocarbons (PAHs) including some positional isomers were investigated using SiImBr as a stationary phase in reversed-phase liquid chromatography. The results showed that SiImBr presented multiple interactions including hydrophobic, π - π , and ion-dipole interactions during the separation of PAHs and dipolar compounds. However, it is proposed that π - π and ion-dipole interactions play important roles in the separation of PAHs and dipolar compounds. These results indicate that the ionic liquid-modified silica stationary phase is promising for future applications. A commercially available monomeric octadecylated silica (ODS) column and a custom-made poly(styrene)-grafted silica (Sil-St_n) column were used as references.

Keywords: Ionic liquid-modified silica; HPLC; PAHs; Ion-dipole interaction.

1. Introduction

Advances in column technologies have contributed to the development of high-performance liquid chromatography (HPLC) as a modern analytical technique [1]. Most reversed-phase HPLC applications are carried out with octadecylated silica (ODS) columns. However, new stationary phases are still emerging and have been studied in recent years [2,3]. Chemical modification of silica packing materials is still a popular method that is used to achieve novel solute selectivity in HPLC [4]. In our earlier study, polyoctadecylacrylate-grafted silica (Sil-ODA_n) as a lipid membrane-analogous stationary phase showed unique separation behaviours with ordered-to-disordered phase transitions. With this phase, high selectivity towards PAHs was observed in the crystalline state [5,6]. Poly(4-vinylpyridine)-modified silica (Sil-VP_n) not only reduces undesirable silanol effects against basic compounds in HPLC [7] but also shows unique shape-selective separation behaviours for PAHs in both the reverse and the normal phases [8].

On the other hand, room-temperature ionic liquids (ILs) [9], which are known as molten salts, are usually composed of a relatively large organic cation (e.g. imidazolium, pyridium) and a small inorganic anion (e.g. Cl⁻, Br⁻, BF₄⁻). Because of their useful and desirable physicochemical properties such as low melting point, low volatility, and high dissolvability, ILs have been widely studied as novel solvents or materials in organic synthesis [10], catalysis [11], and separation science [12]. ILs were also immobilized on silica and other supports and then used as a recycled catalyst [13], a solid-state electrolyte [14], an extractant for solid phase extraction [15], and an additive for a lubricant [16].

Recently, IL-modified silicas have attracted considerable attention from chromatographic workers [17-29]. In 2004, IL-modified silicas were first used as stationary phases in HPLC for the separation of alkaloids [17]. Effective separations were ascribed to both the hydrophobicity and the ionic property of the phases. Imidazolium-based ILs were covalently bonded on silicas via *n*-alkyl chains, and the retention characteristics of these stationary phases were systematically evaluated by the linear solvation free energy relationship (LSER) method developed by Stalcup et al. [18-20]. Colón et al. [21] synthesized two alkylimidazolium-modified silica stationary phases using trimethoxysilane 'ionosilane' derivatives of ILs; they used these phases for separating aromatic carboxylic acids. On the other hand, we prepared anion-exchange phases based on *N*-methylimidazolium- and imidazolium-functionalized silica [23,24] for the separation of inorganic and organic anions with strong anion-exchange interaction; we also prepared two zwitterionic stationary phases based on sulfonated imidazolium for the simultaneous separation of anions and cations [25,26], and it was observed that some bases and vitamins were also separated successfully [25].

Although multiple interactions of IL-modified silica phases have been pointed out by Stalcup et al. [18-20], Colón et al. [21] and our group [17,23-25] etc., considerable work still needs to be done, including conducting extensive studies on the retention mechanism and the application of IL-modified silica phases. In our previous study [26], a 1-allyl-3-butylimidazolium bromide IL-modified silica stationary phase (SiImBr) was prepared by using the synthesis procedure shown Fig. 1. However, SiImBr was used only as a reference column that presented strong anion-exchange interactions when used to separate inorganic anions. In this study, SiImBr was prepared again using a modified method, characterized in detail, and used to separate PAHs containing positional isomers through multiple interactions such as hydrophobic, π - π , and ion-dipole interactions between imidazolium and the analytes.

2. Experimental

2.1. Materials

1-Allylimidazole (99%) was purchased from Alfa Aesar (Lancs, England). 1-Bromobutane (Cica-Reagent) was purchased from Kanto Chemicals (Tokyo, Japan). 3-Mercaptopropyltrimethoxysilane (MPS) was purchased from Azmax (Chiba, Japan). Azobisisobutyronitrile (AIBN) was obtained from Nacalai tesque, Inc. (Kyoto, Japan) and purified by recrystallization from methanol before use. Porous silica particles 120-S5 (diameter 5 μ m, pore size 120 Å, specific surface area 300 m² g⁻¹) were obtained from YMC (Kyoto, Japan). All PAHs, alkylbenzenes, and other positional isomers were commercially available and used without any purification.

2.2. Preparation of stationary phase

SiImBr was prepared by a surface radical chain-transfer reaction according to a method modified from our previous work [26]. Intermediate products were prepared as follows: MPS-modified silica was prepared according to a published procedure [30], and [AyBIm]Br was prepared in the following manner. To 1-allylimidazole (10.8 g, 0.1mol) in a dry 250 mL flask was added an excess of 1-butylbromide (16.4 g, 0.12 mol). The mixture was stirred at room temperature for two days. The obtained [AyBIm]Br was washed with diethyl ether several times and dried under vacuum, giving a light yellow viscous liquid: yield 99%; ¹H NMR (CD₃Cl, 400 MHz, ppm): δ 10.37 (1H, s), 7.61 (1H, s), 7.53 (1H, s), 6.06 (1H, m), 5.48 (2H, m), 5.07 (2H, d), 4.38 (2H, t), 1.94 (2H, m), 1.42 (2H, m), 0.98 (3H, t).

[AyBIm]Br was grafted onto MPS-modified silica through a surface radical chain-transfer reaction as shown in Fig. 1. MPS-modified silica (3.0 g) was added to a 100 mL three-neck round-bottomed container. [AyBIm]Br (3.0 g) dissolved in 30 mL of acetonitrile and 0.03 g of AIBN was added into the container. The mixture was stirred at 60 °C for 6 h. The precipitates were filtered and washed with acetonitrile, methanol, and diethyl ether. The obtained SiImBr was packed into a column and characterized after being dried under vacuum.

2.3 Characterization

Elemental analyses were carried out on a Yanaco CHN Corder MT-6 apparatus (YANACO Co., Ltd., Kyoto, Japan). Diffuse reflectance infrared Fourier transformation (DRIFT) spectra were obtained on a FT/IR-4100 (JASCO Co., Ltd, Tokyo, Japan) in the range of 4000–400 cm^{-1} . Thermogravimetric analysis was performed on a Seiko Exstar 6000 TG/DTA 6200 thermal analyzer (Seiko Instruments Inc., Chiba, Japan) in static air from 35 to 800 °C with a heating rate of 10 °C min^{-1} . Solid-state ^{13}C NMR spectra were measured using a Varian Unity Inova AS400 (Varian, California, U.S.A.) at a static magnetic field of 9.4 T with a Varian 7 mm VT CP/MAS probe. ^1H NMR spectra for [AyBIm]Br were recorded by a JEOLJNM-LA400 instrument (JEOL, Tokyo, Japan).

2.4 Chromatographic conditions

The SiImBr stationary phase was packed into a stainless-steel column (150 × 4.6 mm I.D.). Two reference columns were monomeric ODS (Inertsil ODS-3, 250 × 4.6 mm I.D., GL Science, Tokyo, Japan) and home-made poly(styrene)-grafted silica (Sil-St_n) (250 × 4.6 mm I.D.), respectively [7]. HPLC-graded methanol and Millipore water were used as components of the mobile phase. All samples were directly dissolved in methanol. The chromatographic system (JASCO, Tokyo, Japan) consisted of a LC-NetII/ADC communication device, a DG-2080-53 3 Line degasser, a PU-2080 Plus Intelligent HPLC pump, a CO-2065 Plus column oven, a UV-2075 Plus Intelligent UV/vis detector, and a Rheodyne injector with a 20 μL sample loop. All chromatographic data were obtained by a JASCO ChromNAV Chromatography Data System. The column temperature was controlled at 25 °C. The flow-rate was 1.0 mL min^{-1} , the detection wavelength was UV 254 nm, and the injection volume was 5 μL . The retention time of D_2O was used as the void volume (t_0) marker (The absorption for D_2O was measured at 400 nm, which is actually considered as the injection shock). The retention factor (k) of an analyte was calculated according to the equation: $k = (t_R - t_0)/t_0$, where t_R is the retention time of the analyte. The separation factor (α) is the ratio of the retention factors for the two solutes being analyzed. The water/1-octanol partition coefficient ($\log P_{o/w}$), usually used to represent molecular hydrophobicity, was determined from the retention factor with the ODS column stated above as $\log P_{o/w} = 3.759 + 4.207 \log k$ ($r = 0.99997$), according to the procedure described in our previous work [31]. The structures, properties, and $\log P_{o/w}$ values for alkylbenzenes and PAHs studied in this work are listed in the supporting information (Table S1).

3. Results and discussion

3.1. Preparation and characterization of SiImBr

1-Allyl-3-butylimidazolium IL was synthesized and then covalently bonded onto MPS-modified silica with AIBN as a radical initiator. This is confirmed from the results of the elemental analysis, which are described below.

The degrees of surface coverage for MPS-modified silica and SiImBr were calculated from the following equations [25]:

$$\text{MPS-modified silica } (\mu\text{mol m}^{-2}) = \frac{\%C}{36 \times (1 - \%C - \%H) \times S} = 3.42 \quad (1)$$

$$\text{SiImBr } (\mu\text{mol m}^{-2}) = \frac{\%N}{28 \times (1 - \%C - \%H - \%N - \%Br) \times S} = 1.66 \quad (2)$$

where %C, %H and %N represent the percentages of carbon, hydrogen, and nitrogen respectively. The elemental contents for MPS-modified silica and SiImBr were C 3.52%, H 1.28% and C 8.24%, H 1.75%, N 1.24%, respectively. The %Br (which is 3.54 here) is calculated from the %N in relation to the stoichiometric ratio (%N: %Br = 28: 80), and S is the specific surface area of the silica support ($300 \text{ m}^2 \text{ g}^{-1}$). The amounts of mercaptopropyl and imidazolium moieties attached to the silica surface can thus be calculated as $3.42 \mu\text{mol m}^{-2}$ for MPS-modified silica and $1.66 \mu\text{mol m}^{-2}$ for SiImBr. From these results, it is concluded that this reaction is an addition reaction and not a polymerization reaction. This may be due to the fact that this allyl IL is less-reactive for polymerization [32].

Infrared spectrometry is one of the useful tools to identify the chemical modifications of compounds. Small differences in wave numbers and in the intensities of the absorption bands are observed in the spectra of MPS-modified silica and SiImBr as shown in the supporting information (Fig. S1a). In the spectrum for the SiImBr surface, the peak at 2966 cm^{-1} is assigned to the C–H stretching of the tetrahedral carbon and the peak at 1557 cm^{-1} is attributed the characteristic frequency of the imidazolium groups, which confirms the anchoring of the organic molecule onto the silica surface [33].

Thermogravimetric curves are usually used to determine thermal stability and to confirm the amount of immobilized compounds. The weight loss observed between 200 and $600 \text{ }^\circ\text{C}$ can be associated with the loss of the organic groups attached to the silica surface. As shown in the supporting information (Fig. S1b), MPS-modified silica presented a mass loss of about 6.4% from $200 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$. After covalently bonding with 1-allyl-3-butylimidazolium IL, SiImBr showed a mass loss of about 15.3%, which indicated that the organic content greatly increased. These mass losses are consistent with the immobilized amounts estimated by the elemental analyses.

Solid-state NMR spectroscopy is another powerful tool to evaluate the chemical composition and conformational properties of chemically modified surfaces. The solid-state ^{13}C NMR spectrum for SiImBr was acquired as shown in Fig. 2. Two important signals related to the imidazolium group bonded on the modified silica were observed at 122 and 135 ppm. Signals attributable to the carbons of mercaptopropyl and alkyl groups could also be identified from the spectrum.

3.2. Evaluation of retention mode

It is known that conventional ODS or other alkylated organic stationary phases can recognize the hydrophobicity of solutes in HPLC, which is measured by the selectivity of the stationary phase for the methylene group. This reflects the possibility that the phase may be able to separate two molecules that differ only in methylene group, e.g., amylbenzene and butylbenzene or ethylbenzene and toluene. The retention mode as well as the extent of hydrophobic interactions among the solutes and the packing materials in HPLC can be determined by retention studies using alkylbenzenes as solutes [5]. Fig. 3 shows the relationship between $\log k$ and $\log P_{o/w}$ for SiImBr, Sil-St_n and ODS. It was observed that SiImBr showed higher retention for PAHs than for alkylbenzenes. For instance, the $\log P_{o/w}$ of naphthacene (5.71) is much smaller than decylbenzene (7.36), but the $\log k$ value of naphthacene (0.30) is clearly higher than decylbenzene (0.13). A similar selectivity to PAHs and

alkylbenzenes was also found in Sil-St_n, but for ODS, log *k* vs. log P_{o/w} plots for alkylbenzenes and PAHs were almost on the same line.

The retention mode was further evaluated using the Tanaka test mixture, which included uracil, caffeine, phenol, butylbenzene, amylbenzene, *o*-terphenyl, and triphenylene. Fig. 4 shows the chromatograms for SiImBr, Sil-St_n, and ODS columns. It can be seen that SiImBr presents a special selectivity compared to Sil-St_n and ODS columns. First, uracil and caffeine cannot be separated as basic compounds with SiImBr in these conditions due to the strong electrostatic repulsion from the imidazolium of SiImBr, however caffeine was even eluted after phenol with Sil-St_n. Second, butylbenzene and amylbenzene were not completely separated. With increasing methanol content, the retention of hydrophobic solutes decreased correspondingly as shown in the supporting information (Fig. S2). Third, the retention order for amylbenzene and *o*-terphenyl in SiImBr was the same as that in Sil-St_n, but different from that in ODS. This is likely due to the fact that both the imidazolium of SiImBr and the phenyl of Sil-St_n contain aromatic rings which can present π - π interactions to PAHs. At the same time, good selectivity for *o*-terphenyl and triphenylene was observed in SiImBr, indicating that SiImBr showed good ability to recognize planarity, as will be discussed later.

3.3. π - π interaction

As shown in Table 1, compared with Sil-St_n and ODS, SiImBr presents low retention but similar selectivity for PAHs. This suggests that SiImBr provides specific interactive sites for PAHs which can recognize aromaticity through imidazolium- π interactions. The separation of benzene, naphthalene, anthracene, and naphthacene in SiImBr, Sil-St_n and ODS columns, as well as the effect of methanol in SiImBr, are shown in the supporting information (Fig. S3).

To evaluate the planarity recognition capability of ODS phases, Tanaka et al. [34] and Jinno et al. [35] introduced the selectivity for *o*-terphenyl ($F=9$, $L/B = 1.11$) and triphenylene ($F=9$, $L/B = 1.12$) as the probes. The F number is a molecular size descriptor proposed by Hurtubise et al. [36]. It is defined as follows: $F = (\text{number of double bonds}) + (\text{number of primary and secondary carbons}) - 0.5 (\text{number of nonaromatic rings})$. The selectivity for two-dimensional shape has been further studied with a molecular shape descriptor, defined as the length-to-breadth (L/B) ratio and proposed by Wise et al. [37] and Kaliszán et al. [38]. Since triphenylene and *o*-terphenyl possess the same number of carbons and π -electrons but different molecular planarity in their structures, the separation factor between them has been used as a good indicator to evaluate the selectivity for molecular-planarity [39]. As shown in Fig. 4 and Table 1, we observed that SiImBr ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 3.89$) shows a remarkably enhanced ability to recognize molecular-planarity compared to Sil-St_n ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 2.04$) and ODS ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 1.57$). Data from additional sample sets including phenanthrene/*cis*-stilbene and fluorene/diphenylmethane confirmed this planarity recognition ability of SiImBr, as shown in Table 1.

The ability to recognize planarity is important in the separation of PAHs with geometric isomers. A mixture including benzene, *cis*-stilbene, *trans*-stilbene, *p*-terphenyl, pyrene, chrysene, benzo[a]pyrene and 1,2:3,4-dibenzanthracene were separated with SiImBr, Sil-St_n and ODS columns as shown in Fig. 5. In this case, the greatest challenge is to separate the probe compounds of *cis*-stilbene and *trans*-stilbene. However, we observed that SiImBr ($\alpha_{\text{trans-}/cis\text{-stilbene}} = 1.68$) showed clearly higher selectivity compared with Sil-St_n ($\alpha_{\text{trans-}/cis\text{-stilbene}} = 1.16$) and ODS ($\alpha_{\text{trans-}/cis\text{-stilbene}} = 1.08$). Another important difference between these separations is that the selectivity for *p*-terphenyl and pyrene was completely different for SiImBr compared with Sil-St_n and ODS. The retention of pyrene on SiImBr was longer than that of *p*-terphenyl ($\alpha_{\text{pyrene}/p\text{-terphenyl}} = 1.43$), but a reversed order

and smaller selectivity were observed in Sil-St_n ($\alpha_{\text{pyrene}/p\text{-terphenyl}} = 0.82$) and ODS ($\alpha_{\text{pyrene}/p\text{-terphenyl}} = 0.87$). The order of retention on Sil-St_n and ODS can be explained by the fact that the hydrophobicity of *p*-terphenyl ($\log P_{\text{o/w}} = 5.15$) is stronger than that of pyrene ($\log P_{\text{o/w}} = 4.88$) [40], and therefore the specificity of SiImBr should be attributed to non-hydrophobic effects such as π - π interactions.

3.4. Ion-dipole interaction

The SiImBr phase was also investigated in the separation of various positional isomers. The retention and separation factors for different isomers on SiImBr, Sil-St_n and ODS are shown in Table 2. We observed that SiImBr showed high selectivity for isomers with electron-withdrawing groups such as dinitrobenzenes and dinitropyrenes, but low selectivity for those with electron-donating groups. SiImBr always showed a higher retention factor for *o*-dinitrobenzene, but Sil-St_n and ODS did not show such selectivity. Chromatograms for the separation of three kinds of mixtures (*p*-, *m*- and *o*-dinitrobenzene; 2- and 1-chloronaphthalene; 1,5- and 1,3-dinitronaphthalene) using SiImBr and ODS are shown in the supporting information (Fig. S4). These results indicate that the selectivity for isomers with electron-withdrawing groups in SiImBr cannot be explained by hydrophobic or π - π interactions. It should be noted that the dipoles of *o*- and *p*-dinitrobenzenes are 7.80 and 0.02, and thus the difference corresponds to 7.78. These facts imply that in SiImBr, the difference of dipoles is important for isomer selectivity. Ion-dipole interaction is an attractive force that results from the electrostatic attraction between an ion and a neutral molecule with a dipole. Therefore, we suggest that the ion-dipole interaction between imidazolium and dipolar compounds could bring about positive effects in the separation of dipolar isomers using SiImBr.

4. Conclusions

Previously, we found that the SiImBr phase shows strong anion-exchange interactions in the separation of inorganic and organic anions [26]. In this paper, we found SiImBr is less sensitive to the hydrophobicity of samples, or only has weak hydrophobic interactions with neutral samples compared to Sil-St_n and ODS. However, SiImBr is more sensitive to aromaticity than hydrophobicity. These phenomena lead to the suggestion that IL-modified silica stationary phase (SiImBr) is similar to a phenyl phase such as Sil-St_n. And SiImBr shows better planarity recognition than Sil-St_n. Another interest is that SiImBr is also sensitive for the dipoles of samples with ion-dipole interactions, especially for nitro-group-containing substances. In conclusion, the IL-modified silica stationary phase is like a phenyl phase in the separation of hydrophobic compounds such as alkylbenzenes and PAHs, but still possesses some special characteristics such as anion-exchange and ion-dipole interactions compared to conventional ODS and phenyl phases. For these reasons, its applicability may be expanded.

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Figure Captions:

Fig. 1. Synthesis of ionic liquid-modified silica stationary phase (SiImBr).



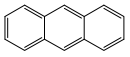
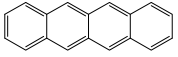
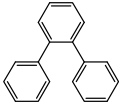

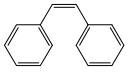
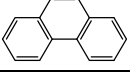
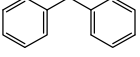
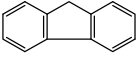
Fig. 2. Solid-state ^{13}C NMR spectrum of SiImBr.

Fig. 3. The relationships of $\log k$ and $\log \text{Po/w}$ for SiImBr (red line), Sil-St_n (blue line), and ODS (green line) stationary phases. Mobile phase: SiImBr, 60% CH₃OH; Sil-St_n, 80% CH₃OH; ODS, 90% CH₃OH. Elutes: including ethylbenzene (1), butylbenzene (2), hexylbenzene (3), octylbenzene (4), decylbenzene (5), dodecylbenzene (6), benzene (7), naphthalene (8), anthracene (9), and naphthacene (10). Flow-rate: 1.0 mL min⁻¹. Detection: UV 254 nm. Column temperature: 25 °C. Injection volume: 5 μL.

Fig. 4. Chromatograms for the separation of Tanaka test mixture including uracil (1), caffeine (2), phenol (3), butylbenzene (4), amylbenzene (5), *o*-terphenyl (6), and triphenylene (7). Stationary phase: (a) SiImBr, (b) Sil-St_n, (c) ODS. Mobile phase: (a) 50% CH₃OH, (b) 80% CH₃OH, and (c) 90% CH₃OH. Other chromatographic conditions were the same as in Fig. 3.

Fig. 5. Chromatograms for the separation of benzene (1), *cis*-stilbene (2), *trans*-stilbene (3), *p*-terphenyl (4), pyrene (5), chrysene (6), benzo[a]pyrene (7) and 1,2:3,4-dibenzanthracene (8). Stationary phase: (a) SiImBr, (b) Sil-St_n, (c) ODS. Mobile phase: (a) 60% CH₃OH, (b) 80% CH₃OH, and (c) 90% CH₃OH. Other chromatographic conditions are the same as in Fig. 3.

Table 1. Retention and separation factors of PAHs for SiImBr, Sil-St_n and ODS.^a

| PAHs | Structure | SiImBr | | Sil-St _n | | ODS | |
|----------------------|---|----------|----------|---------------------|----------|----------|----------|
| | | <i>k</i> | α | <i>k</i> | α | <i>k</i> | α |
| Benzene |  | 0.17 | | 0.37 | | 0.62 | |
| | | | 2.46 | | 2.19 | | 1.81 |
| Naphthalene |  | 0.42 | | 0.82 | | 1.13 | |
| | | | 2.21 | | 2.47 | | 2.01 |
| Anthracene |  | 0.93 | | 2.03 | | 2.28 | |
| | | | 2.15 | | 2.53 | | 2.17 |
| Naphthacene |  | 2.01 | | 5.12 | | 4.94 | |
| <i>o</i> -Terphenyl |  | 0.66 | | 2.14 | | 2.56 | |
| | | | 3.89 | | 2.04 | | 1.57 |
| Triphenylene |  | 2.56 | | 4.36 | | 4.02 | |
| <i>cis</i> -Stilbene |  | 0.41 | | 1.34 | | 1.77 | |
| | | | 1.84 | | 1.25 | | 1.08 |
| Phenanthrene |  | 0.75 | | 1.68 | | 1.91 | |
| Diphenylmethane |  | 0.38 | | 0.89 | | 1.44 | |
| | | | 1.44 | | 1.36 | | 1.26 |
| Fluorene |  | 0.54 | | 1.21 | | 1.82 | |

^a Mobile phases: 60% CH₃OH for SiImBr, 80% CH₃OH for Sil-St_n, 90% CH₃OH for ODS.

Table 2. Retention and separation factors of position isomers for SiImBr, Sil-St_n and ODS.

| Isomers | SiImBr | | Sil-St _n | | ODS | |
|---------------------------|-------------------|----------|-----------------------|----------|-----------------------|----------|
| | <i>k</i> | α | <i>k</i> ^c | α | <i>k</i> ^c | α |
| <i>p</i> -Dinitrobenzene | 0.42 ^a | (1) | 0.29 | (1) | 0.47 | (1) |
| <i>m</i> -Dinitrobenzene | 0.55 ^a | 1.33 | 0.37 | 1.25 | 0.58 | 1.25 |
| <i>o</i> -Dinitrobenzene | 1.36 ^a | 3.26 | 0.29 | 1.00 | 0.37 | 0.79 |
| <i>p</i> -Dichlorobenzene | 1.43 ^a | (1) | 0.51 | (1) | 3.26 | (1) |
| <i>m</i> -Dichlorobenzene | 1.67 ^a | 1.16 | 0.54 | 1.06 | 3.94 | 1.21 |
| <i>o</i> -Dichlorobenzene | 2.00 ^a | 1.39 | 0.51 | 1.00 | 3.26 | 1.00 |
| 2-Chloronaphthalene | 1.63 ^b | (1) | 0.96 | (1) | 5.07 | (1) |
| 1-Chloronaphthalene | 1.85 ^b | 1.14 | 0.99 | 1.03 | 5.45 | 1.08 |
| 1,4-Diacetylbenzene | 0.33 ^b | (1) | 0.22 | (1) | 0.30 | (1) |
| 1,3-Diacetylbenzene | 0.35 ^b | 1.06 | 0.22 | 1.00 | 0.29 | 0.97 |
| 1,2-Diacetylbenzene | 0.35 ^b | 1.06 | 0.15 | 0.70 | 0.17 | 0.56 |
| <i>p</i> -Cresol | 0.39 ^b | (1) | 0.09 | (1) | 0.39 | (1) |
| <i>m</i> -Cresol | 0.45 ^b | 1.15 | 0.09 | 1.00 | 0.38 | 0.98 |
| <i>o</i> -Cresol | 0.46 ^b | 1.20 | 0.11 | 1.21 | 0.44 | 1.12 |
| <i>p</i> -Xylene | 0.57 ^b | (1) | 0.45 | (1) | 2.57 | (1) |
| <i>m</i> -Xylene | 0.58 ^b | 1.02 | 0.46 | 1.02 | 2.56 | 1.00 |
| <i>o</i> -Xylene | 0.59 ^b | 1.03 | 0.45 | 1.00 | 2.36 | 0.92 |
| <i>p</i> -Nitrotoluene | 0.48 ^b | (1) | 0.38 | (1) | 1.02 | (1) |
| <i>m</i> -Nitrotoluene | 0.49 ^b | 1.02 | 0.42 | 1.10 | 1.11 | 1.08 |
| <i>o</i> -Nitrotoluene | 0.50 ^b | 1.04 | 0.40 | 1.05 | 0.96 | 0.93 |
| 5-Amino-2-naphthol | 1.37 ^b | (1) | 0.11 | (1) | 0.09 | (1) |
| 6-Amino-2-naphthol | 1.47 ^b | 1.08 | 0.13 | 1.17 | 0.08 | 0.90 |
| 8-Amino-2-naphthol | 1.55 ^b | 1.13 | 0.15 | 1.44 | 0.19 | 2.03 |
| 1,5-Dinitronaphthalene | 0.14 ^c | (1) | 0.90 | (1) | 1.38 | (1) |
| 1,3-Dinitronaphthalene | 0.81 ^c | 5.63 | 0.99 | 1.10 | 1.87 | 1.35 |

Mobile phase: ^a 20% CH₃OH; ^b 40% CH₃OH; ^c 80% CH₃OH.

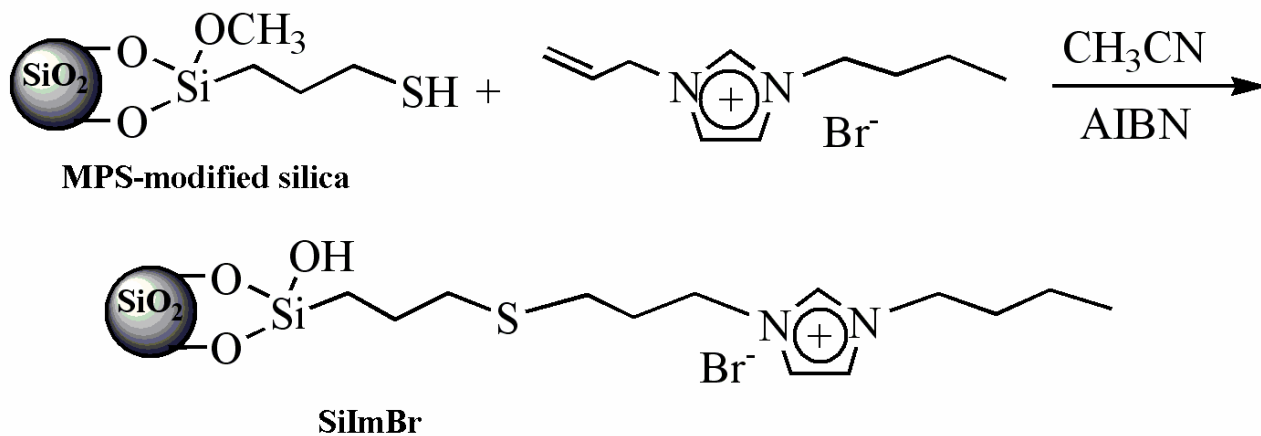


Fig. 1

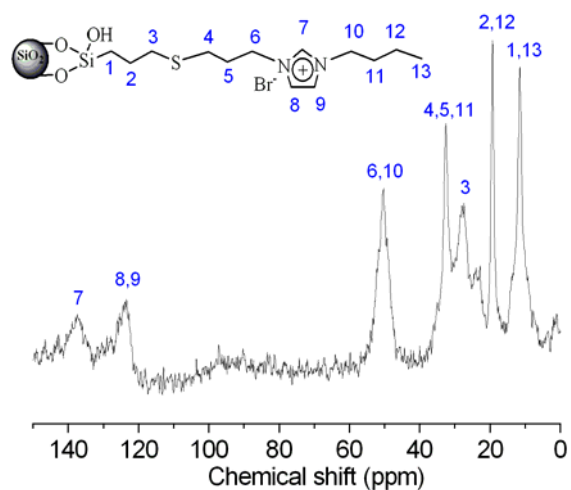


Fig. 2

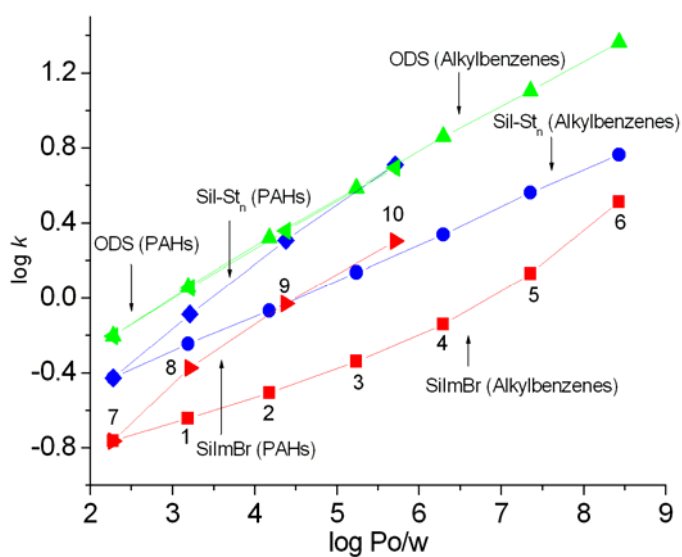


Fig. 3

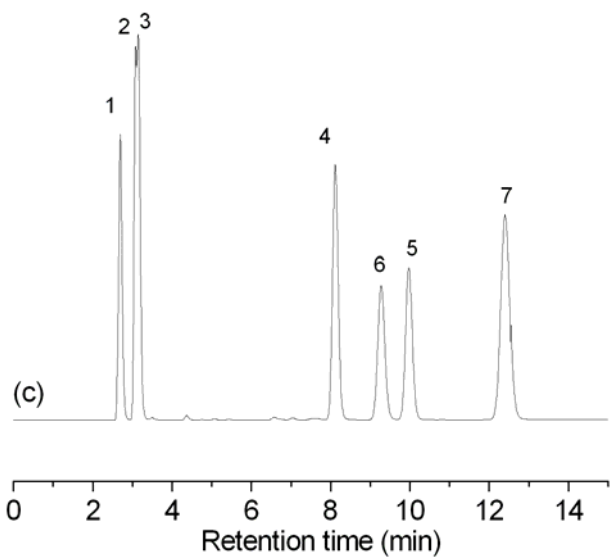
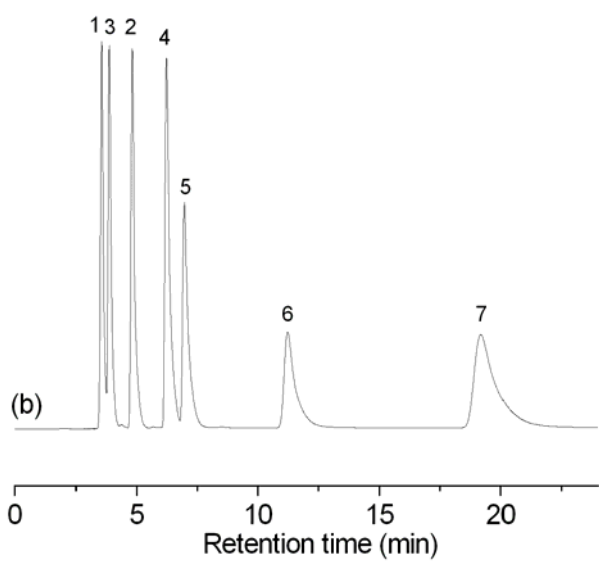
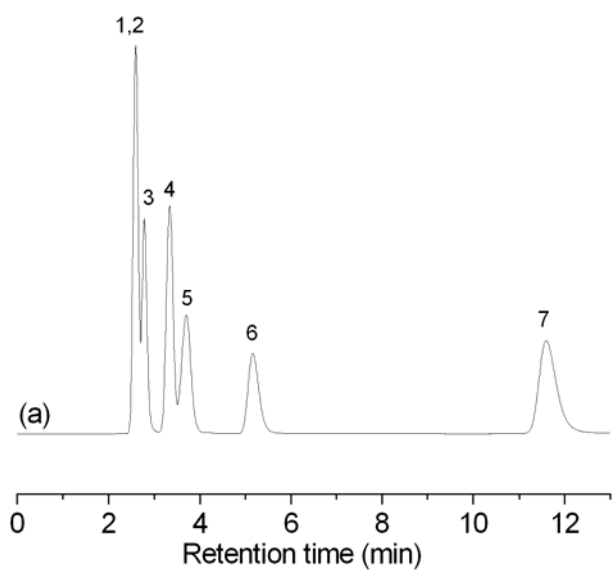


Fig. 4

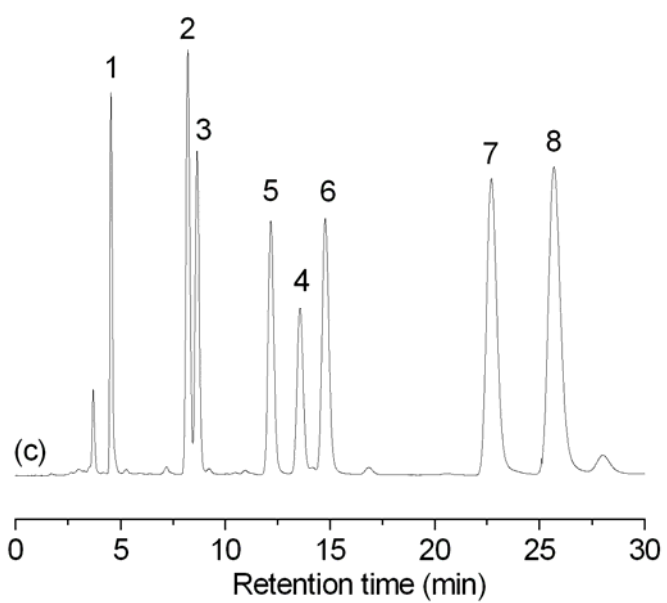
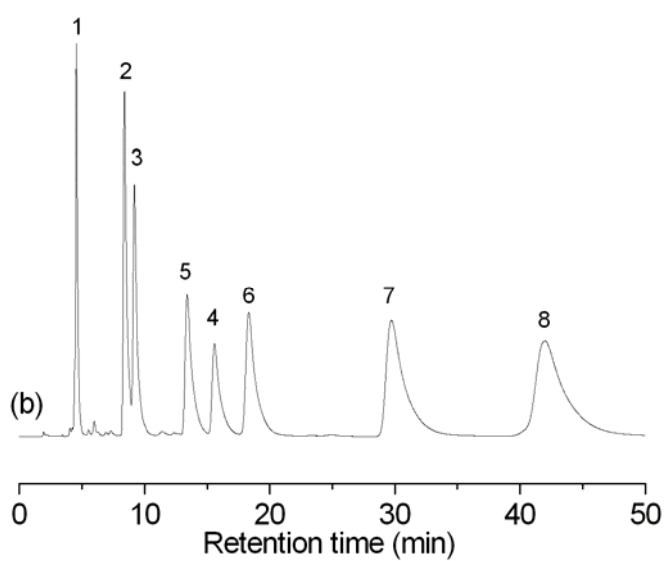
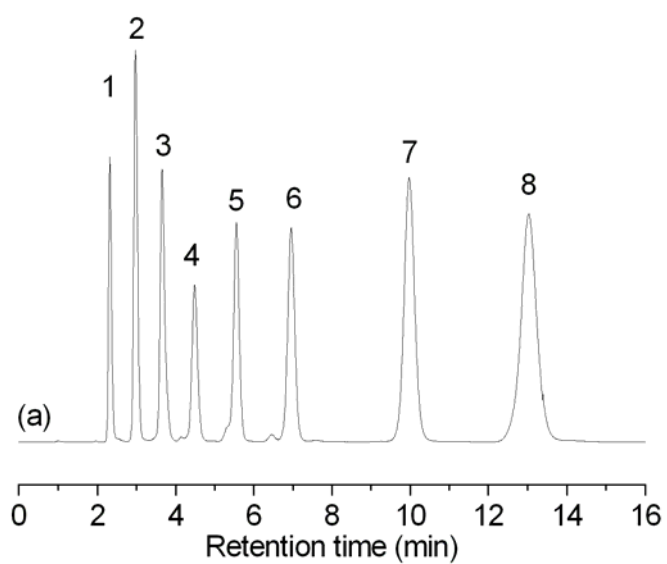


Fig. 5