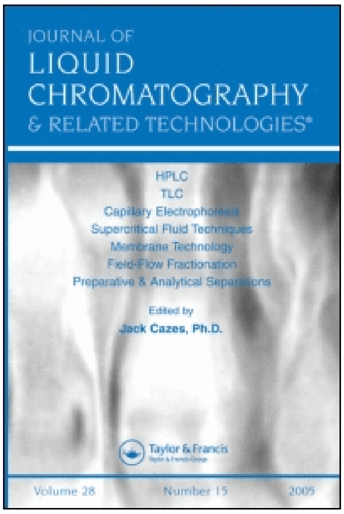

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SEPARATION OF C_{60} AND C_{70} FULLERENES WITH A TRIPHENYL BONDED SILICA PHASE IN MICROCOLUMN LIQUID CHROMATOGRAPHY

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ABSTRACT

C_{60} and C_{70} fullerenes were chromatographically separated with triphenyl, diphenyl and monophenyl bonded silica phases in microcolumn liquid chromatography. The results indicate that the triphenyl bonded phase having the narrowest pore size possesses the best separation performance among the evaluated phases. The retention power of the triphenyl bonded phase for C_{60} and C_{70} was much greater than that of typical octadecylsilica (ODS) phases, although the separation factor between C_{60} and C_{70} was almost comparable to that of ODS phases. With the triphenyl bonded phase, a smaller temperature dependence than ODS phases was observed for the separation of C_{60} and C_{70}.

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INTRODUCTION

Retention behaviours of fullerenes in high performance liquid chromatography (HPLC) have been studied concentrically in recent years [1-6], because the separation and purification of fullerenes are inevitable procedures to characterize those interesting compounds to use in various wide fields. Hawkins *et al.* [1,2] reported the liquid chromatographic separation of C_{60} and C_{70} on a phenylglycine-derivartized bonded phase ("Pirkle Column"), and Cox *et al.* [3] used a dinitroanilinopropylsilica stationary phase to separate them. Pirkle *et al.* [4] have synthesized a new stationary phase, the so-called "buckyclutcher", and obtained an excellent separation of C_{60} and C_{70}. For this separation, pyrenylethyl [5] and nitro-derivartized phenylethyl [5,6] bonded phases have been introduced by Kimata and Tanaka *et al.* All of the phases described above include phenyl ring(s) in their bonded phase structures and some of them possesses nitro group(s) on the ring in order to enhance the interaction between bonded phase ligands and fullerene molecules.

In our previous investigations we studied the retention behaviour of fullerenes with various stationary phases such as commercially available monomeric and polymeric ODS phases [7-12], multi-legged phenyl bonded phases [12,13] and methoxyphenylpropyl bonded stationary phases [12,14]. This is because the fact that fullerene molecules can be considered to be very big polycyclic aromatic hydrocarbons (PAHs) with specific shape and size, and therefore, they are regarded as good sample probes to investigate the retention

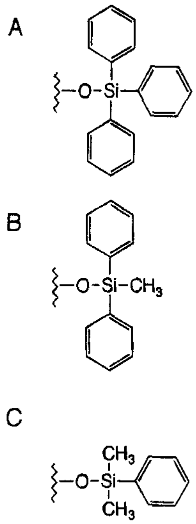

FIGURE 1 Chemical structures of triphenyl (Triph; A), diphenyl (Diph; B) and monophenyl (Monoph; C) bonded phases.

behaviour of PAHs in liquid chromatography. On the other hand, if the chromatographic separation mechanism of fullerenes with the stationary phases is elucidated, a new design of the stationary phase to effectively separate them can be developed by the concept based on the mechanism.

In this work, three types of stationary phases, triphenyl (Triph), diphenyl (Diph) and monophenyl (Monoph) bonded silica phases were evaluated as stationary phases to separate C_{60} and C_{70} fullerenes in microcolumn liquid chromatography, since microcolumns are ideal for use in these studies because of limited amounts of experimentally synthesized bonded phases.

EXPERIMENTAL

Bonded Phase Synthesis

The syntheses of these bonded phases were described previously [15]. The basic characteristics of these bonded phases are summarized in Table 1.

Chromatographic Measurements.

The bonded phases were packed using a slurry method into a fused-silica capillary (Tokyo Kasei, Tokyo, Japan) of 0.53 mmi.d. x 150

TABLE 1

Basic Characteristics of the Bonded Phases Investigated in This Study.

bonded phase	pore size (Å)	carbon content (%)	surface coverage (μmol/m^2)
Triph	70	11.2	1.14
Triph	150	4.79	1.19
Triph	300	1.64	0.94
Diph	70	13.7	2.20
Diph	150	6.11	2.16
Diph	300	2.57	2.23
Monoph	70	10.8	3.40
Monoph	150	5.35	3.81
Monoph	300	3.28	5.77

mm length. The microcolumn HPLC system consisted of a microfeeder MF-2 pump (Azuma Electric, Tokyo, Japan), a Rheodyne 7520 injector (Cotati, CA, USA) with a 0.2 μL injection volume and a Uvidec 100-III UV detector (Jasco, Tokyo, Japan) set at 320 nm. The mobile phase was guaranteed reagent grade n-hexane (Kishida Chemical, Osaka, Japan). The typical flow-rate was 2 μL/min., and a mixture of toluene and cyclohexane was used as the sample solvent. The chromatographic measurements were done at least three times. The column temperature was controlled using a modified Hewlett-Packard Model 5820-II Gas Chromatographic oven (Yokogawa Analytical Systems, Mitaka, Tokyo, Japan).

RESULTS and DISCUSSION

The Separation Performance of Triphenyl, Diphenyl and Monophenyl Bonded Stationary Phases.

Figs.2a, 2b and 2c show chromatograms of the separation of C_{60} and C_{70} on Triph, Diph and Monoph bonded phases prepared with different pore size silica gels. These retention data are also summarized in Table 2. With the phases having a 70 Å pore size, the Triph phase exhibited the best retention power and separation performance, although good separation was obtained with all phases, as shown in Fig.2a. In the cases of 150 Å (Fig.2b) and 300 Å (Fig.2c) pore size, the retentions of C_{60} and C_{70} are shorter than those of the 70 Å phases.

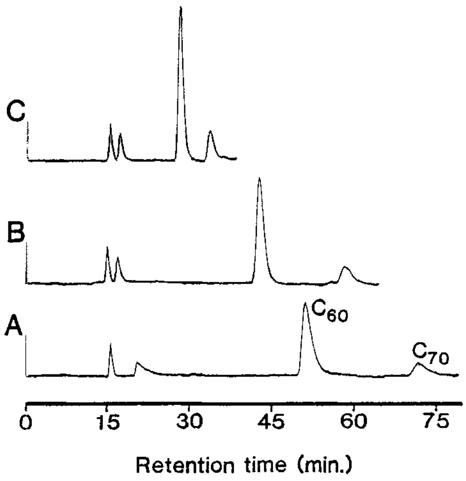

FIGURE 2a Chromatograms for the separation of C_{60} and C_{70} with Triph (A), Diph (B) and Monoph (C) bonded phases. Pore size, 70 Å; mobile phase, n-hexane; column temperature, 30 °C.

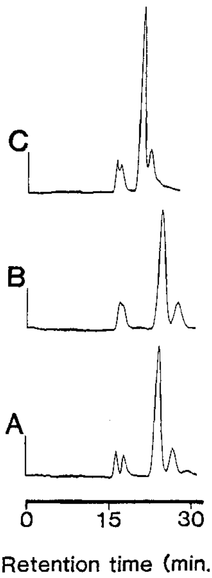

FIGURE 2b Chromatograms for the separation of C_{60} and C_{70} with Triph (A), Diph (B) and Monoph (C) bonded phases. Pore size, 150 Å; mobile phase, n-hexane; column temperature, 30 °C.

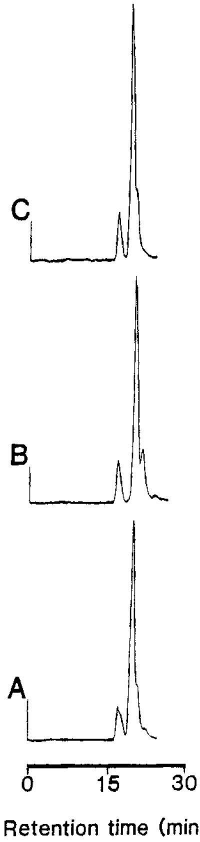

FIGURE 2c Chromatograms for the separation of C_{60} and C_{70} with Triph (A), Diph (B) and Monoph (C) bonded phases. Pore size, 300 Å; mobile phase, n-hexane; column temperature, 30 °C.

This can be attributed to the lower carbon loadings of these wider pore phases.

It can be said from the above results that the three phenyl rings of Triph bonded phases' ligands possess a strong retentivity based on the π-π interaction with fullerene molecules, because these bonded phases

TABLE 2

Retention Data for the Separation of C_{60} and C_{70} with Triphenyl (Triph), Diphenyl (Diph) and Monophenyl (Monoph) Bonded Phases. Mobile Phase, n-hexane; Column Temperature, 30℃.

bonded phase	pore size (Å)	capacity factor (k')		separation factor
		C_{60}	C_{70}	α (C_{70}/C_{60})
Triph	70	2.28	3.59	1.57
Diph	70	1.85	2.89	1.56
Monoph	70	0.863	1.24	1.44
Triph	150	0.454	0.633	1.39
Diph	150	0.452	0.639	1.41
Monoph	150	0.273	0.370	1.36
Triph	300	0.157	0.217	1.38
Diph	300	0.203	0.266	1.31
Monoph	300	0.152	0.194	1.28

indicate the best retention capability in spite of the lowest surface coverage value among the three phases having the same pore size. Furthermore, the chromatographic characteristics of these three phases (i.e. Triph, Diph and Monoph) are most evident in 70 Å silica gel phases.

Table 3 shows the retention data for C60 and C70 with various bonded stationary phases. In this table, the BP phase is a multi-legged

TABLE 3

Retention Data for C_{60} and C_{70} with Five Different Bonded Phases. Mobile Phase, n-hexane; Column Temperature, 30°C.

bonded phase	capacity factor (k')		separation factor
	C_{60}	C_{70}	$\alpha (C_{70}/C_{60})$
Tiph 70 Å	2.28	3.59	1.57
BP	2.76	5.25	1.90
DMPP	3.09	5.77	1.87
Develosil ODS-5	0.87	1.60	1.84
Capcell Pak C18 SG120*	0.34	0.53	1.56

*Conventional monomeric ODS column with polymer coated silica (4.6 mmi.d. x 250 mm; Shiseido, Tokyo, Japan); flow rate, 1mL/min.

bonded silica phase [12,13] and DMPP bonded phase is a multi-methoxy phenyl stationary phase [12,14], and these two phases have been found to have an excellent separation performance for fullerene mixtures in our previous investigations. In addition, Develosil ODS-5 (Nomura Chemical, Seto, Japan) is the phase that exhibited the best separation factor of C_{60} and C_{70} among various commercially-available ODS phases in our previous evaluation [9].

Consequently, Table 3 demonstrates that the Triph 70 Å phase has a much higher retention power than commercially-available ODS phases, although the retentivity of the triphenyl phase is somewhat less than those of BP and DMPP bonded phases.

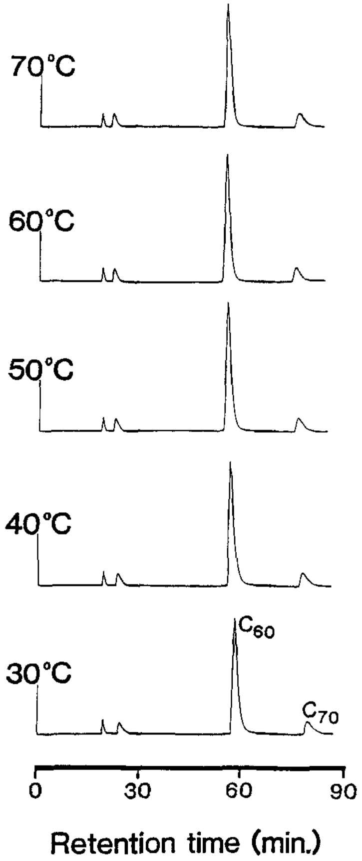

FIGURE 3 Chromatograms for the separation of C_{60} and C_{70} with the Triph 70Å phase at different column temperatures. Mobile phase, n-hexane.

Effect of Temperature on the Separation of C_{60} and C_{70} with the Triphenyl Bonded Phase.

Fig.3 depicts chromatograms for the separation of C_{60} and C_{70} with the Triph 70 Å bonded phase at different column temperatures. These chromatograms indicate the small temperature dependence of

TABLE 4

Capacity Factors of C_{60}, C_{70} and Five PAHs with Triph 70 Å Phase at Different Column Temperatures. Mobile Phase, n-hexane.

	column temperature (℃)				
	30	40	50	60	70
naphthalene	0.763	0.707	0.634	0.582	0.538
phenanthrene	1.52	1.38	1.20	1.07	0.971
o-terphenyl	2.32	2.07	1.77	1.57	1.40
pyrene	1.66	1.54	1.41	1.30	1.21
triphenylene	3.02	2.77	2.44	2.22	2.02
C_{60}	1.98	1.97	1.94	1.93	1.93
C_{70}	3.10	3.09	3.03	3.02	3.02

this separation with the triphenyl phase. For comparison, retention data for five PAHs were also measured and summarized in Table 4. Because the capacity factors of PAHs decrease with increasing the column temperature, the slight variation in the retention data of C60 and C70 may be specific for fullerenes.

Separation factors of C60 and C70 with various phases at different temperatures were tabulated in Table 5 and these data were also plotted in Fig.4 with some additional data. The separation factors with ODS phases, especially in the case of the polymeric phase, decrease significantly when the column temperature is elevated. However, as reported previously [12], the BP phase indicates a very small temperature dependence for the separation of C60 and C70, and

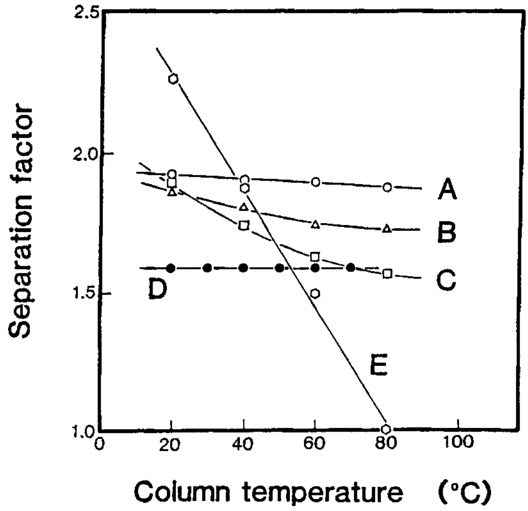

FIGURE 4 Relationships between separation factors for C60 and C70 with five different bonded phases versus column temperature. (A) BP, (B) DMPP, (C) monomeric ODS, (D) Triph 70 Å and (E) polymeric ODS. In this figure plots (A), (B), (C) and (E) were reported in our previous paper [12]. Mobile phase, n-hexane.

TABLE 5

Separation Factors of C_{60} and C_{70} with Five Bonded Phases at Different Column Temperatures. Mobile Phase, n-hexane.

	separation factor $\alpha(C_{70}/C_{60})$		
bonded phase	20 ℃	40 ℃	60 ℃
Triph 70Å	1.57	1.57	1.56
BP	1.92	1.90	1.89
DMPP	1.86	1.80	1.74
Develosil ODS-5	1.89	1.74	1.62
Wakosil-II5C18AR*	2.26	1.87	1.49

*Conventional polymeric ODS column (4.6 mmi.d. x 250 mm; Wako Pure Chemical, Osaka, Japan).

the DMPP stationary phase also exhibits a relatively smaller variation than the ODS phases, because of conformational rigidity of the BP and DMPP phases.

Therefore, it can be assumed from the above results that the Triph 70 Å phase also possesses a conformational rigidity which is not witnessed using the ODS phases.

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