

Dimethoxyphenylpropyl bonded silica phase for higher fullerenes separation by high-performance liquid chromatography

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ABSTRACT

Fullerenes were separated using three chemically bonded phases, dimethoxyphenylpropyl (DMP), monomeric octadecyl and polymeric octadecyl modified silicas (ODS), with *n*-hexane as the mobile phase. DMP and the monomeric ODS are the best choices for the separation of C₆₀ and C₇₀ compounds, while DMP is the only phase that has high temperature stability while maintaining the resolution. For the separation of higher fullerenes, DMP offers faster analysis at higher temperatures while maintaining its high resolution, whereas ODS phases cannot provide similar run times while offering the same resolution. In conclusion, DMP is the most suitable and promising stationary phase for fullerenes analysis because of the short run time and its superior separation efficiency.

INTRODUCTION

Since the existence of all-carbon molecules such as C₆₀ and C₇₀ was confirmed in 1985, there have been many publications dealing with the separation and analysis of these compounds, called fullerenes, using various analytical techniques [1–18]. The unique properties and structures of these molecules have been widely

studied, and now studies on their usefulness in materials science fields are the driving force that attract many scientists to this field of chemistry. In order to further scientific investigations of fullerenes, chromatographic separation techniques are required to separate and purify these molecules. High-performance liquid chromatography (HPLC) is probably the best method one can choose for this application.

Although novel stationary phases based on nitrophenyl groups have proved to be useful for C₆₀ and C₇₀ separation and a few are now commercially available [19–21], a basic approach to optimize separation systems for higher ful-

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lerenes is still urgently required. Studies of the separation of C_{60} and C_{70} using multi-legged biphenyl bonded phase (BP) [22], commercially available octadecyl silica (ODS) phases (polymeric and monomeric phases) [23–26] and a novel dimethoxyphenylpropyl silica bonded phase (DMP) [27] have been previously conducted in our laboratory. The separation of higher fullerenes such as C_{76} , C_{78} and C_{84} with ODS phases was also reported in previous papers [25,26]. These investigations indicated that there is still potential for further studies to obtain higher selectivity with the above-mentioned stationary phases using their characteristic chromatographic properties. In this communication, we describe an approach to enhance the selectivity of separation with varying column temperature in order to get better resolution for C_{60} , C_{70} and other higher fullerenes using various stationary phases, especially DMP phase.

EXPERIMENTAL

The HPLC system used consisted of a Tosoh CCPE pump (Tokyo, Japan), a Hewlett-Packard 1040 A photodiode array detector (Yokogawa Analytical Systems, Musashino, Japan) controlled by an HP 9000 computer, and a Rheodyne 7520 injector (Cotati, CA, USA) with 20- μ l loop volume for injection. The column temperature was controlled by a Tosoh RE-8000 oven at temperatures between 30 and 80°C and by a LAB-Thermo Model LH-1000E (Toyo Seisakusho, Tokyo, Japan) at temperatures lower than 30°C. Separation columns evaluated herein were as follows: Develosil ODS-5 (monomeric type, 5 μ m, Nomura Chemicals, Seto, Japan), 250 mm \times 4.6 mm I.D.; Wakosil II 5C18AR (polymeric type, 5 μ m, Wako Chemicals, Tokyo, Japan), 250 mm \times 4.6 mm I.D.; and DMP (monomeric type, 5 μ m, laboratory made), 150 mm \times 4.6 mm I.D. In this work, DMP was used as the primary stationary phase and others were used as references for the comparison of the chromatographic performance for fullerene separations, since it has been found previously [27] that DMP is very promising stationary phase for fullerenes separation (C_{60} and C_{70}). The

mobile phase was *n*-hexane at a flow-rate of 1 ml/min.

Carbon soot was produced by a common arc discharge in an inert gas environment. The soot was extracted with toluene in order to obtain the C_{60} and C_{70} fraction and the residue was extracted with 1,2,4-trichlorobenzene to get highly concentrated higher fullerenes [25]. The solution was then evaporated to dryness and then redissolved in toluene for use as the test sample for the injection.

RESULTS AND DISCUSSION

Separation of C_{60} and C_{70}

In general, in HPLC, high temperature results in lower retention and high resolution. However, Pirkle and Welch [19] reported an unusual temperature dependence of their special column (the so-called Pirkle column) for C_{60} and C_{70} separation, *i.e.* higher temperature causes higher retention and high resolution. In this work, therefore, the first step was to separate C_{60} and C_{70} with various stationary phases and varying column temperature. In Fig. 1, the separation factors for C_{60} and C_{70} are plotted against temperature. With the polymeric ODS phase, the separation factors changed drastically with the column temperature: decreasing the temperature increased selectivity. Low temperature makes it possible to separate both fullerenes with low retention and resolution. At temperatures greater than 40°C, the same separation cannot be achieved because of very low retention and co-elution of C_{60} and C_{70} . This means that polymeric ODS is not suitable for separating C_{60} and C_{70} even at low column temperatures, because the retentions of two fullerenes are very short and the separation efficiency is very sensitive to small changes in temperature. With the monomeric ODS phase, the change in the separation factors with temperature is not as drastic as found when using the polymeric ODS phase, but the tendency for the selectivity to increase at lower temperatures is clearly seen. From the practical point of view, the monomeric phase is preferable to the polymeric, although at low temperatures the polymeric ODS phase can offer much higher separation factors than the monomeric ODS. Actual

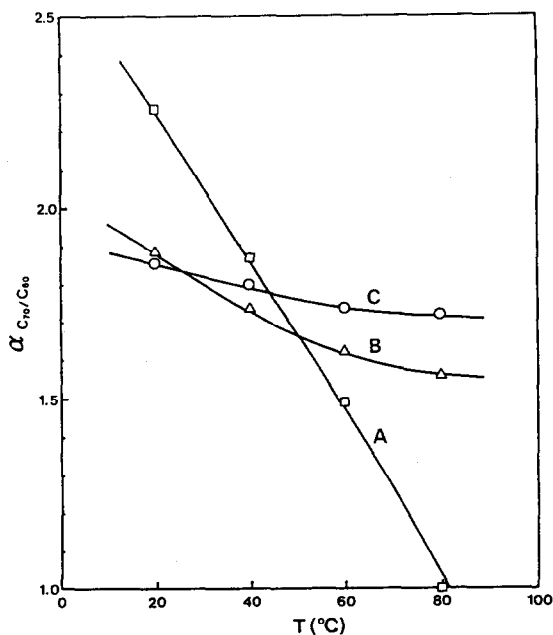


Fig. 1. Relationships between separation factors (α) for C_{60} and C_{70} with four different stationary phases and column temperature. (A) Polymeric ODS; (B) monomeric ODS; (C) DMP.

retention values with the polymeric phase are always lower than those with the monomeric, and this fact demonstrates that the monomeric material is the better stationary phase for fullerene separations. As previously reported by Pirkle and Welch [19] different retention mechanisms are affected to varying degrees by temperature change. With the DMP phase, the temperature dependency is very minimal, not as low as the Pirkle column, but the lowest temperature dependency of the three phases studied.

Higher fullerenes separation

In our previous work [26], polymeric and monomeric ODS phases with toluene-acetonitrile as the mobile phase were evaluated for the separation of higher fullerenes such as C_{76} , C_{78} , C_{82} and C_{84} . Interesting results were obtained in that work: the elution order of C_{76} and one of three isomers of C_{78} , *i.e.*, $C_{78}-C_{2v'}$, with the monomeric phase was reversed by using the polymeric phase. Also, the elution order of C_{82} and C_{84} with the monomeric ODS was reversed when compared with the polymeric phase, *i.e.*,

the order with the latter is C_{84} then C_{82} . These differences in the elution characteristics of the monomeric and the polymeric phases can be explained by the molecular planarity recognition capability of the phases, as discussed in our previous paper [26]. Here we will compare three stationary phases with *n*-hexane as the mobile phase in determining elution orders and temperature dependence as it relates to the retention of higher fullerenes.

In Fig. 2, the temperature dependency of the separation of higher fullerenes with the DMP phase is demonstrated. The results clearly show that with this phase the elution characteristics of fullerene isomers do not change dramatically even at different column temperatures. Increasing the temperature only allows faster analysis with similar resolution for those higher fullerenes. The thermal stability of the separation with the DMP phase is apparently seen in the results. For comparison, the chromatograms obtained with the monomeric and the polymeric ODS phases are summarized in Figs. 3 and 4, respectively. The elution behaviours with both ODS phases show higher temperature dependency than is the case with the DMP phase. The polymeric phase shows a drastic elution change with temperature. Even at 20°C, the temperature which offers the highest resolution with the polymeric ODS, only partial separation was realized for higher fullerenes. This means that the polymeric phase is very poor for separation of the higher fullerenes with *n*-hexane as the mobile phase. With the monomeric phase the resolution is a little better. At 20°C with the monomeric ODS, only three major peaks which range from C_{76} to C_{84} in the chromatogram appear, and these peaks merge into two major peaks at 80°C. Therefore, the monomeric phase is better than the polymeric phase but neither is good for higher fullerenes separations.

Two important and conclusive facts are obtained from the experimental results: (1) the resolution of higher fullerenes with the DMP phase is better than with other phases using *n*-hexane as the mobile phase and (2) increasing the temperature with the DMP phase results in slightly faster analysis without loss of resolution. It is clear that the DMP phase is the best

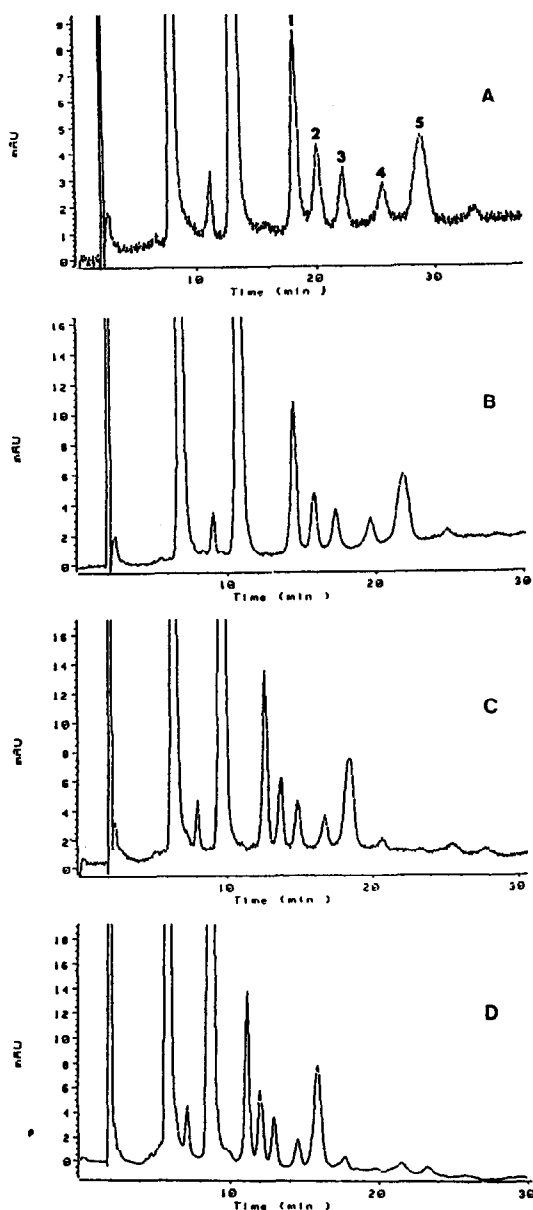


Fig. 2. Separations of higher fullerenes with the DMP phase at different temperatures. (A) 20°C; (B) 40°C; (C) 60°C; and (D) 80°C. Peak assignments are described in the caption of Fig. 5.

stationary phase for the separation of isomers of higher fullerenes.

UV-Vis spectra obtained by the separation with the DMP phase reveal that the elution order of higher fullerenes is C_{76} (peak 1 in Fig. 2), $C_{78}-C_{2v} + C_{78}-D_3$ (peak 2), $C_{78}-C_{2v'}$ (peak

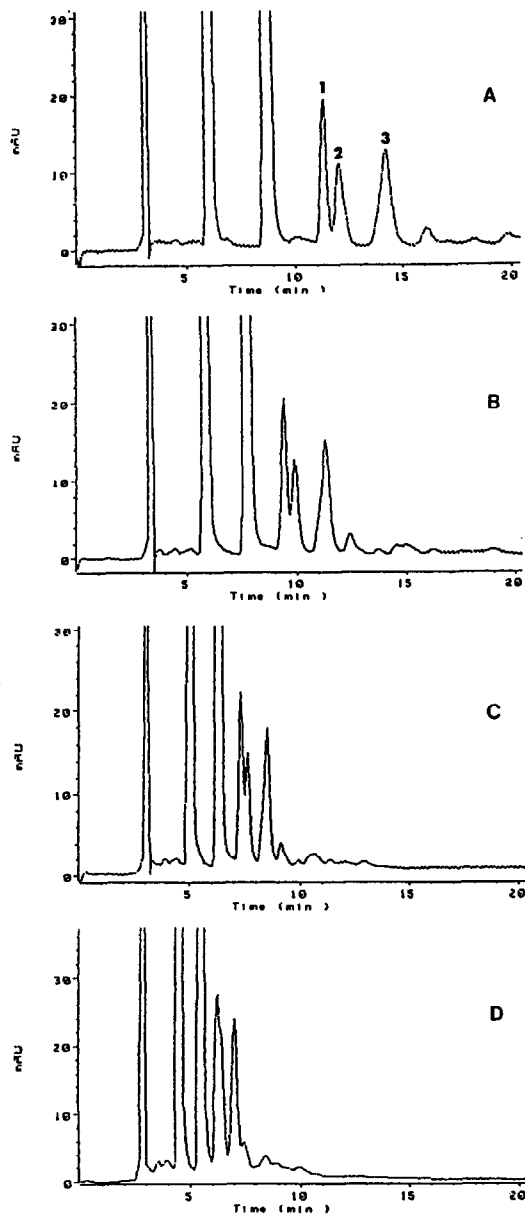


Fig. 3. Separations of higher fullerenes with the monomeric ODS phase. (A) 20°C; (B) 40°C; (C) 60°C; and (D) 80°C. Peak assignments are given in the text.

3), C_{82} (peak 4) and C_{84} (peak 5), as seen in those spectra summarized in Fig. 5. This order is different from those with ODS phases when toluene-acetonitrile was used as the mobile phase [26], *i.e.*, with the monomeric phase the order is C_{76} , $C_{78}-C_{2v'}$, $C_{78}-C_{2v} + C_{78}-D_3$, C_{82} and C_{84} , and with the polymeric phase it is

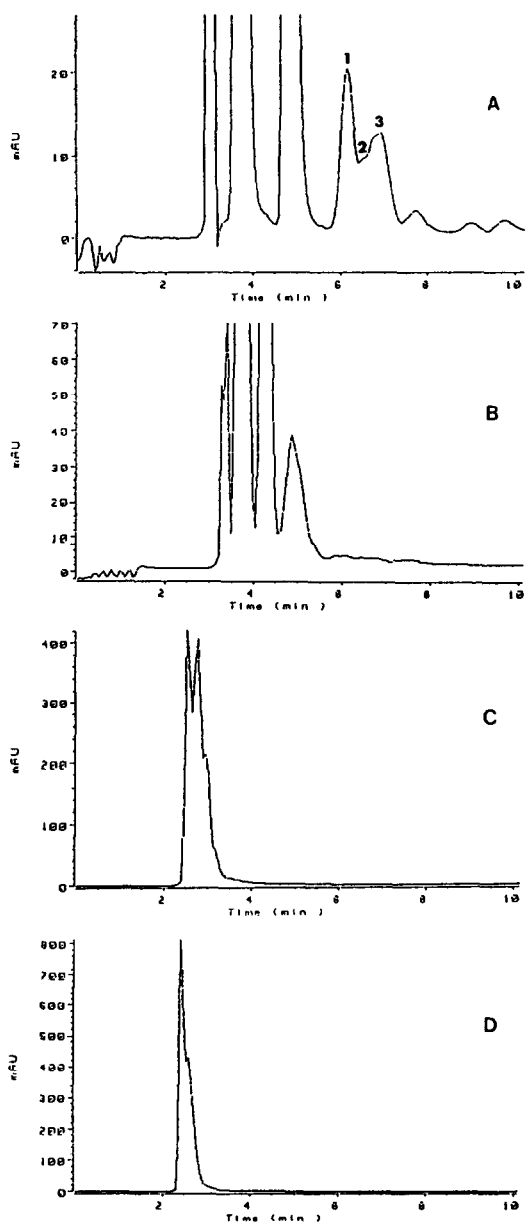


Fig. 4. Separations of higher fullerenes with the polymeric ODS phase. (A) 20°C; (B) 40°C; (C) 60°C; and (D) 80°C. Peak assignments are given in the text.

$C_{78}-C_{2v}$, C_{76} , $C_{78}-C_{2v}$, $C_{78}-D_3$ and $C_{84} + C_{82}$. With *n*-hexane as the mobile phase, the order with the polymeric phase is not clearly seen because of low resolution for these fullerenes. By measuring spectra at several points from 6 to 8 min of the chromatogram obtained at 20°C, it

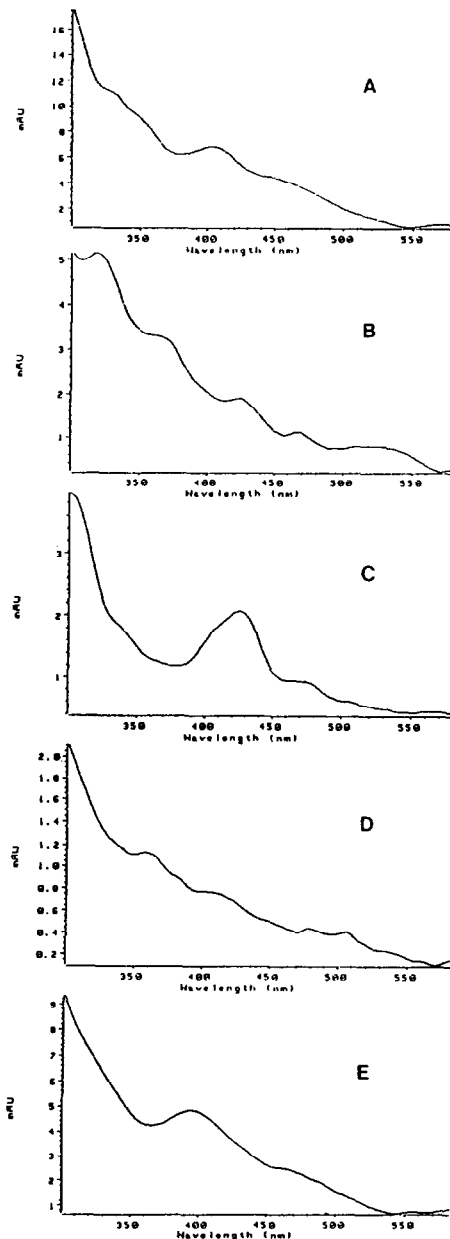


Fig. 5. UV-Vis spectra of the peaks in the chromatograms shown in Fig. 2. (A) Peak 1; (B) peak 2; (C) peak 3; (D) peak 4; and (E) peak 5. By careful examination the spectra can be assigned as follows: (A) C_{76} ; (B) $C_{78}-C_{2v} + C_{78}-D_3$; (C) $C_{78}-C_{2v}$; (D) C_{82} ; (E) C_{84} .

was determined that the order was similar to that with the toluene-acetonitrile mobile phase. Peak 1 in Fig. 4 is $C_{78}-C_{2v} + C_{76}$, peak 2 is $C_{78}-C_{2v}$ and peak 3 includes C_{84} , $C_{78}-D_3$ and C_{82} . With

the monomeric phase the order is also similar to the case with the toluene–acetonitrile mobile phase, although with *n*-hexane even at 20°C three isomers of C₇₈ elute together and C₈₂ makes a little shoulder at the left side of the C₈₄ peak. This means that the peak assignments in Fig. 3 are as follows: peak 1 is C₇₆, peak 2 is three C₇₈ isomers in the order C₇₈–C_{2v'}, C₇₈–C_{2v} and C₇₈–D₃, and peak 3 is C₈₂ + C₈₄. In conclusion, it has been found that the elution order of the higher fullerenes from C₇₆ to C₈₄ is very different with different stationary phases. This is a very important finding and indicates that HPLC separations can be used not only to isolate and purify fullerenes, but also to identify their size and shape. The different order seen for C₇₈–C_{2v'} and C_{2v} isomers is caused by the cavity-like shape of the DMP phase, which might be much better suited to catch C_{2v'} isomer than C_{2v} isomer because the former is a little bulkier than the latter. The polymeric ODS phase, which has the largest molecular planarity recognition capability, retains C_{2v'} less than even C₇₆, and these small differences of shape and structure of the higher fullerenes isomers can be recognized by different types of stationary phases in HPLC. This indicates that HPLC separations are performed under molecular level interactions such as solute–stationary phase interaction. If one can choose a series of appropriate stationary phases and determine the elution order of unknown fullerene isomers, the shape and size of those molecules can be predicted by systematic HPLC analyses. For fullerenes higher than C₈₄ this approach is very promising if one can combine LC–MS technique to determine the isomers' molecular masses [28,29]. This research is under way in our laboratory using the stationary phases mentioned in this work in addition to other different types which can offer different selectivity, such as liquid-crystal bonded phases [30–32].

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