Original Paper

Development of a C₇₀-Fullerene Bonded Silica-Monolithic Capillary and Its Retention Characteristics in Liquid Chromatography

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Abstract

In this report, C₇₀-fullerene (C70), which has aspheric structure and greater π electrons compared to C₆₀-fullerene (C60), was effectively immobilized onto the surface of a silica-monolithic capillary, and then the retention characteristics for polycyclic aromatic hydrocarbons (PAHs) due to π - π interaction were evaluated in liquid chromatography (LC). For the immobilization of C70, a C70 derivative *via* thermal reactive agent, perfluorophenylazide (PFPA) and *N*-hydroxysuccinimide (NHS) was synthesized. In comparison with a typical thermal reaction in an oil bath and a microwave, the latter reaction provided higher yield. Then, both the C70 and C60 monoliths were evaluated by LC with a variety of PAHs as the solutes. The results suggested that the specific interactions, such as dipole and induced dipole interactions were contributed between the bonded C70 and PAHs. Absorption spectra of PAHs with C60 or C70 and a computer simulation also supported these interactions. Furthermore, the comparison of the separations for PAHs and brominated benzenes with the C70 column and a porous graphite carbon packed column suggested that the interactions based on the polarization of the molecules contributed the separations.

Keywords: C₇₀-Fullerene; Silica monolith; π - π Interaction; Dipole interaction; Polycyclic aromatic hydrocarbons

1. Introduction

In liquid chromatography (LC), the reverse-phase chromatography using the hydrophobic packing materials is not suitable for the separation of aromatic compounds, and π - π interaction in normal phase chromatography is more suitable for its separations [1-3]. Kayillo *et al.* previously reported that a phenyl group bonded silica provided more effective separation of polycyclic aromatic hydrocarbons (PAHs) compared to a typical hydrophobic adsorbent, octadecylsilyl bonded silica [4]. Furthermore, Kimata *et al.* reported that a pyrene moiety bonded silica showed the separation of allotropes of fullerenes [5]. These specific columns are now commercially available for the separation of the complicated aromatic compounds in advanced researches and the necessity of the separation media based on π - π interaction is still increased [6-8].

Generally, the π - π interaction, by which a pair of aromatic rings is stabilized as an overlapping shape, is caused mainly by the London dispersion [9]. London dispersion is an attraction force worked between the dipole moment of nonpolar molecule caused by momentary

fluctuation of the electrons and the induce dipole moment of another nonpolar molecule, and strongly depending on the polarizability of each molecule [10-12]. Aromatic compounds with larger π -conjugation surface provide higher polarity, in fact a simulation was reported that the strength of the π - π interaction between benzene and PAHs in vacuum depended on the number of carbon atoms in PAHs [13].

On the other hand, based on the unique properties, such as high specific surface area, physical strength, and conductivity [14-16], nano-carbon materials have been widely applied for a variety of fields, including electronic materials, reinforced materials, medicines, and so on [17-21]. Additionally, most of the nano-carbon materials show a specific π -stacking property based on their huge π -conjugated surface. Therefore, the possibility of separating aromatic compounds by nano-carbon materials is expected [22-26]. However, the chemical modifications toward the nano-carbon materials must be necessary to obtain the reactivity and solubility, and the modifications cause the defection of the specific characteristics of the

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carbon materials. Yan *et al.* suggested that perfluorophenyl azide (PFPA) is effectively worked for the immobilization of the carbon materials [27-31] and we also reported the immobilization of C₆₀-fullerene (C60) on the surface of a silica monolith [32-34]. Additionally, we recently reported similar silica-monolithic capillary modified with C₇₀-fullerene (C70), which has aspheric structure and greater π electrons compared to C60 [35-37], for the separation medium in LC [38]. In these our studies, the fullerene bonded monoliths provided the specific retention behavior, in brief, the C70 bonded monolith provided the higher selectivity for hemispherical molecule, corannulene (Crn) by the induced dipole interaction between C70 and Crn. But, the detailed retention selectivity for typical PAHs has not been evaluated.

In this study, in order to understand the retention characteristics of the C70 bonded monolithic capillary, a variety of PAHs were evaluated in LC with non-polar solvents as the mobile phases. Also, the retention selectivity was compared to other columns containing a C60 monolithic capillary, a pyrene bonded column (PYE), and a porous graphite carbon packed column (PGC).

2. Experimental

2.1. Chemicals and reagents

n-Hexane, methanol, toluene, chlorobenzene, ethyl acetate, acetone, diethylether, magnesium sulfate, sodium hydroxide, and chloroform were purchased from Nacalai Tesque (Kyoto, Japan), methyl pentafluorobenzoate, PAHs, alkylbenzenes, diethyl amine, urea, acetic acid, and 3-aminopropyltrimethoxysilane (APTMS) from Tokyo Chemical Industry (Tokyo, Japan), sodium azide, *N*-hydroxysuccinimide (NHS), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) from Wako Pure Chemical Industries (Osaka, Japan), polyethylene glycol (PEG) (*M_n*=10,000), C₆₀-fullerene, and C₇₀-fullerene from Sigma-Aldrich Japan (Tokyo, Japan), respectively. Deionized water was obtained from a Milli-Q Direct-Q 3UV system (Merck Millipore, Tokyo, Japan). A COSMOSIL PYE® was purchased from Nacalai Tesque, and a fused-silica capillary from Polymicro Technologies Inc. (Phoenix, AZ). Hypercarb™ was purchased from Thermo Fisher Scientific Inc. (Waltham, MA, USA).

2.2. Instruments

A capillary liquid chromatographic system consisted of a DiNa S (KYA Technologies Co., Tokyo, Japan) as a pump, CE-2070 (JASCO, Tokyo, Japan) as a UV detector, CHEMINERT (Valco Instruments Co., Huston, TX) as a sample injector, and Chemco capillary column conditioner Model 380-b (Chemco Co. Osaka, Japan) as a column oven. An HPLC system consisted of a Prominence series (Shimadzu Co., Kyoto, Japan). FT-IR, NMR, elemental

analysis, and fast atom bombardment mass spectrometry (FABMS) were carried out by a Nicolet iS5 ATR (Thermo Fisher Scientific Inc., Waltham, MA, USA), JNM-ECA500 spectrometer (JEOL, Tokyo, Japan), Flash EA1112 (Thermo Fisher Scientific), and JMS-700 (JEOL), respectively.

2.3. Synthesis of C70-PFPA-NHS

As well as the previous studies [34,38], a C70 bonded silica-monolithic capillary was prepared. To modify C70 *via* PFPA, a C70 conjugated molecule with PFPA and NHS was synthesized as follows (Scheme 1-a). C70 of 100 mg (0.12 mmol) and NHS conjugated PFPA (PFPA-NHS) of 78.7 mg (0.24 mmol) were dissolved in chlorobenzene (40 mL). After N₂ bubbling for 3 min, the mixture was stirred at 108 °C for 120 h under N₂ atmosphere. After removal of the solvent, the products were purified by a silica gel chromatography with toluene/ethyl acetate (=20/1) as a mobile phase. Finally, the objective product was further purified by precipitation with toluene and *n*-hexane. Additionally, to improve the reaction efficiency, the microwave reaction was also employed. C70 of 20 mg (0.03 mmol) and PFPA-NHS of 15.6 mg (0.047 mmol) were dissolved in chlorobenzene (8 mL), and then the mixture was treated at 130 °C for 2 h by microwave (2.45 GHz). The final product was purified by same method as above.

Scheme 1. Preparation of a C70 bonded silica monolith. (a) synthesis scheme of a C70-PFPA-NHS. (b) preparation of a C70 bonded monolith *via* C70-PFPA-NHS.

2.4. Preparation of a C70 bonded silica-monolithic capillary

A fused-silica capillary (2-3 m in length, 100 μ m i.d.)

was treated with a 1.0 M aqueous sodium hydroxide solution at 40 °C for 3 h, followed by washing with water and acetone, and then dried. TMOS (56 mL) was added to a solution of PEG (11.9 g) and urea (9.0 g) in 0.01 M acetic acid (100 mL), and the mixture stirred at 0 °C for 30 min. The resultant homogeneous solution was charged into a fused-silica capillary and stayed to react at 30 °C for overnight at the same temperature. Then, the temperature was increased, and the monolithic silica column was treated at 120 °C for 3 h to form mesopores with ammonia generated by the hydrolysis of urea, followed by washing with water and methanol. After drying, a heat treatment was carried out at 330 °C for 25 h, resulting in the decomposition of the organic moieties in the capillary.

As shown in Scheme 1-b, the silica-monolithic capillary was treated with 1.0 M aqueous sodium hydroxide at 40 °C for 3 h. After washing with water and methanol, APTMS in methanol (10%, v/v) was passed through the silica-monolithic capillary for 24 h and washed with methanol (NH₂-monolith). C70-PFPA-NHS in toluene (3.0 mg mL⁻¹) was charged into the NH₂-monolith for 24 h at room temperature, and washed with toluene and methanol. To evaluate by elemental analysis, the bulk type silica monolith was also prepared with the same compositions as the capillary. The bulk monolith was crashed and similar surface modification was also carried out with C70-PFPA-NHS.

2.5. Computer simulations of atomic charges in fullerenes

To understand the polarity of fullerenes, the atomic charges of each carbon atom in C60 and C70 were calculated by a computer simulation. B3LYP and 6–311 (d) were employed as a general function and basis function, respectively. In addition, a continuous dielectrics of *n*-hexane for consideration of solvent effect were carried out. All the simulations were operated by a software, Gaussian 09 Rev. D01.

3. Results and discussions

3.1. Characterizations of C70-PFPA-NHS and modified silica-monoliths

As comparison between a typical thermal reaction in an oil bath and a microwave reaction, the yield against C70 were 18.2% and 24.5%, respectively. Although the reaction time by the microwave was significantly shorter than that of the oil bath, the yield was much higher [39]. In both reactions, similar FT-IR spectrum, mass spectrum, and the results of elemental analysis were identified as well as our previous study [38].

The immobilized fullerenes were estimated by elemental analysis with the monoliths, which were prepared with a bulk type monolith by modification of the C60- or C70-PFPA-NHS. As results, the density of C60 and C70

was estimated at 0.83 $\mu\text{mol mg}^{-1}$ and 0.44 $\mu\text{mol mg}^{-1}$, respectively. The reason of the lower density in C70 is that the steric exclusion might be caused by larger size of C70. Furthermore, both the fullerene bonded monolithic capillaries provided the retention toward alkylbenzenes in reverse-phase LC. The results also supported that the immobilized C60 or C70 contributed the retention by hydrophobic interaction. These fundamental results were corresponded to our previous studies [34,38].

3.2. Retention properties of the C70 bonded silica-monolithic capillaries

In our previous study, the C70 bonded monolith allowed the significantly higher retention selectivity toward hemispherical molecule, Crn. In brief, Crn was strongly retained in the C70 column compared to the C60 column and a PYE column. We concluded that the effective retention caused by induced dipole interaction between C70 and Crn was occurred. In this study, we further evaluated the fundamental retention characteristics with typical PAHs as the solutes in several mobile phase conditions.

3.2.1. Effect of the mobile phases

In our previous study, we confirmed that the retention strength on fullerenes was strongly depended on the mobile phases. In brief, when polar solvents, such as methanol containing water was employed, the retentions toward PAHs became greater by hydrophobic interaction. On contrary, when water-immiscible polar solvents, such as chloroform and toluene were employed, the retentions were dramatically decreased by the interruption of π - π interaction due to chlorine atoms or solvation. Therefore, in order to understand the effect of the mobile phases, further investigations were carried out using several non-polar

Fig. 1. Retention factors of phenanthrene and triphenylene with the C70 monolith in several solvents. LC conditions: column, C70 bonded silica-monolithic capillary (66.5 cm $\times$ 100 μm i.d.); flow rate, 2.0 $\mu\text{L min}^{-1}$.

solvents. In this evaluation, the retention factors of phenanthrene and triphenylene were compared in each solvent. We anticipated that the solubility of fullerenes should contribute the retention strength. Therefore, the saturated solubility of C70 in each solvent referred by literatures are summarized in Table 1 [40]. The retention factors of the solutes are summarized in Fig. 1. Firstly, the retention factors were much higher by using methanol. The reason can be easily considered that hydrophobic interaction was dominant of these retentions, although the solubility of C70 was zero. On the other hand, with non-polar solvents, the retention strengths were corresponded to the order of the saturated solubility. It seemed that higher compatibility between the mobile phases and fullerenes helped more accessibility of each PAH toward C70. In other words, the wettability by the solvents are very important, and we concluded the solvents with non-polar structure and without aromatic moieties/halogen atoms are suitable for obtaining the effective π - π interaction by fullerenes.

Table 1. Saturated solubility of C70 in the solvents.

Solvents	Saturated solubility / mg mL ⁻¹
methanol	0.00
<i>n</i> -hexane	0.01
cyclohexane	0.08
<i>n</i> -octane	0.04

3.2.2. Retention selectivity on the C70 fullerene toward PAHs

As described in our previous study, both the C60 and C70 bonded columns showed selective retention to hemispherical Crn. As well, the base line separation of PAHs in *n*-hexane as a mobile phase was achieved.

Fig. 2. Retention factors of PAHs in the C60, C70, and PYE columns. LC conditions: column, C60 or C70 bonded silica-monolithic capillary (12.1 cm × 100 μm i.d.), PYE (100 mm × 4.6 mm i.d.); mobile phase, *n*-hexane; flow rate, C60 or C70 2.0 μL min⁻¹, PYE 2.0 mL min⁻¹.

Additionally, the retention strength to PAHs were slightly different between the C60 and C70 columns. Then, in order to understand the differences among the fullerenes, the detailed evaluations were carried out. Fig. 2 shows the retention factors of PAHs containing phenanthrene, pyrene, triphenylene, and benzo[a]pyrene in the C60, C70, and PYE columns. As we expected, the retention strength of PAHs was related to the number of π electrons in the PYE column, the simple π - π interaction was worked between pyrene moiety in the column and solutes. In contrast, the C60 and C70 columns provided non-linear relations to the number of π electrons. Especially, the retention of PAHs having larger π electrons were much higher in the C70 column. Here, as well as our previous study, we anticipated that the alteration of electrons density was concerned to these strong retentions.

Thereat, the absorption spectra of PAHs with fullerenes were evaluated. The absorption spectra of phenanthrene of 40 μM or triphenylene of 45 μM with /without C60 or C70 (saturated) in *n*-hexane are summarized in Fig. 3. Interestingly, the spectra were dramatically changed when either C60 or C70 was added to the solutions. Especially, with adding C70 to the solutions, the absorption around 250 nm was completely disappeared. As shown in the previous study [41], the absorption around 250 nm is depended on π - π^* transition on aromatic rings, so that we assumed that

Fig. 3. Absorption spectra of PAHs with C60 or C70. (a) Phenanthrene (40 μM) or (b) triphenylene (45 μM) with/without the saturated C60 or C70 in *n*-hexane.

the larger decrease was observed on C70 by the higher dipole of C70. These results suggested that the strong retentions in the fullerene bonded columns were caused not only by π - π interactions but also weaker interactions, such as dipole and induced dipole interactions. To support the hypothesis, the atomic charges of carbon atoms in C60 and C70 were estimated by a computer simulation. The results are summarized in Fig. 4. The figure clearly showed the presence of dipole and unique HOMO/LUMO orbitals in C70, whereas any dipoles were identified in C60. These differences seemed to be associated toward the retention behaviors in LC evaluations. We believe that further investigations will contribute to understand the retention mechanism among the aromatic compounds and the separations for a great number of aromatic compounds.

Fig. 4. Atomic charges of carbon atoms and HOMO/LUMO orbitals in C70. (a) view from the edge in long axis, (b) view from the side.

3.3. Separation of the aromatic compounds with C70 column and porous graphite carbon

As well known, the carbon based materials are useful for the separation of aromatic compounds. Porous graphite carbon (PGC) is the best adsorbent for the separation, in brief, HypercarbTM has been widely applied for the separation of aromatic compounds, racemic mixture, and polymers [42-46]. Then, we finally demonstrated the separation of aromatic compounds with the C70 column compared to the separation by the PGC column. The results of chromatographic separation of PAHs and brominated benzenes are summarized in Figs. 5, 6. As we expected, the PGC column provided the significantly strong retention ability toward PAH described in Fig. 5-a. Although the separation of PAHs was also achieved in the C70 column, the absolute retention was much lower than that of the PGC column (Fig. 6-a). The PGC column was packed with the spherical porous graphite carbon, so that the total amount of graphite is much higher than any other

Fig. 5. Separations of PAHs and brominated benzenes in the PGC column. (a) separations of PAHs, (b) separations of brominated benzenes, LC conditions: PGC column, Hypercarb (30 mm $\times$ 2.1 mm i.d.); flow rate, 2.0 mL min⁻¹; mobile phase, *n*-hexane / chloroform = 7 / 3.

Fig. 6. Separations of PAHs and brominated benzenes in the C70 column. (a) separations of PAHs, (b) separations of brominated benzenes, LC conditions: column, C70 bonded silica-monolithic capillary (66.5 cm $\times$ 100 μ m i.d.); flow rate, 2.0 μ L min⁻¹; mobile phase, *n*-hexane / chloroform = 7 / 3.

silica-gel based columns. Accordingly, the higher retention was obtained in the PGC column. On the other hand, similar separations were obtained for brominated benzenes in both columns (Figs. 5-b, 6-b). Compared to the separation of PAHs, the relative retention to brominated benzenes in C70 was much higher. In other words, C70 provided the selective retention ability for the polarized aromatic ring or electrons-rich bromine atoms. In either cases, the weaker dipole interactions seemed to be contributed the selective retentions. Consequently, we expect that the C70 bonded column is useful not only for PAHs but also polarized aromatic compounds in non-polar solvents by LC. Further investigations will contribute the effective separations based on the weak interaction, such as dipole or induced dipole interactions.

4. Conclusions

We successfully prepared a C70 bonded silica-monolithic capillary for LC separations. For the synthesis of a C70 conjugated molecule with PFPA and NHS, higher yield was obtained by using microwave reaction. The C70 monolith showed the higher retention ability for several PAHs, and the results by the absorption spectra and the computer simulation suggested that the specific retentions were caused by the weaker interaction, such as dipole interaction. Comparison of the LC separations between the C70 and PGC column supposed that the C70 column showed the unique separation ability for brominated aromatic compounds by the dipole or induced dipole interactions. We believe that these results will contribute for the development of new media aid in separation of a variety of aromatic compounds by weak interactions based on polarization of the molecules.

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