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High-performance liquid chromatography of C_{60} , C_{70} , and higher fullerenes on tetraphenylporphyrin–silica stationary phases using strong mobile phase solvents

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Abstract

The HPLC separation of C_{60} , C_{70} , and higher fullerenes on a tetraphenylporphyrin–silica stationary phase is investigated using pure carbon disulfide, chlorobenzene, *p*-xylene, and toluene as mobile phases. Selectivity factors (α) for C_{70}/C_{60} separations using these solvents are determined to be 1.8, 3.2, 3.8, and 4.3, respectively. Thermodynamic studies reveal that an exothermic interaction takes place between the fullerene and porphyrin stationary phase in the presence of such solvents. Higher fullerenes (up to C_{94}) can be separated quickly at 90°C using CS_2 –toluene (45:55, v/v) as the mobile phase. The high solubility of fullerenes in these solvents dramatically increases the overall potential with regard to preparative fullerene purification. The inability of an alternative protoporphyrin–silica phase to separate C_{60}/C_{70} using the same mobile phases supports a retention mechanism based on simultaneous face-to-face and face-to-edge π – π interactions between the immobilized tetraphenylporphyrin and the fullerenes.

1. Introduction

The discovery of Buckminster fullerene [1], C_{60} , and related higher fullerene structures has evoked a flurry of research in the fields of chemistry, physics, and materials science [2]. This increase in research activities has necessitated the development of improved purification methods for this new class of molecules [3–5]. Currently, HPLC techniques play an integral role in the separation and purification of fullerenes and several stationary phases have been

developed specifically for fullerene (including higher fullerenes) separations [4,6–21].

The difficulty in chromatographic purification of fullerenes lies in their relative insolubility. As pointed out previously by Sun and co-workers [23] as well as Pirkle and Welch [24], this low solubility [22] in organic solvents commonly used as eluents (e.g., hexane, *n*-pentane, dichloromethane, and acetonitrile) makes preparative fullerene separations on conventional supports tedious. Only the use of strong solvents [i.e., toluene or carbon disulfide (CS_2)] as mobile phases would enable large-scale purification of the higher fullerenes [14,15,24–27]. Thus, a faster and more efficient chromatographic process, not curbed by solubility limitations, is urgently

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needed to increase the amount of isolated fullerenes obtained from a single crude soot extract.

Recently it has been reported [28,29] that stationary phases based upon tetraphenylporphyrin immobilized on silica gel supports can be useful in anion-exchange separations of aromatic carboxylates/sulfonates, and in reversed-phase separations of polycyclic aromatic hydrocarbons (PAHs) by HPLC. In addition, preliminary data demonstrated that the tetraphenylporphyrin–silica stationary phase can achieve the highest reported selectivity factor for the separation of C_{60}/C_{70} in 100% toluene [30]. Further, we have also shown that single-step HPLC separation of metallofullerenes (e.g., $La@C_{82}$ and $Y@C_{82}$) can be achieved using a 10-cm column packed with zinc(II) tetraphenylporphyrin–silica [31].

In continuing the investigation of this new stationary phase, we report herein: (i) the separation of C_{60} and C_{70} with four strong fullerene solvents, i.e., toluene, *p*-xylene, chlorobenzene, and carbon disulfide, as mobile phases; (ii) thermodynamic studies for these separations; and (iii) the separation of higher fullerenes (up to C_{94}) in a single injection of crude extract with a very strong mobile phase of CS_2 –toluene (45:55, v/v), within 8 min at 90°C. We further illustrate that the phenyl group of the immobilized porphyrin is critical for separation of fullerenes by reporting results for similar separations using a protoporphyrin–silica phase.

2. Experimental

2.1. Apparatus

The HPLC system consisted of a Spectra Physics (San Jose, CA, USA) SP 8700 solvent delivery system, a Spectra-Physics SP 4290 computing integrator, a Kratos (Ramsey, NJ, USA) Spectroflow 773 variable-wavelength UV–Vis detector, and a Rhyodyne (Cotati, CA, USA) Model 7010 sample valve. Columns were thermostated using a Fisher Scientific water jacket connected to a Fisher Scientific (Pittsburgh, PA,

USA) Model 80 Isotemp constant-temperature circulator. Dead volume of the column was determined by the injection of a CS_2 solution in toluene while using toluene as the mobile phase.

2.2. Chemicals

Fullerenes were produced via a d.c. carbon arc method similar to that described by Parker et al. [32]. The reactor featured water-cooled collection surfaces, variable arc gap, and forced helium flow across the gap to decrease slag formation. The fullerene-containing soot was Soxhlet extracted for 16 h with toluene, followed by a second extraction with pyridine. The resulting deep-red solutions were filtered through a 0.45- μ m cellulose nitrate filter (Millipore, Bedford, MA, USA) prior to drying at 130°C under vacuum. The total yield of crude fullerene extract was approximately 8.0 wt.%, with the pyridine extract containing a greater percentage of higher fullerenes. HPLC-grade toluene, *p*-xylene, and carbon disulfide as well as analytical-reagent grade chlorobenzene were obtained from Aldrich (Milwaukee, WI, USA).

2.3. Preparation of the stationary phase

The zinc(II) tetraphenylporphyrin–silica [$Zn(pCPTPP)$ –silica] stationary phase was prepared in a manner similar to that described elsewhere [28]. In brief, the unsymmetrical phenyl-substituted tetraphenylporphyrin, [5-(*p*-carboxyphenyl)-10,15,20-triphenyl]porphyrin [H_2 -(*pCPTPP*)], was covalently attached to aminopropyl silica gel (10 μ m) via an amide bond. The residual amine sites on the stationary phase were acetylated by refluxing the support in acetic anhydride. Finally, to prepare the metallated support, 2 g of H_2 (*pCPTPP*)–silica was refluxed in 50 ml dimethylformamide containing 0.8 g $ZnCl_2$. Typical porphyrin surface coverages were in the range 0.2–0.4 μ mol/m², based on data from elemental analysis of the final stationary-phase material [28]. The porphyrin–silicas were packed into 250 × 4.6 mm I.D. stainless-steel

tubes by the downfall slurry method at a pressure of 41.4 MPa.

2.4. Matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF-MS)

MALDI-TOF-MS was performed on a VESTEC-2000 instrument (Houston, TX, USA). The wavelength of the laser was 337 nm. A saturated 2,5-dihydrobenzoic acid solution (about 50 mM) with 50% aqueous acetonitrile containing 0.1% TFA was used as the matrix. An amount of 1 μ l of fullerene solution in carbon disulfide was analyzed on the flat surface of the probe tip (2 mm diameter) with the matrix. The insulin A chain (FW = 2531.6) was used as the internal standard to calibrate the m/z output of the system.

3. Results and discussion

In order to fully explore the versatility of columns packed with tetraphenylporphyrin–silica and to acquire more information regarding the nature of the interactions between the immobilized tetraphenylporphyrin and fullerenes, four different strong solvents, i.e. toluene, *p*-xylene, chlorobenzene, and carbon disulfide, were examined as mobile phases to separate C_{60} and C_{70} . Typical chromatograms for C_{60} and C_{70} separations using these solvents are shown in Fig. 1. Table 1 summarizes the solubility of C_{60} , capacity factors (k'), and selectivity factors ($\alpha_{C_{70}/C_{60}}$) in these solvents. To keep the chromatographic conditions consistent, a detector wavelength of 430 nm was selected, which is above the UV cutoff of carbon disulfide (390 nm), although fullerenes do not absorb strongly in this region. To perform the separation, a 20- μ l solution of C_{60} and C_{70} in toluene (1 mg/ml each) was injected into a 250 \times 4.6 mm I.D. column packed with zinc(II) tetraphenylporphyrin–silica (10 μ m). As shown in Table 1, retention times of C_{60} and C_{70} follow a trend that correlates with the inverse of their solubilities in the given mobile-phase solvent; that is, fullerene retention time in CS_2 < in

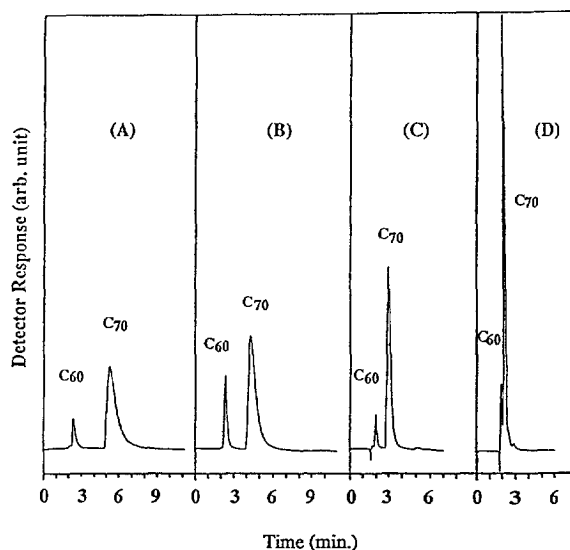


Fig. 1. Separation of C_{60} and C_{70} on the Zn(pCPTPP)–silica stationary phase. Column: 250 \times 4.6 mm I.D. stainless-steel column. Flow-rate: 2 ml/min. Detection: UV, 430 nm (0.100 AUFS). Injection: 20 μ l of fullerene solution in toluene. Temperature: 30°C. Mobile phase: (A) toluene, (B) *p*-xylene, (C) chlorobenzene, and (D) carbon disulfide.

chlorobenzene < in *p*-xylene < in toluene. These results are consistent with other reports on less selective columns [14,26], where increasing the percentage of a stronger fullerene solvent, usually toluene, in the mobile phase decreases the retention of the fullerenes. Interestingly, it has been reported that the separation on poly(styrene-divinylbenzene) gel switches from an adsorption (i.e., C_{70} elutes after C_{60}) to a size-exclusion (i.e., C_{70} elutes before C_{60}) type of mechanism when the carbon disulfide content in a CS_2 – CH_2Cl_2 mobile phase is increased beyond 60% [27]. The porphyrin-based stationary phase, however, still behaves as a normal adsorption-type column, even when using 100% CS_2 as the mobile phase, suggesting that the fullerene interaction with the immobilized porphyrin is quite strong. Although only complete solubility data for C_{60} has appeared in the literature, retention of C_{70} on the porphyrin-based column indicates that its solubility follows the same pattern as that of C_{60} . In comparing the selectivity achieved for C_{70} and C_{60} separation on the tetraphenylporphyrin–silica stationary phase to that obtained

Table 1
Solubility of C₆₀, capacity factors (*k'*) of C₆₀ and C₇₀, and selectivity factors (α) for C₇₀ and C₆₀ using different mobile-phase solvents^a

| Mobile phase | Solubility of C ₆₀ (mg/ml) ^b | Capacity factor of C ₆₀ | Capacity factor of C ₇₀ | Selectivity factor for C ₇₀ /C ₆₀ |
|------------------|---|---------------------------------------|---------------------------------------|--|
| Toluene | 2.8 | 0.56 | 2.43 | 4.3 |
| <i>p</i> -Xylene | 5.2 | 0.51 | 1.92 | 3.8 |
| Chlorobenzene | 7.0 | 0.27 | 0.87 | 3.2 |
| Carbon disulfide | 7.9 | 0.17 | 0.31 | 1.8 |

^a HPLC conditions as in Fig. 1.

^b From Ref. [22].

on two commercial columns (“Buckyrep” and “Buckyclutcher”), which have been touted as the best for fullerene separations, the tetraphenylporphyrin column has an $\alpha_{C_{70}/C_{60}}$ of 4.3 using 100% toluene, compared to $\alpha_{C_{70}/C_{60}} = 1.8$ for the “Buckyrep” column [15] (packed with 2-pyrenal-1-ethyl-silica) and $\alpha_{C_{70}/C_{60}} = 1.45$ for the “Buckyclutcher” column [33] (packed with 3,3,3-tri-dinitrobenzoxyl-propyl-silica) under the same conditions. Therefore, the tetraphenylporphyrin stationary phase is capable of operating with fullerene solvents even stronger than toluene as the mobile phase while still yielding excellent separation of C₇₀ and C₆₀.

Some peak asymmetry (tailing) is observed for the C₆₀ and C₇₀ bands in the chromatograms shown in Fig. 1. This was typical for all columns studied. Peak tailing decreased as the solvent strength of the mobile phase increased, i.e., tailing in CS₂ < in chlorobenzene < in *p*-xylene < in toluene (see Fig. 1). Injection of mixtures made from pure C₆₀ and C₇₀ eliminated the possibility that the presence of higher fullerenes, which elute after C₇₀, contributed to C₇₀ tailing. One possible factor that can influence peak profiles is the kinetics of fullerene interaction with the immobilized porphyrin on the silica support. Indeed, slow “off” and/or “on” adsorption rate constants may contribute to the asymmetric peak profiles observed. In this situation, a stronger solvent used as the mobile phase can increase the rate of a slow kinetic step, and thereby improve the symmetry of peak profiles. In addition, since kinetics are temperature dependent, increasing the column temperature is

an effective means of improving peak symmetry (see below). Another possible explanation for the tailing observed is the self-complexing of fullerenes in solution, which has been recently reported by researchers [34]. A small amount of this complex may be retained longer on porphyrin column, resulting in a tailing after the “parent” peak. Higher solubility and an increase in operating temperature are also unfavorable for the formation of such self-complexes [34].

Although carbon disulfide is a very strong solvent for fullerenes, the Zn(pCPTPP)-silica column exhibits an $\alpha_{C_{70}/C_{60}} = 1.8$ using this solvent as a mobile phase (see Table 1). To our knowledge, no existing HPLC column is capable of separating C₆₀ and C₇₀ in 100% CS₂. Unfortunately, due to the low efficiency of the porphyrin-silica column used here, C₆₀ and C₇₀ are not baseline resolved. However, it is likely that better resolution could be achieved with a more efficiently packed column (the current column typically has $N = 700$). It should also be noted that the capacity factors of C₆₀ and C₇₀ (0.16 and 0.31) in this separation are much lower than the optimum value (5–10). If the surface coverage (ϕ) of porphyrin stationary phase could be increased from the present 0.2 $\mu\text{mol}/\text{m}^2$ to 2 $\mu\text{mol}/\text{m}^2$ (e.g., increasing the ϕ value ten-fold) via an improved porphyrin immobilization method, the capacity factors ($k' = K \cdot \phi$) for C₆₀ and C₇₀ would be 1.6 and 3.1, respectively. This would improve the resolution (R_s) by a factor of three in accordance with the classical equation defining the resolution of solutes on chromatographic columns.

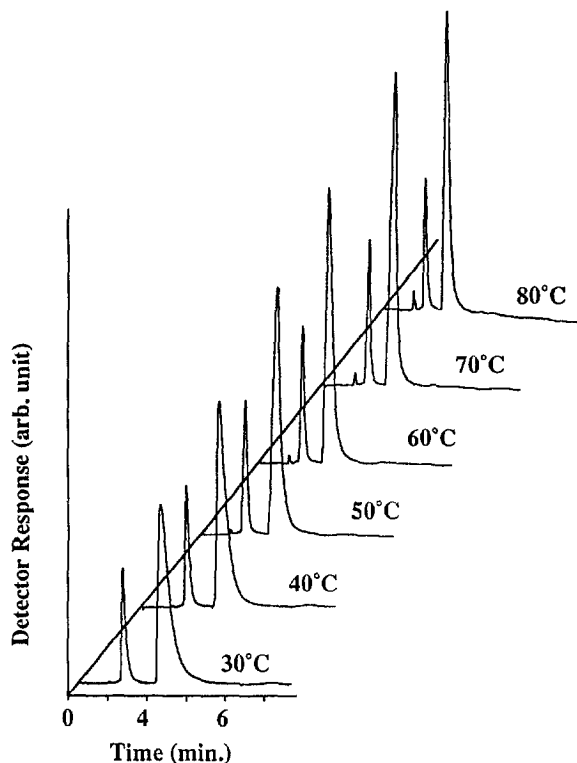


Fig. 2. Temperature effect on separation of C_{60} and C_{70} . Column: 250×4.6 mm I.D. Zn(pCPTPP)–silica. Mobile phase: *p*-xylene. Flow-rate: 2 ml/min. Detection: UV–Vis, 430 nm (0.100 AUFS). Injection: $20 \mu\text{l}$ of fullerene solution in toluene. Temperatures: 30, 40, 50, 60, 70, and 80°C .

To evaluate the thermodynamic parameters governing fullerene adsorption onto the tetraphenylporphyrin stationary phase, chromatograms were obtained at various temperatures. Fig. 2 shows chromatograms of C_{60} and C_{70} with *p*-xylene as the mobile phase at different temperatures. The profile of the C_{70} peak improves as the temperature is elevated. This may be a further indication (see above) that the tailing of the C_{70} peak is due to slow kinetics for fullerene interaction with the immobilized porphyrin as well as self-complexation of fullerenes.

Fig. 2 clearly demonstrates that increasing the column temperature results in a decrease in retention and asymmetry of both the C_{60} and C_{70} peaks when employing *p*-xylene as the mobile phase. Moreover, the van 't Hoff plots of C_{60} and C_{70} , Figs. 3A and 3B, show the same trend for the other three solvents examined. Due to the low boiling point of CS_2 , it was studied only over the temperature range 30 – 70°C , while the range 30 – 80°C was examined for the other solvents. In the temperature range studied, the van 't Hoff plots are all quite linear. The enthalpies of transfer (see Table 2) are calculated from the slopes of the van 't Hoff plots according to the equation

$$\ln(k') = -\frac{\Delta G}{RT} + \ln \phi = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \phi \quad (1)$$

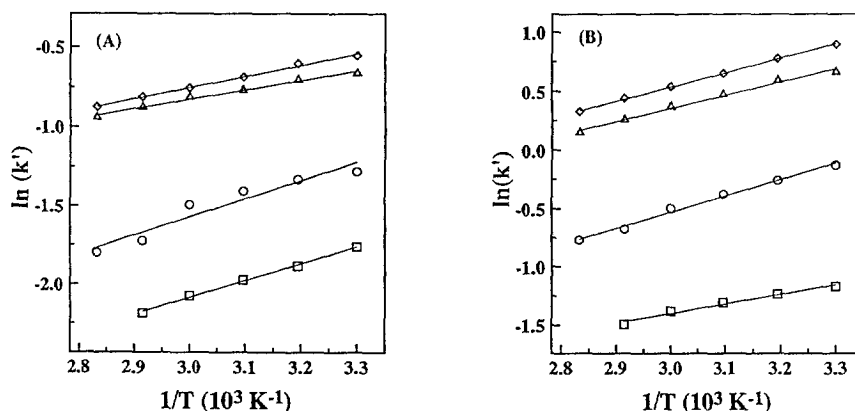


Fig. 3. Plot of $\ln(k')$ vs. $1/T$ for C_{60} (A) and C_{70} (B) on the Zn(pCPTPP)–silica stationary phase. Mobile phase: toluene (\diamond), *p*-xylene (Δ), chlorobenzene (\circ), and carbon disulfide (\square). Flow-rate: 2 ml/min. Detection: UV–Vis, 430 nm (0.100 AUFS). Injection: $20 \mu\text{l}$ of fullerene solution in toluene.

Table 2

Enthalpy of transfer (ΔH) for the separation of fullerenes on tetraphenylporphyrin–silica stationary phase using different mobile-phase solvents (kJ/mol)

| Enthalpy | Mobile phase | | | |
|------------------------|------------------|---------------|------------------|---------|
| | Carbon disulfide | Chlorobenzene | <i>p</i> -Xylene | Toluene |
| ΔH of C_{60} | –9.4 | –10.1 | –5.7 | –6.1 |
| ΔH of C_{70} | –7.2 | –11.9 | –9.8 | –10.2 |

A similar normal temperature dependence of fullerene separation has been reported previously for a dimethoxyphenylpropyl-bonded silica phase [18]. However, an unusual temperature effect on the retention of C_{60} and C_{70} has been reported for a CSP 1 support [24], the “Buckyclutcher 1” stationary phase [33], the dinitrobenzoylphenylglycine (DNBPG), as well as the (*R*)-(–)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy propionic acid (TAPA) stationary phase [14]. Retention times for C_{60} and C_{70} on these stationary phases increase, rather than decrease, as the column temperature is raised. The authors did not propose a clear explanation for this unusual behavior. From Table 2, the negative sign of the ΔH s means that the adsorption of C_{60} and C_{70} on the immobilized porphyrin column is exothermic. In addition, the separation of PAHs, the planar analogs of fullerenes, on the tetraphenylporphyrin–silica stationary phase [29] has the same temperature dependence as that of fullerenes. This consistency in the temperature dependence of fullerenes and PAHs supports a proposed π – π interaction retention mechanism (see below).

An unusual temperature effect with CS_2 is shown in Fig. 4, in which selectivity factors for C_{70}/C_{60} are plotted versus temperature. With toluene, *p*-xylene, or chlorobenzene as the mobile phase, elevating the temperature decreases the selectivity factor. However, the selectivity factor for C_{70} over C_{60} increases rather than decreases, as column temperature is raised when using CS_2 as the eluent. The relationship between the change in selectivity factor $\alpha_{i,j}$ ($=k'_i/k'_j$) and temperature can be expressed as

$$\frac{\alpha_{T_1}}{\alpha_{T_0}} = \exp \left[\frac{(T_1 - T_0) \Delta(\Delta H)}{T_1 T_0 R} \right] \quad (2)$$

where $\Delta(\Delta H)$ is $\Delta H_i - \Delta H_j$ (solute *i* is more retained than solute *j*). Usually in chromatography as observed with toluene, *p*-xylene, and chlorobenzene as mobile phases, the ΔH s for C_{60} (–6.1, –5.7, and –10.1 kJ/mol, respectively) are smaller than those of C_{70} (–10.2, –9.8, and –11.9 kJ/mol, respectively); thus, according to Eq. 2, the higher the column temperature, the smaller the α value. However, the ΔH of C_{60} in carbon disulfide (–9.4 kJ/mol) is larger than that of C_{70} (–7.2 kJ/mol), so that increasing the

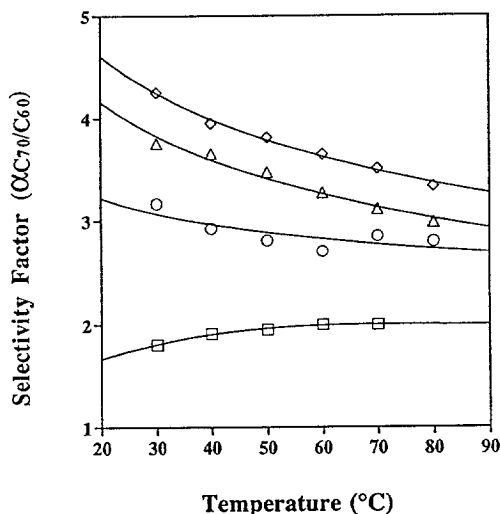


Fig. 4. Plot of $\alpha_{C_{70}/C_{60}}$ versus temperature on the Zn(pCPTPP)–silica stationary phase. Mobile phase: toluene (◇), *p*-xylene (△), chlorobenzene (○), and carbon disulfide (□). Flow-rate: 2 ml/min. Detection: UV–Vis, 430 nm (0.100 AUFS). Injection: 20 μ l of fullerene solution in toluene.

temperature results in an increase, rather than a decrease, in the selectivity factor (α). This unusual behavior reveals that the entropy effect predominates retention in carbon disulfide, whereas the enthalpy effect predominates retention in the other three solvents. It is speculated that the high electronic density of the π -orbitals of the sulfur atoms in carbon disulfide somehow interacts differently with the π -electrons of fullerenes when compared with π -electrons of toluene, xylene, and chlorobenzene. It is also possible, however, that CS_2 more effectively solvates the porphyrin stationary phase, and this may further contribute to the unusual temperature dependence observed. A clearer understanding of this abnormal behavior will require a more detailed investigation.

Using a stronger solvent as the mobile phase in fullerene separations on the porphyrin–silica columns dramatically increases the solubility of the higher fullerenes, enabling both the detection and purification of higher fullerenes to be achieved much more rapidly than with conventional columns. Fig. 5 shows a typical rapid separation obtained for a single injection of a pyridine extract of crude soot, which contains higher fullerenes. Matrix-assisted laser desorption time-of-flight mass spectra (MALDI-TOF-MS) of each of the six fractions collected are shown in Fig. 6. Due to the very low laser power used, fragmentation of fullerene ions is minimized. Thus, the bands in the chromatogram shown in Fig. 5 can easily be assigned. In some spectra, a small portion of previous peak components are seen because of peak tailing. Further, due to the great similarity between higher fullerenes (i.e., only two carbon atoms difference (2.5%) between C_{76} and C_{78}), C_{76} and C_{78} are not baseline resolved and C_{82} and C_{84} co-elute. It should be noted, however, that a mixture of very strong fullerene solvents (45% CS_2 –55% toluene) was used as the mobile phase, and better resolution of these components is possible by using a weaker mobile phase (e.g., toluene or toluene–hexane).

In our previous work [29], the tetraphenylporphyrin-based stationary phase was demonstrated to have a shape (planar versus nonpla-

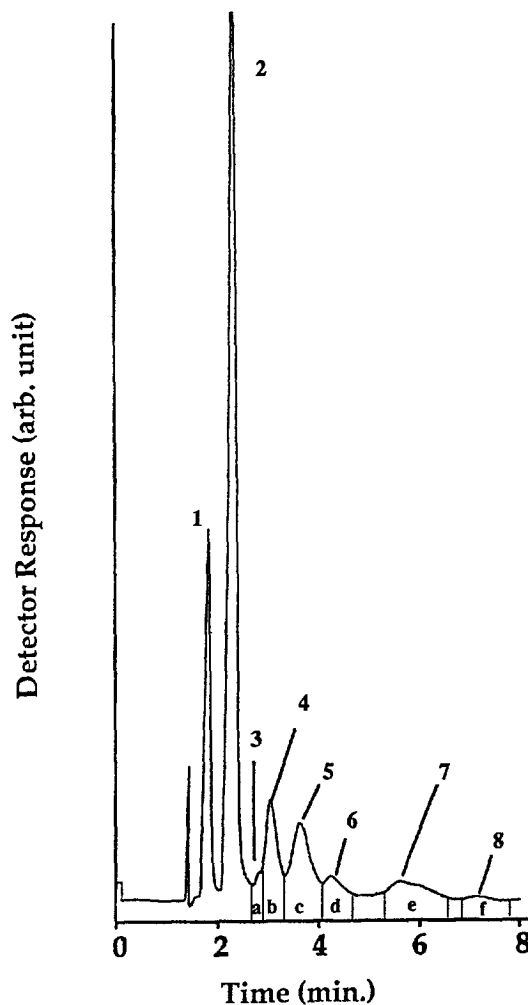


Fig. 5. HPLC chromatogram of higher fullerenes on the Zn(pCPTPP)–silica stationary phase. Mobile phase: carbon disulfide–toluene (45:55, v/v). Injection: 50 μl toluene solution of a pyridine extract of graphite soot. Flow-rate: 2 ml/min. Detection: UV, 430 nm (0.150 AUFS). Temperature: 90°C. Peak identity: (1) C_{60} , (2) C_{70} , (3) C_{76} , (4) C_{78} , (5) C_{82} , and C_{84}^* , (6) C_{86} , (7) C_{88} , C_{90}^* , and C_{92} , (8) C_{94} ; (a)–(f) are fractions for mass spectrometry in Fig. 6 (* indicates the major components).

nar) selectivity for PAHs, based on face-to-face π – π interactions between π -electron systems on the porphyrin ring and the PAH. It is thought that the *meso* phenyl groups do not play a significant role in PAH retention. However, the unique convex surface of fullerenes may render

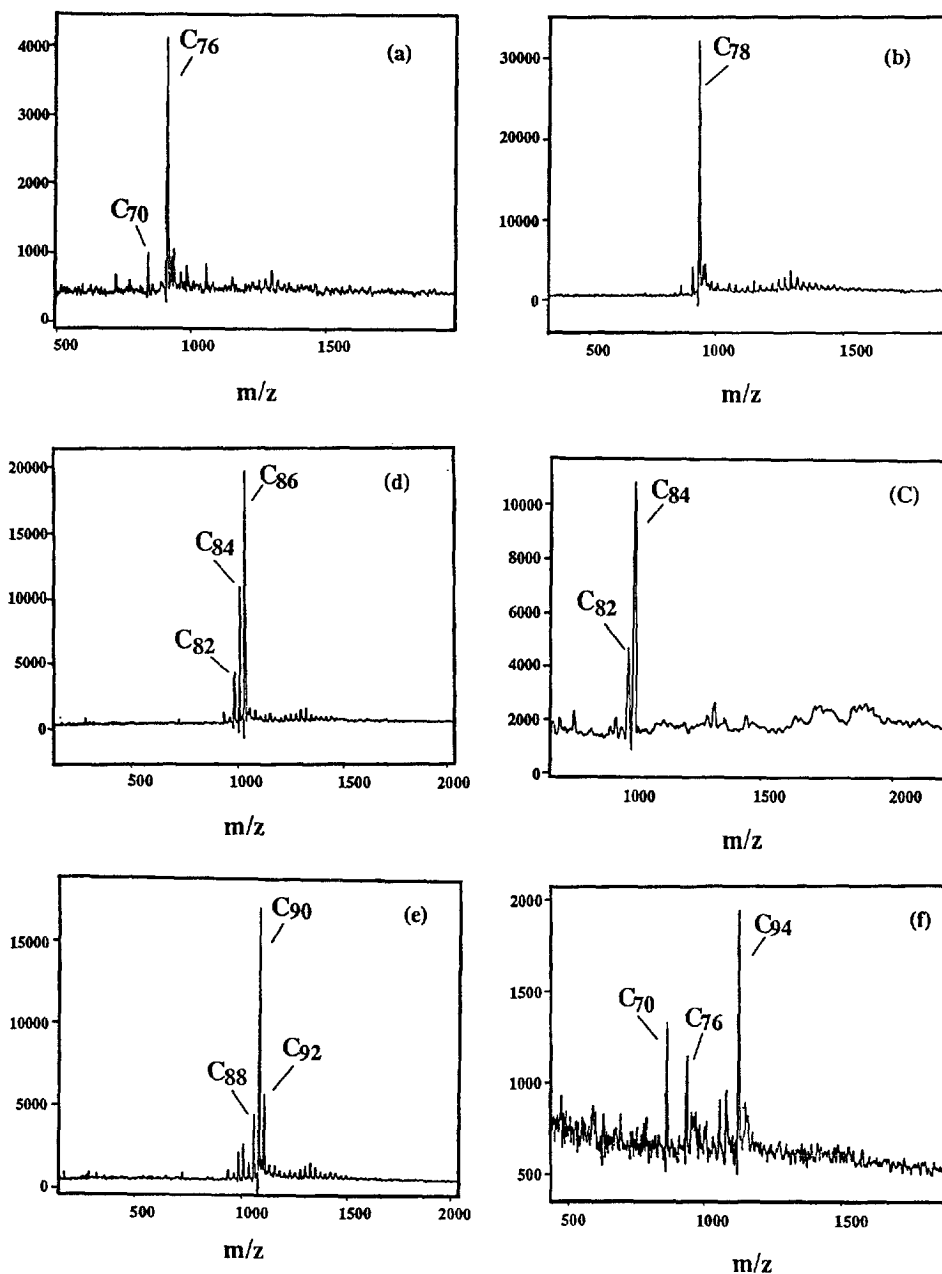


Fig. 6. MALDI-TOF-MS of six fractions (a)–(f) in Fig. 5. Mass spectrometry conditions are described in the Experimental section.

these analytes better able to undergo three-dimensional (3D) interaction with immobilized tetraphenylporphyrin stationary phase than planar PAH molecules. Single-crystal X-ray studies [35] reveal that the four *meso* phenyl rings in

tetraphenylporphyrin are perpendicular to the porphyrin ring, rather than co-planar. Therefore, another interaction is possible, between the fullerene “face” and the “edge” of the *meso* phenyl groups. This type of face-to-edge π - π

interaction in chromatographic recognition has been reported previously by Pirkle et al. [36], and such arrangements are found in the crystal structures of proteins [37], peptides [38], and small molecules [39], and also have been the subject of theoretical calculations [40]. Since tetraphenylporphyrin may be capable of simultaneous face-to-face and face-to-edge π - π interactions with the fullerenes, this extra dimension with respect to the interaction between the immobilized tetraphenylporphyrin and fullerene may account for the very high selectivity achieved. In Fig. 7, the 3D structures of C_{60} and zinc(II) tetraphenylporphyrin (ZnTPP) are shown at the same scale to reveal their relative sizes. Buckminsterfullerene (C_{60}) with a diameter of 7.1 Å looks like a soccer ball [41], while C_{70} with a central diameter of 6.9 Å and a longitudinal axis of 7.8 Å looks like a football [42]. Theoretical simulations predict that even C_{100} has a longitudinal length of only 15 Å. ZnTPP with its 6.8 × 6.8 Å porphyrin ring and four *meso* phenyl groups, that are diagonally approximately 11 Å apart, appears to form a π -electron cavity and behaves as a half of "basket" to host fullerenes. As shown in Fig. 7a, the larger the fullerene cage (C_{70} versus C_{60}), the more contact area the solute has to interact with the ZnTPP cavity, resulting in a stronger π - π interaction and, therefore, a longer retention

time. Indeed, the molecular-shape selectivity observed on the tetraphenylporphyrin-silica phase is so sensitive that even the small difference in shape between C_{70} and C_{60} yields a very large difference in retention.

To further support this retention mechanism, we have prepared a protoporphyrin-silica stationary phase [43]. Compared with the tetraphenylporphyrin structure, protoporphyrin does not possess four phenyl rings at the *meso* positions. As shown in Fig. 8, under similar conditions, C_{60} and C_{70} can still be separated but with much poorer selectivity. Because the higher surface coverage of protoporphyrin [2.8 versus 0.2 $\mu\text{mol}/\text{m}^2$ for Zn(pCPTPP)] rules out the possibility that these results are due to less coverage of stationary phase ($k' = K \cdot \phi$), the shorter retention time and poorer C_{70}/C_{60} selectivity appears due to a much smaller partition coefficient (K) for each solute. As illustrated in Fig. 7b, the absence of the π -electron cavity in the protoporphyrin stationary phase results in less π - π interaction sites, further suggesting the critical contribution of the *meso* phenyl groups (see Fig. 7a) to the fullerene separations on tetraphenylporphyrin-silica columns.

4. Conclusion

In summary, immobilized tetraphenylporphyrins offer unprecedented selectivity for the separation of fullerenes over previously reported columns. With this newly developed stationary phase, the strong fullerene solvents carbon disulfide, chlorobenzene, and *p*-xylene, in addition to toluene, can be used for the first time as mobile phases to efficiently separate C_{60} and C_{70} and higher fullerenes. Higher fullerenes (up to C_{94}) can be quickly separated within 8 min using a 45% CS_2 -55% toluene mixture as the mobile phase while operating the column at 90°C. This work demonstrates the great potential of tetraphenylporphyrin-silica stationary phase for the large-scale purification of higher fullerenes. In contrast to other fullerene selectors, the separation of fullerenes on tetraphenylporphyrin-silica behaves normally as the temperature in-

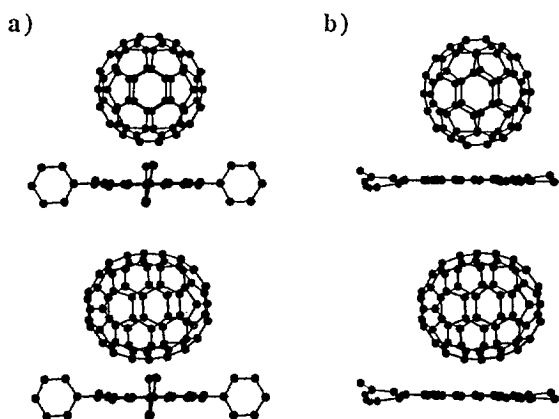


Fig. 7. Three-dimensional molecular modeling for the interaction of zinc tetraphenylporphyrin (ZnTPP) (a) and protoporphyrin IX (b) with Buckminsterfullerene (C_{60}) (top) and C_{70} (bottom).

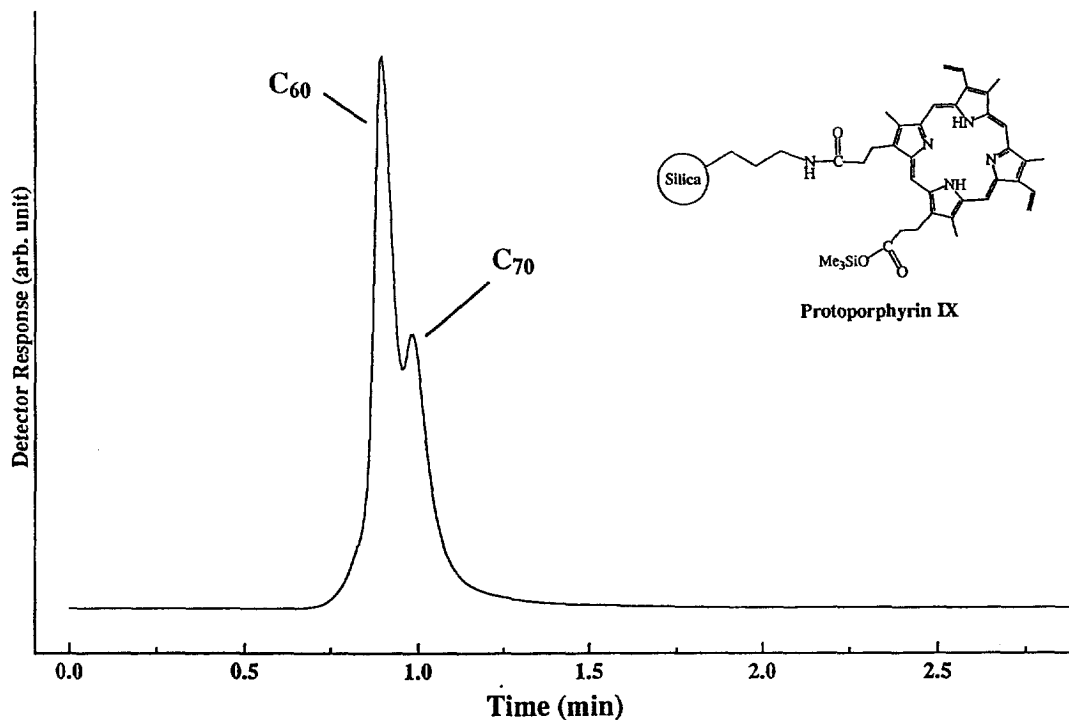


Fig. 8. Separation of C_{60} and C_{70} on the column packed with immobilized protoporphyrin-silica. Mobile phase: toluene. Flow-rate: 1 ml/min. Detection: UV-Vis, 430 nm (0.100 AUFS). Injection: 20 μ l of fullerene solution in toluene. Temperature: ambient.

creases, indicating that the adsorption interaction is exothermic. An unusual temperature effect on the selectivity factor of C_{60} and C_{70} in carbon disulfide is observed. At present, the reason for this atypical behavior is not clear. A possible retention mechanism that relies upon simultaneous face-to-face and face-to-edge π - π interactions between fullerenes and tetraphenylporphyrin is further supported by new results obtained with columns packed with a protoporphyrin-silica phase.

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