

Adsorption isotherms of the fullerenes C₆₀ and C₇₀ on a tetraphenylporphyrin-bonded silica

Fabrice Gritti^{a,b}, Georges Guiochon^{a,b*}

^a Department of Chemistry, University of Tennessee, 415 Buehler Hall, Knoxville, TN 37996-1600, USA

^b Division of Chemical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120, USA

Available online 28 July 2004

Abstract

The single-component adsorption isotherms of the C₆₀ (from 0 to 15 g/L) and C₇₀ (from 0 to 8 g/L) buckminsterfullerenes on a tetraphenylporphyrin-bonded silica were acquired by frontal analysis, using a solution of toluene–1-methylnaphthalene (40:60, v/v) as the mobile phase. The best isotherm model derived from the fitting of these adsorption data was the bi-Langmuir model, a choice supported by the bimodal affinity energy distribution (AED) obtained for C₆₀. The isotherm parameters derived from the inverse method (IM) of isotherm determination (by fitting calculated profiles to experimental overloaded band profiles of C₆₀ and C₇₀) are in very good agreement with those derived from the FA data. According to the isotherm parameters found by these three methods (FA, AED, IM), the tetraphenylporphyrin-bonded silica can adsorb 54 and 42 mmol/L of C₆₀ and C₇₀ fullerenes, respectively, a result that is consistent with the relative molecular size of these two compounds. The 20% lower surface accessibility for C₇₀ is compensated by a three times higher equilibrium constant on the low-energy sites, giving a selectivity $\alpha_{C_{70}/C_{60}} = 3.6$. Large volumes (0.2, 0.8 and 1.7 mL) of mixtures of C₆₀ (3.2 g/L) and C₇₀ (1.3 g/L) were injected and their elution profiles compared to those calculated from the competitive bi-Langmuir model derived from the single-component isotherm data. A good agreement is obtained between calculated and experimental profiles, which supports the two-site adsorption mechanism derived from the single-component adsorption data. The measurements of the influence of the pressure on the retention of C₆₀ and C₇₀ demonstrate that the partial molar volumes of the two buckminsterfullerenes are 12 mL/mol larger in the stationary than in the mobile phase.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Preparative chromatography; Adsorption isotherms; Frontal analysis; Band profiles; Affinity energy distribution; Stationary phases, LC; Mathematical modelling; Buckminsterfullerenes; Fullerenes; Tetraphenylporphyrin; Methylnaphthalene; Toluene

1. Introduction

Materials based upon buckminsterfullerenes have proven to be interesting in many application fields, with regards to their new structure, stability and important physical properties. The preparation of new carbon materials with original structures is part of a vast research area (fullerenes, carbon nanotubes, functionalized fullerenes, ...) and the development of methods for the separation and purification of the original compounds becomes necessary in order to allow the physical characterization of these objects. High-performance liquid chromatography (HPLC) seems to be the most valuable method of purification [1,2].

Many attempts were made to develop a separation process and extract the most abundant fullerenes, C₆₀ and C₇₀, from the soot generated by electrical discharges. Excellent resolutions were obtained with several conventional chemically bonded silicas for reversed-phase chromatography (all bonded with hydrocarbon ligands), using mixtures of poor solvents of these fullerenes (toluene, n-heptane, methanol, dichloromethane, ...) as the mobile phase. However, the production rate of the purification process was always very small because the solubility of fullerenes in these solvents is low (<3.2 g/L). The need of systems using better solvents of the fullerenes was compelling, despite the possible loss of resolution. Kele et al. [3] proposed 1-methylnaphthalene which has a 10 times higher solubility for C₆₀ (33 g/L) than pure toluene. This solvent fulfills other important requirements for a mobile phase to be used in preparative liquid chromatography: it has a low toxicity (in spite of a strong, unpleasant odor),

* Corresponding author. Tel.: +1 865 974 0733; fax: +1 865 974 2667.
E-mail address: guiochon@utk.edu (G. Guiochon).

a moderate viscosity and density, and a low melting point. The optimization of the operational conditions regarding the nature of the stationary phase, the mobile phase composition, the mobile phase velocity, and the temperature was discussed by Kele et al. in great detail [3]. A strong solvent can be used only with a stationary phase that interacts strongly with the feed. The best adsorbent used so far consists in a bonded amino-silica onto which is grafted a tetraphenylporphyrin ligand. A 4.75 mg mixture of C₆₀/C₇₀ was completely resolved on this system, using a toluene–1-methylnaphthalene mixture (50:50, v/v), at an optimum flow rate of 0.3 mL/min (for high column efficiency), at all temperatures between 25 and 70 °C.

However, little information was available on the adsorption behavior of either C₆₀ or C₇₀ on this tetraphenylporphyrin stationary phase. The overloaded band profiles of C₆₀ and C₇₀ published by Kele et al. [3] exhibit front shock layers and diffuse rear boundaries that clearly suggest that the isotherms of both fullerenes are convex upward. However, no systematic study in the literature were ever devoted to the determination of these isotherms. The goal of this paper was to measure and model adsorption data of these two fullerenes. The data were to be acquired by frontal analysis. The best model of adsorption isotherm derived from these data was to be validated by comparing calculated and experimental overloaded band profiles, by calculating the adsorption energy distribution, and by estimating the best isotherm parameters from the experimental band profiles, using the inverse method of isotherm determination. Finally, the competitive isotherm model was to be determined by comparing calculated and experimental band profiles for binary mixtures of C₆₀ and C₇₀.

2. Theory

2.1. Models of isotherm used

2.1.1. Single-component isotherm model

The isotherm model used to describe the adsorption of C₆₀ and C₇₀ on tetraphenylporphyrin-bonded silica is the bi-Langmuir model, the simplest model for adsorption on nonhomogeneous surface [4]. The surface is assumed to be paved by two different types of adsorption sites, acting independently. The isotherm equation is written as follows:

$$q^* = q_{s,1} \cdot \frac{b_1 C}{1 + b_1 C} + q_{s,2} \cdot \frac{b_2 C}{1 + b_2 C} \quad (1)$$

where q^* and C are the equilibrium concentrations of the compound considered in the adsorbed and in the liquid phases, respectively, and $q_{s,1}$, $q_{s,2}$, b_1 and b_2 are the monolayer saturation capacities and the equilibrium constants, respectively. The equilibrium constants b_1 and b_2 are associated with the adsorption energies $\epsilon_{a,1}$ and $\epsilon_{a,2}$, respectively, through the following classical equation [5]:

$$b_i = b_0 e^{\epsilon_{a,i}/RT} \quad (2)$$

where $\epsilon_{a,i}$ is the adsorption energy, R is the universal ideal gas constant, T is the absolute temperature and b_0 is a pre-exponential factor that could be derived from the molecular partition functions in the bulk and the adsorbed phases. b_0 is often considered to be independent of the adsorption energy [5].

2.1.2. Two-component isotherm model

For binary mixtures, the competition for access to the adsorbent was accounted for by using a simple extension of the single-component bi-Langmuir model, e.g. the competitive bi-langmuir model. For component i ($i = 1$ or 2), the amount adsorbed per volume unit of adsorbent is:

$$q_i^* = \frac{q_{s,i,1} b_{i,1} C_i}{1 + b_{1,1} C_1 + b_{2,1} C_2} + \frac{q_{s,i,2} b_{i,2} C_i}{1 + b_{1,2} C_1 + b_{2,2} C_2} \quad (3)$$

where $q_{s,i,j}$ is the single-component saturation capacity of component i on site j and $b_{i,j}$ the single-component equilibrium constant of component i on site j . Three other similar models were applied depending whether or not the competition for adsorption happens on the two types of sites (see Section 4).

2.2. The inverse method of isotherm determination

The inverse method of isotherm determination has the great advantages of requiring less time and smaller amounts of chemicals than the conventional methods of FA or perturbation. It consists in fitting calculated to experimental overloaded band profiles, using an appropriate model of band profile calculation (see next section). However, in the calculations, the equation of the isotherm model must be selected first. Thus, the inverse method can be used to confirm the numerical isotherm parameters found by direct methods or to determine these parameters in wide range of experimental conditions. A more detailed description of this method is given elsewhere [6].

2.3. Modeling of band profiles in HPLC

The overloaded band profiles of the buckminsterfullerenes (pure or in mixtures) were calculated using the equilibrium-dispersive model (ED) of chromatography [7–9]. The ED model assumes instantaneous equilibrium between the mobile and the stationary phases and a finite column efficiency originating from an apparent axial dispersion coefficient that accounts for the dispersive phenomena (molecular and eddy diffusion) and for the non-equilibrium effects (mass transfer kinetics) that take place in the chromatographic column. The axial dispersion coefficient is related to the column efficiency under linear conditions.

At $t = 0$, the stationary phase is in equilibrium with the pure mobile phase and the solute concentrations in both phases in the column are uniformly equal to zero. The boundary conditions used are the classical Danckwerts-type boundary conditions [10] at the inlet and outlet of the column.

The ED model was solved using the Rouchon program, based on a finite difference method [7,11–13].

3. Experimental

3.1. Chemicals

The mobile phase used in this work was a mixture of toluene–1-methylnaphthalene (60:40, v/v). Both toluene (HPLC grade) and 1-methylnaphthalene (95%) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The solutes studied were the purified buckminsterfullerenes C₆₀ (99.9%) and C₇₀ (99.0%), both purchased from SES Research (Houston, TX, USA).

3.2. Columns

We used a 250 mm × 4.6 mm column packed with tetraphenylporphyrin(TPP)-bonded silica given by Selective Technologies (Ann Arbor, MI, USA). Its main characteristics are summarized in Table 1. This column was already used by Kele et al. [3] for the optimization of the experimental chromatographic parameters. The performance and characteristics of the column were found unchanged. The column void volume was derived from the average of the retention times of two consecutive toluene injections (3.21 mL). This volume remained unchanged when different average column pressures were applied (18, 132 and 252 bar).

3.3. Apparatus

All the breakthrough curves and the overloaded band profiles were acquired using a Hewlett-Packard (now Agilent Technologies, Palo Alto, CA, USA) HP 1090 liquid chromatograph. This instrument includes a multi-solvent delivery system (volume of each tank, 1 L), an auto-sampler with a 250 μL sample loop, a diode-array UV detector, a column thermostat and a data station. Compressed nitrogen and helium bottles (National Welders, Charlotte, NC, USA) are connected to the instrument to allow the continuous operations of the pump, the auto-sampler, and the solvent sparging. The extra-column volumes are 0.057 and 0.35 mL as measured

Table 1
Physico-chemical properties of the tetraphenylporphyrin bonded silica column (250 mm × 4.6 mm)

Particle size	10 μm
Particle shape	Irregular
Pore size	Unknown
Surface area	200 m ² /g
Surface coverage	0.2–0.4 μmol/m ²
Total column porosity ^a	0.770

Data from [3].

^a Data from toluene injections in a toluene–1-methylnaphthalene mobile phase (60:40, v/v).

from the auto-sampler and from the pump system, respectively, to the column inlet. All the retention data were corrected for these two contributions. The flow-rate accuracy was controlled by pumping the pure mobile phase at 23°C and 1 mL/min during 50 min, from each pump head, successively, into a volumetric glass of 50 mL. The relative error was less than 0.4%, so that we can estimate the long-term accuracy of the flow-rate at 4 μL/min at flow rates around 1 mL/min. All measurements were carried out at a constant temperature of 23°C, fixed by the laboratory air-conditioner. The daily variation of the ambient temperature never exceeded ±1°C.

3.4. Measurements of the adsorption isotherm of the buckminsterfullerenes by FA

The adsorption isotherms of the fullerenes C₆₀ and C₇₀ were all measured in solutions of toluene–1-methylnaphthalene (60:40, v/v). The retention factors of these compounds are 0.55 and 1.91 (see Fig. 1). These values are relatively low and the breakthrough curves were recorded at the low flow rate of 0.5 mL/min (instead of the usual 1 mL/min) in order to maximize the column efficiency and acquire more accurate adsorption data. The maximum concentrations of C₆₀ and C₇₀ applied in FA were fixed at 15 and 8 g/L, respectively, to avoid any precipitation in the instrument. One master solution was prepared at this maximum concentration for each compound. One pump of the HPLC instrument was used to deliver a stream of the pure mobile phase (toluene–1-methylnaphthalene, 60:40, v/v) and the second pump a stream of the master solution. The feed concentration in the FA stream is proportional to the concentration of the sample in the master solution

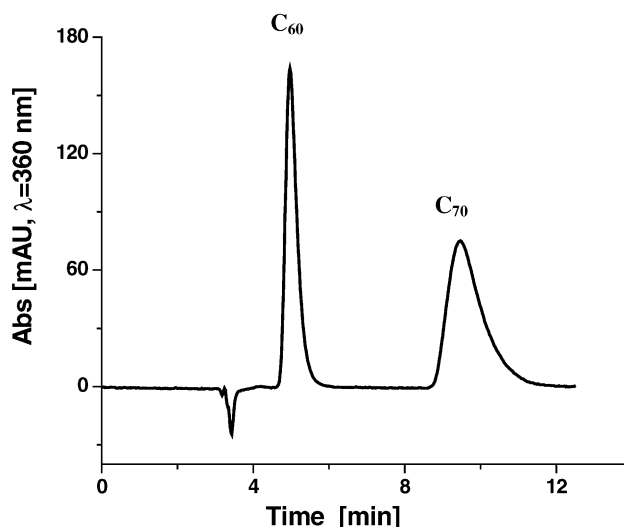


Fig. 1. Analytical chromatogram of C₆₀ and C₇₀ on the TPP stationary phase with a mixture of toluene–1-methylnaphthalene (60:40, v/v) as the mobile phase, at a flow rate of 1 mL/min. Room temperature, injection of 10 μL of a solution of 1 g/L of C₆₀ and C₇₀ each. Note the slower mass transfer (larger peak) between the mobile and stationary phase for C₇₀.

and to the flow rate fractions delivered by the two pumps. Twenty-two data points were acquired between 0.15 and 15 g/L for C_{60} and twenty data points between 0.04 and 8 g/L for C_{70} .

The breakthrough curves were recorded with a sufficiently long time delay between them (35 min) to allow for the complete re-equilibration of the column with the pure mobile phase after the elution of each breakthrough curve. The injection time of the sample was fixed at 7 min for all FA steps in order to reach a stable plateau at the column outlet, whatever the feed concentration used. The signal was detected at 598 nm (highest wavelength available). For concentrations larger than 4.0 and 1.5 g/L the response of the detector for C_{60} and C_{70} , respectively, exceeds 2500 mAU and the signal becomes useless. Below these concentrations, the detector response was calibrated by measuring the UV absorbance at the plateaus observed on the breakthrough curves. At higher fullerene concentrations, although calibration is impossible, the position of the front shock of the breakthrough curve can still be measured clearly from the rapid increase of the UV signal corresponding to the elution of the shock layer and the adsorption isotherm could be measured accurately within the whole concentration range.

3.5. Measurements of overloaded band profiles

High-concentrations bands were injected with the pump. For single-component bands, the injections of a solution of C_{60} (1.50 g/L during 1 min) and of C_{70} (1.44 g/L during 1.5 min) were performed using the pump delivery system. For binary mixtures, the injection of three different volumes (0.2, 0.8 and 1.7 mL) of a feed made with C_{60} (3.2 g/L) and C_{70} (1.3 g/L) were performed. All the band profiles were recorded at 598 nm.

4. Results and discussion

4.1. Single-component isotherms

Fig. 2 shows the adsorption data of C_{60} (top) and its Scatchard representation (bottom), the data being measured by frontal analysis. Fig. 3 shows the same results for C_{70} . As expected from the overloaded band profiles reported by Kele et al. [3], both isotherms are strictly convex upward. However, the simple and popular Langmuir isotherm model cannot account for the experimental data, as shown by a comparison between the data (symbols) and the best Langmuir and bilangmuir isotherms (solid lines). The adsorption energy distributions (AEDs) calculated from the isotherm data confirmed this conclusion since a bimodal energy distribution was obtained C_{60} (Fig. 4). However, because the solubility of C_{70} is low (8 g/L instead of 15 g/L for C_{60}), the adsorption data could not be measured in a sufficiently wide range of concentrations, the low-energy range of the AED was not properly samples, and the calculation did not converge (Fig. 5).

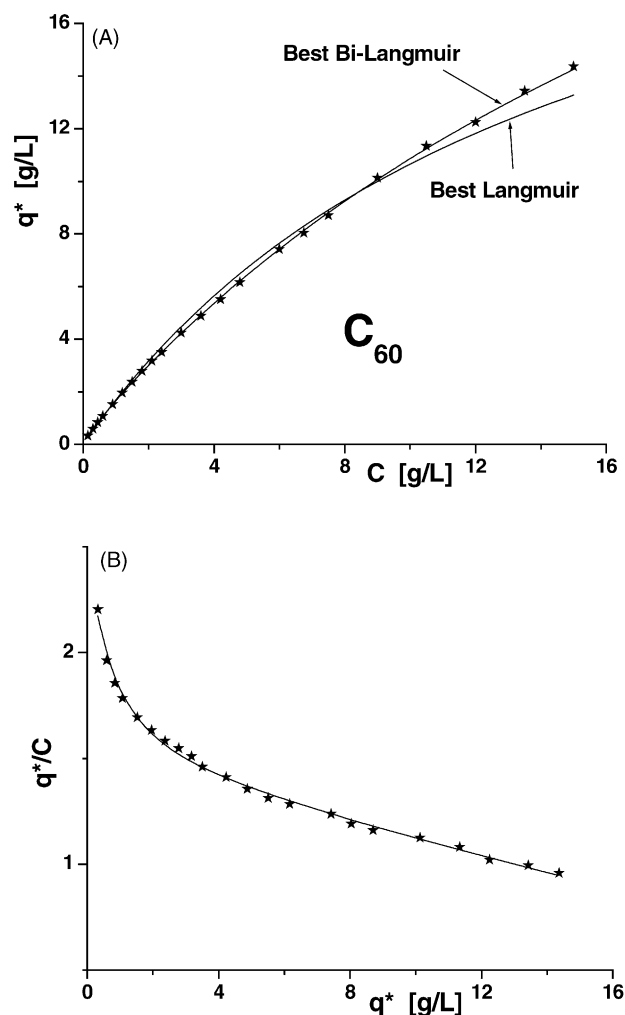
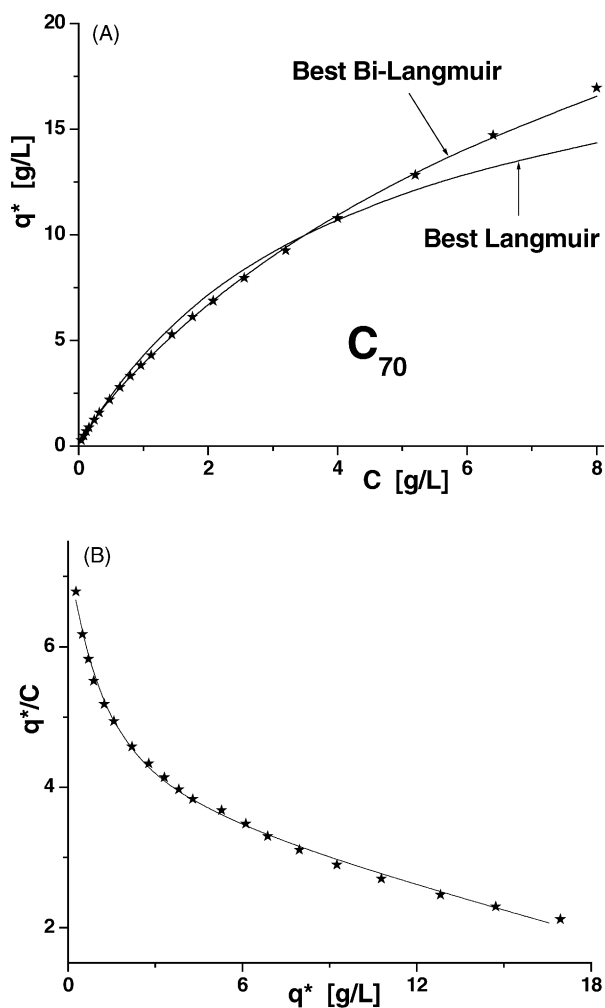


Fig. 2. Adsorption data (star plot) of C_{60} measured by frontal analysis and best isotherm model (solid lines) derived by linear regression. Same experimental condition as in Fig. 1. (A) Isotherm plot. Note the poor agreement with the simple Langmuir model. (B) Scatchard plot. The solid line represents the best bi-Langmuir model. Note the obviously non-linear behavior of the plot, confirming the rejection of the Langmuir model.

The incomplete results suggest, however, that the energy distribution is not unimodal but at least bimodal. The surface of the stationary phase used appears to be heterogeneous, at least regarding the adsorption of fullerenes. The low bonding density of this phase (between 0.2 and 0.4 $\mu\text{mol}/\text{m}^2$) might generate sufficiently large inter-ligand space accessible to the fullerenes. Note that the average diameter of C_{60} is about 7 Å, which makes this molecule small enough either to adsorb on a single TPP ligand or to be adsorbed between two neighboring TPP groups, interacting with both. Accordingly, the isotherm model chosen to account for the adsorption of the buckminsterfullerenes C_{60} and C_{70} was the bi-langmuir model. Neither the heterogeneous Toth nor the heterogeneous Langmuir–Freundlich isotherm models could describe properly the adsorption of the fullerenes because their AEDs are both unimodal.

Fig. 3. As Fig. 2 except for C_{70} .

The best values of the bi-Langmuir isotherm parameters were first derived from the least-square fitting of the FA adsorption data, minimizing the relative error $\sum(1 - q_{i,calc}/q_{i,exp})^2$. The values of the parameters are listed in Table 2. We observe, first and most importantly, that the total saturation capacity of C_{60} is larger than that of C_{70} (54 mmol/L versus 42 mmol/L of adsorbent), a result that is qualitatively consistent with the larger molecular volume of C_{70} . Assuming a density of 2 g/L for the adsorbent, 1 L of

Table 2

Best bi-Langmuir isotherm parameters obtained by FA, AED and the IM, regarding the adsorption of C_{60} and C_{70} on the TPP stationary phase using a toluene–1-naphthalene mixture (60:40, v/v)

	C_{60}			C_{70}		
	FA	IM	AED	FA	IM	AED ^a
$q_{s,1}$ (mmol/L)	53.8	57.4	63.6	41.0	37.8	n.a
b_1 (L/mol)	26.8	25.3	19.7	89.3	95.0	n.a
$q_{s,2}$ (mmol/L)	0.5	0.5	1.5	0.9	0.9	n.a
b_2 (L/mol)	2101	1982	331	4226	4183	n.a

^a Non available data because of no convergence of the AED calculation.

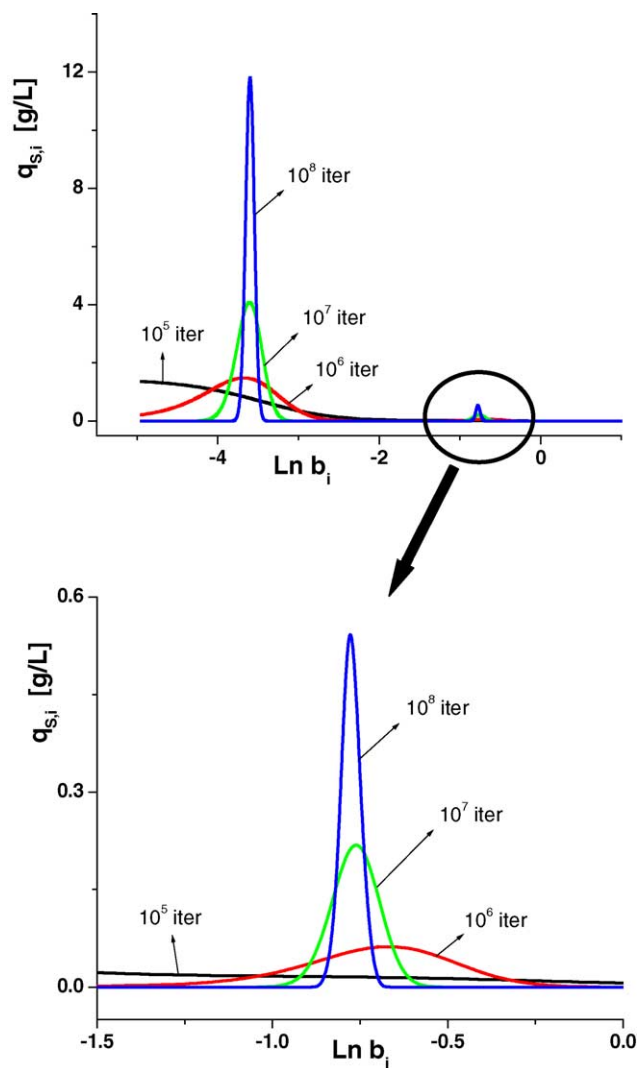


Fig. 4. Adsorption energy distribution of C_{60} on the TPP stationary phase calculated by the expectation-maximization method, directly from the adsorption data shown in Fig. 2. Note the bimodal energy distribution suggesting the existence of two distinct adsorption sites on the TPP stationary phase.

adsorbent develop approximately 400 m² of surface area and contains between 80 and 160 μ mol of TPP ligands. Accordingly, at saturation, there is one adsorbed fullerene molecule for between two and three TPP ligands. This suggests that a significant fraction of the TPP ligands are ineffective, either for steric reasons, because they interfere with neighbors, or for some other reasons.

The good separation obtained between C_{70} and C_{60} ($\alpha = 3.5$) is now easily explained by the adsorption strength or adsorption constant of the former which are much stronger than those of the latter on the low-energy sites (three times larger), compensating the somewhat lower surface accessibility (one fifth lower). Also, the high-energy equilibrium constant b_2 as well as the saturation capacity $q_{s,2}$ of C_{70} are double those of C_{60} , which contribute to the stronger tailing of its band, as shown in Fig. 6. Note in this figure the

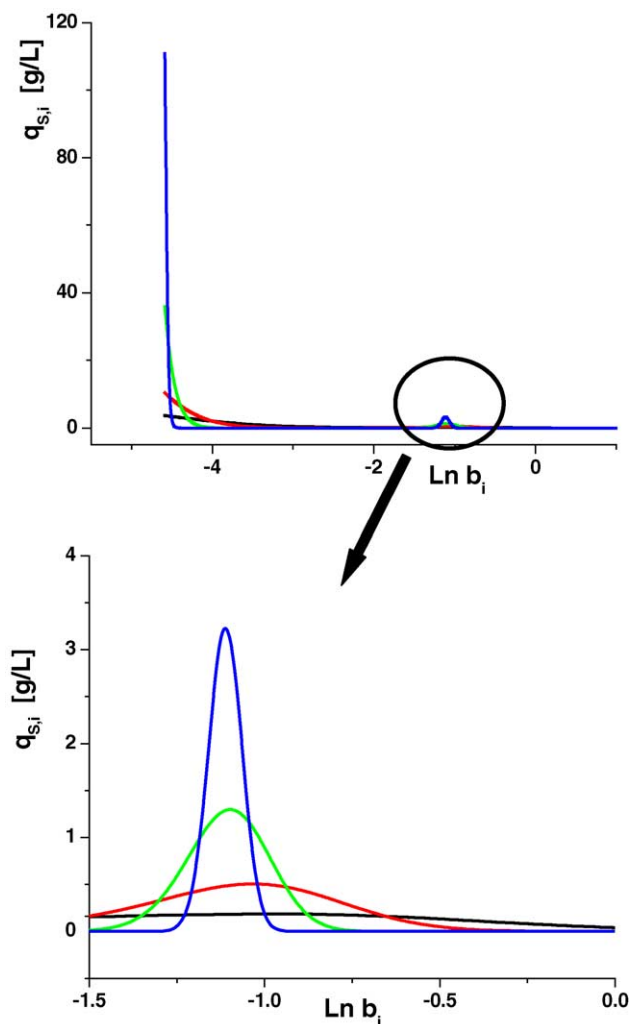


Fig. 5. As Fig. 4 except for C_{70} . Note that the calculation did not converge to a bimodal distribution as for C_{60} . However, the distribution is clearly not unimodal.

very good agreement between the experimental band profiles (symbols) and those calculated using the FA isotherm parameters. Not surprisingly, the IM method of isotherm determination gives nearly the same values of the isotherm parameters than the FA method. Those derived from the AED of C_{60} are slightly different but remain of the same order. All these results comfort the two-sites model of adsorption for the buckminsterfullerenes on the TPP bonded phase.

4.2. Binary competitive isotherms

From the precedent results, derived from the single-component adsorption data of both C_{60} and C_{70} , we can build up four different two-component adsorption isotherm models under different specific assumptions. All the numerical coefficients given below are consistent with the concentrations being expressed in g/L.

- (I) There is no competition for adsorption between the two compounds on either the low- or the high-energy sites.

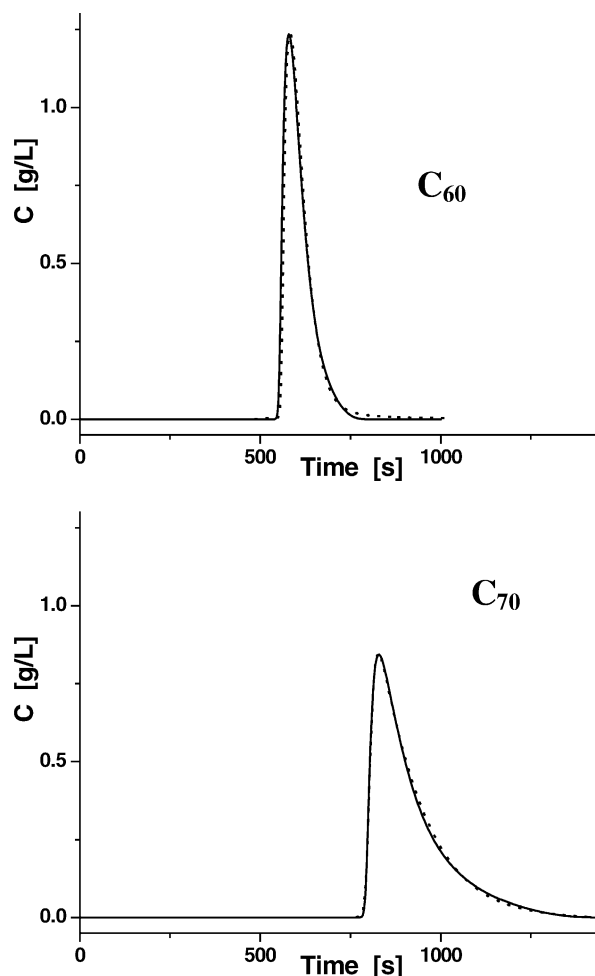


Fig. 6. Experimental (dotted lines) and calculated (from the parameters of the isotherm model fitting best the FA data, solid lines) band profiles of C_{60} and C_{70} on the tetraphenylporphyrin column. Flow rate 0.5 mL/min. Same experimental conditions as in Fig. 1. Note the very good agreement between experimental and calculated profiles as well as the strong tailing of the band of C_{70} , suggesting a stronger adsorption constants.

Accordingly, the “competitive” isotherms are the same as the single-component ones:

$$q_{C_{60}}^* = \frac{1.442[C_{60}]}{1 + 0.037[C_{60}]} + \frac{1.059[C_{60}]}{1 + 2.92[C_{60}]}$$

and

$$q_{C_{70}}^* = \frac{3.661[C_{70}]}{1 + 0.106[C_{70}]} + \frac{3.623[C_{70}]}{1 + 5.03[C_{70}]}$$

- (II) There is competition for adsorption between the two compounds only on the low-energy adsorption sites, 1. Accordingly, the competitive isotherm is written as follows:

$$q_{C_{60}}^* = \frac{1.442[C_{60}]}{1 + 0.037[C_{60}] + 0.106[C_{70}]} + \frac{1.059[C_{60}]}{1 + 2.92[C_{60}]}$$

and

$$q_{C_{70}}^* = \frac{3.661[C_{70}]}{1 + 0.037[C_{60}] + 0.106[C_{70}]} + \frac{3.623[C_{70}]}{1 + 5.03[C_{70}]}$$

(III) There is competition for adsorption between the two compounds only on the high-energy adsorption sites, 2. Accordingly, the competitive isotherm is written as follows:

$$q_{C_{60}}^* = \frac{1.442[C_{60}]}{1 + 0.037[C_{60}]} + \frac{1.059[C_{60}]}{1 + 2.92[C_{60}] + 5.03[C_{70}]}$$

and

$$q_{C_{70}}^* = \frac{3.661[C_{70}]}{1 + 0.106[C_{70}]} + \frac{3.623[C_{70}]}{1 + 2.92[C_{60}] + 5.03[C_{70}]}$$

(IV) There is competition for adsorption between the two compounds on both types of adsorption sites. Accordingly, the competitive isotherm is written as follows:

$$q_{C_{60}}^* = \frac{1.442[C_{60}]}{1 + 0.037[C_{60}] + 0.106[C_{70}]} + \frac{1.059[C_{60}]}{1 + 2.92[C_{60}] + 5.03[C_{70}]} \quad (4)$$

and

$$q_{C_{70}}^* = \frac{3.661[C_{70}]}{1 + 0.037[C_{60}] + 0.106[C_{70}]} + \frac{3.623[C_{70}]}{1 + 2.92[C_{60}] + 5.03[C_{70}]} \quad (5)$$

Three large samples of a mixture of C_{60}/C_{70} containing 3.2 and 1.3 g/L, respectively, were injected and the band profiles recorded. Unfortunately, it was impossible to inject more concentrated solutions (and then maximize the competition effect), because of the maximum detection limit (<2500 mAU). The duration of the injection varied between 0.4 and 3.7 min, in order to obtain two chromatograms with a complete separation and one chromatogram exhibiting band overlap. Since the resolution is complete in the first two chromatograms, it is easy to derive the experimental band profiles of the two components from the experimental record and the calibration curves. Then, they can easily be compared to the calculated band profiles. The last chromatogram is the sum of the absorbance signals due to C_{60} and C_{70} at 598 nm. To compare

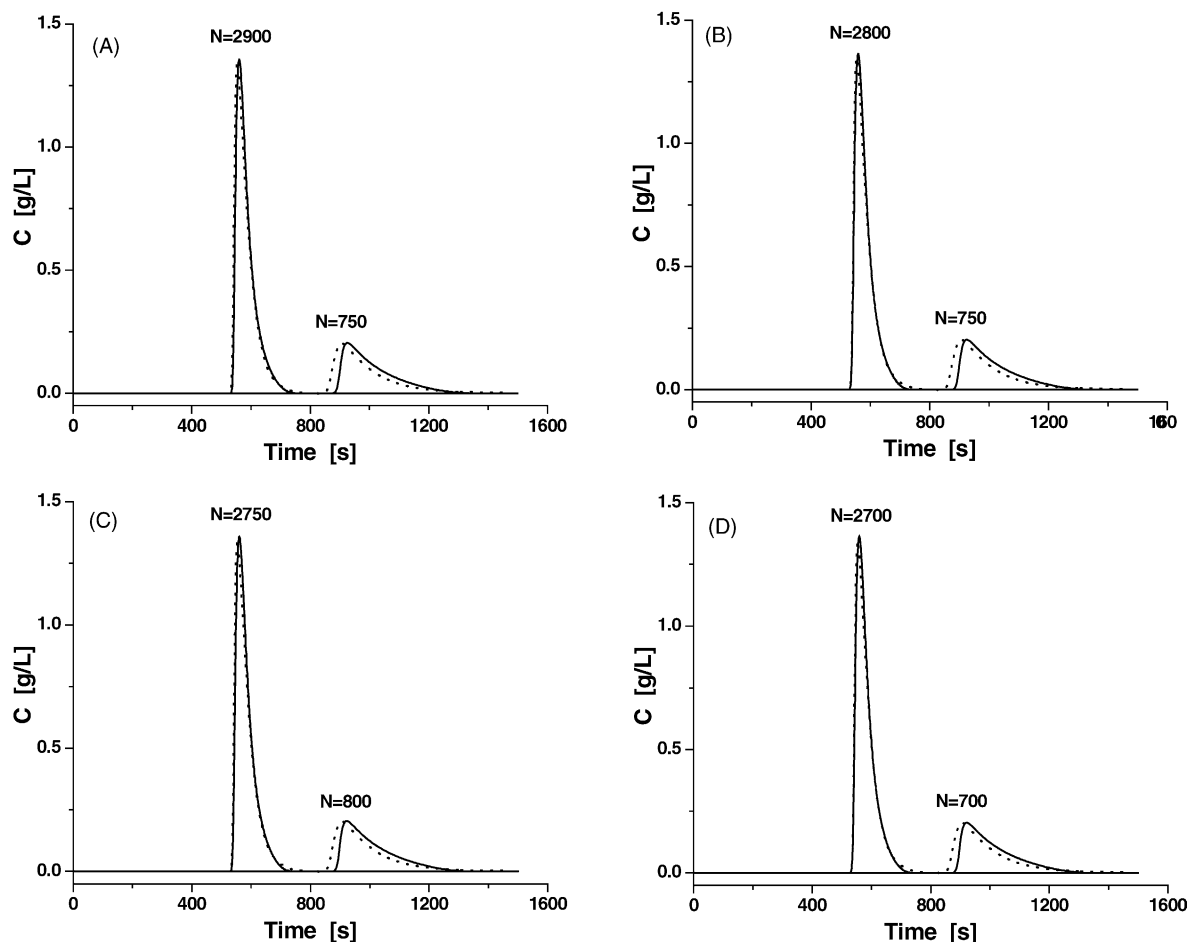


Fig. 7. Comparison between experimental (dotted line, injection 0.2 mL of a mixture of 3.2 and 1.3 g/L of C_{60} and C_{70} , respectively) and calculated overloaded band profiles (solid line). Same experimental conditions as in Fig. 6. Different hypothesis were made regarding the theoretical adsorption model (see equation in the text). (A) No competition on either sites 1 or 2. The single-component isotherm equations were used simply in the equilibrium-dispersive model. (B) Only competition was considered on sites 1. (C) Only competition was considered on sites 2. (D) Competition was considered on types of both sites.

experimental and calculated chromatograms, it was assumed that the absorbance contributions were additive so the two single-component profiles were transformed into absorbance profiles, using the calibration curves, and the sum of these two calculated absorbance profiles was compared to the experimental band profile. All these calculations were performed with the four competitive adsorption models listed earlier. For the two lowest column loadings (0.2 and 0.8 mL injected), different column efficiencies had to be considered for the calculations of the profiles of C_{60} and C_{70} because the mass transfer kinetics of these two compounds seem to be quite different. For the highest column load (injection of 1.7 min), the same column efficiency ($N = 2000$) was chosen because the influence of kinetics on the band profiles becomes small compared to that of thermodynamics.

Figs. 7–9 compare the calculated and the experimental band profiles. Because the column overloading is too small in Fig. 7, it is difficult to find any significant differences between the profiles calculated with the four different models. The non-competitive model and the three competitive models give all the same single-component band profiles for the two compounds. In Fig. 8, the profiles calculated with any of the

three competitive models seem slightly better than the profile obtained with the non-competitive model but the difference is still small and none of the three competitive models appears better than any other. The improvement concerns only the band of the C_{70} fullerene. Finally, in Fig. 9, where the column loading is maximum, it is possible to recognize significant differences between the profiles calculated with the four models. First, the experimental band of C_{60} reaches a concentration plateau (at 3.5 g/L) that is higher than the injection concentration (3.2 g/L). This higher concentration is typical of a competition for adsorption between compounds having convex upward isotherms [7]. This plateau is commonly called the intermediate plateau when the breakthrough curves of mixtures are recorded in FA. The reversed situation of a higher concentration plateau for the more retained compound was observed with convex downward isotherms [14]. This competition explains why, in the calculation of the chromatograms in Figs. 7 and 8, a higher column efficiency has to be considered to compensate the incomplete competitive nature of the isotherm model and to match the height of the experimental band profile when the isotherm model becomes less competitive (compare the results of model IV to those

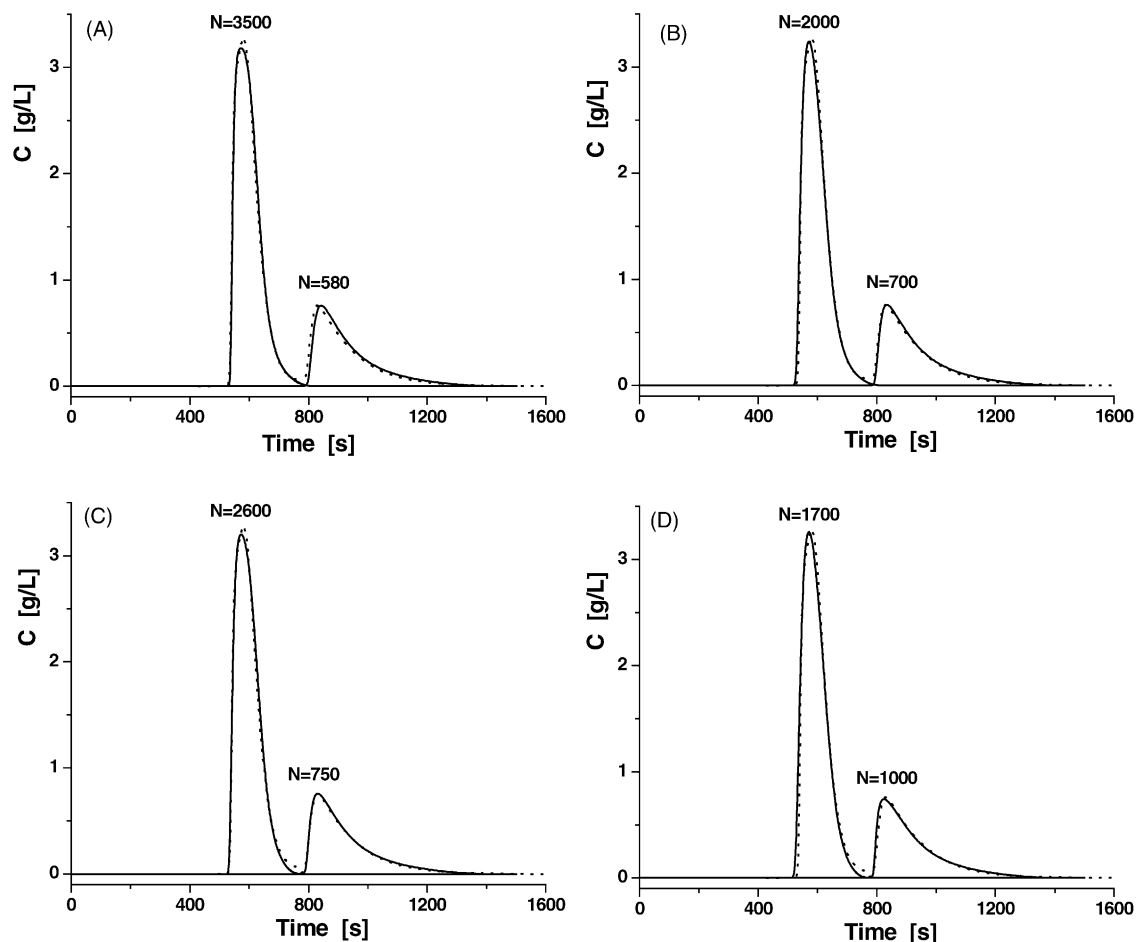


Fig. 8. As Fig. 7, except volume injected: 0.4 mL.

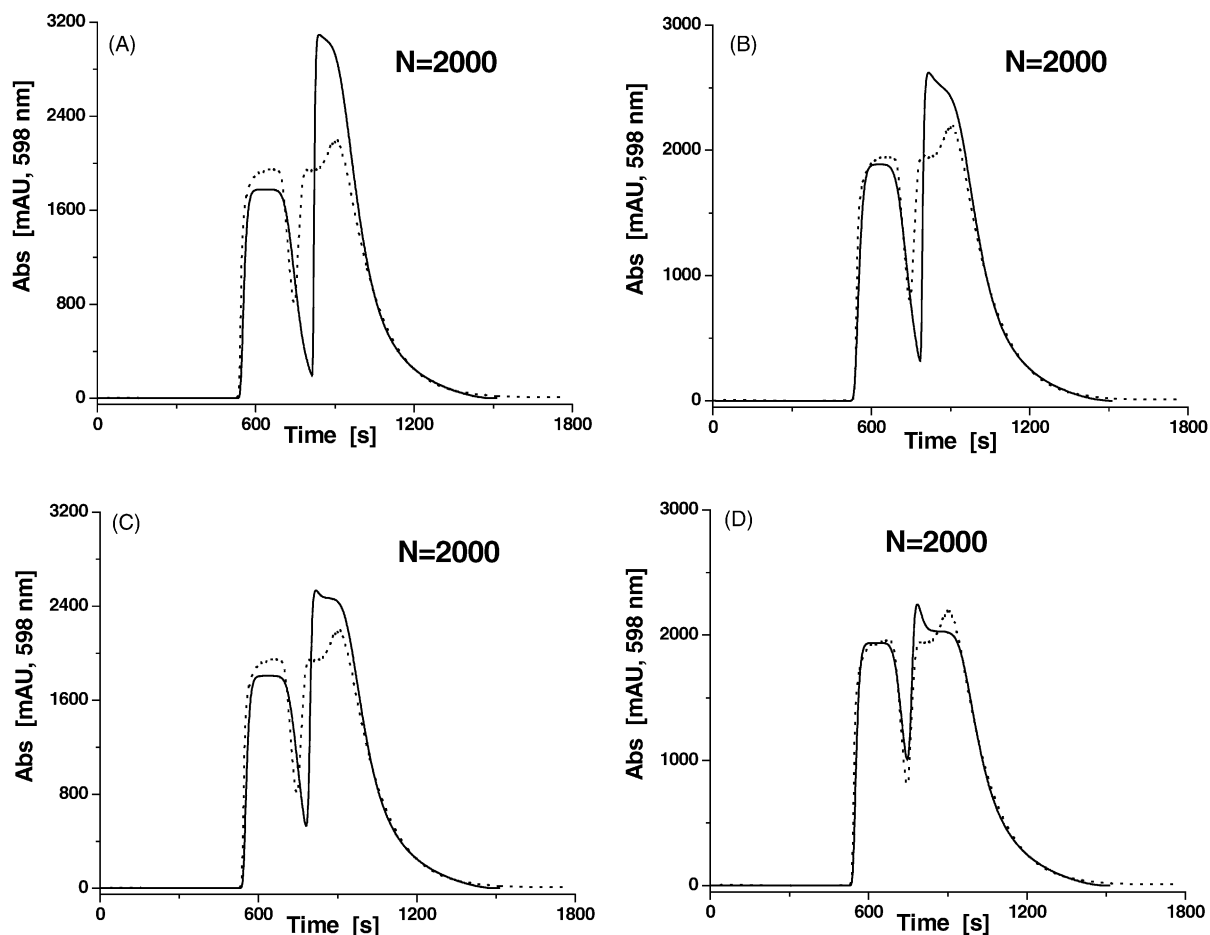


Fig. 9. As Fig. 7, except volume injected: 1.7 mL.

of model I). In Fig. 9, whatever the efficiency considered, the calculated value of the concentration of the intermediate plateau remains unchanged and this informs on the pertinence of the model used to describe the experiments. With the non-competitive model I, the height of the plateau for C_{60} is obviously at 3.2 g/L, the injected concentration. When no competitive adsorption is assumed on sites 2 or 1, the heights of the intermediate plateau are 3.25 and 3.40 g/L, respectively, values closer and closer to the experimental one (3.5 g/L). Finally, if adsorption competition is assumed on both sites 1 and 2, the agreement is excellent regarding the height of the intermediate plateau of the band of C_{60} .

The differences regarding the shape of the band of C_{70} are more pronounced. The agreement is only approximate with the profiles derived from models I, II and III which all predict too high a retention of this band, and, accordingly, too deep a valley between the two bands. This shows that the competition for adsorption must take place on the two sites. In so doing (model IV), the agreement becomes excellent, except for the position of a hump on the intermediate plateau of C_{70} . In summary, the experimental band profiles of mixtures of the two most abundant fullerenes are now well understood. They are accounted for by a competitive adsorption isotherm

based on the competitive bi-Langmuir model of isotherms. This result supports the two-sites adsorption model for the adsorption mechanism of the fullerenes on TPP bonded silica. This model could easily be used to calculate overloaded band profiles and to optimize the production rate of fullerenes.

4.2.1. Effect of the average column pressure on the retention of C_{60} and C_{70}

A significant influence of the pressure, P , on the retention of peptides [15] or proteins [16] has already been observed experimentally. The change in the retention factor of these analytes is fundamentally related to the change in the partial molar volume of the analyte when it is transferred from the liquid to the adsorbed phase. Basic thermodynamic considerations, explained in more details elsewhere [17,18], allow the derivation of a relationship accounting for the variation of the retention factor k with the local pressure in the system:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V}{RT} + \left(\frac{\partial \ln \phi}{\partial P}\right)_T \quad (6)$$

where ΔV is the variation of the partial molar volume, ϕ the column phase ratio and T the temperature.

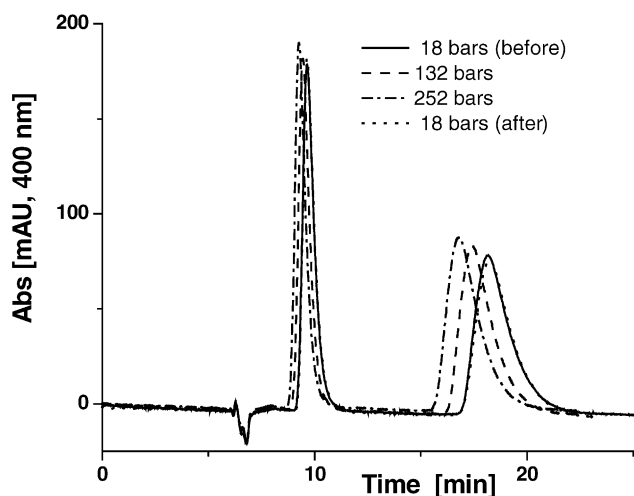


Fig. 10. Effect of the average column pressure on the retention time of C_{60} and C_{70} . Same mobile phase condition as in Fig. 6. Note the decrease of the retention times with increasing pressure.

The second term in the right hand side of Eq. (6) is related to the variation of the hold-up column volume with the pressure. Experiments were carried out under three different values of the average column pressure. The pressure was adjusted by connecting capillary tubes of different lengths to the outlet of the detector. The values were 18 bar (no capillary added), 132 bar (capillary 1) and 252 bar (capillary 1 + capillary 2 in series). Since the bonding density of TPP to the silica support is relatively small (between 0.2 and 0.4 $\mu\text{mol/L}$), no significant variation of the hold-up column volume was expected and none was observed (see the first baseline perturbation in Fig. 10). However, the positions of the peaks of C_{60} and C_{70} shift significantly toward the low retention times when the pressure increases. By contrast to what was observed with peptides [15,16] and with simpler organic compounds [17], the partial molar volume of the two fullerenes is larger in the adsorbed phase (TPP bonded silica) than in the mobile phase (toluene–1-methylnaphthalene, 60:40, v/v). From the slope of the plot of the logarithm of the retention factor k versus the average column pressure P , it is easy to derive values of ΔV of 12.32 and 12.75 mL/mol for C_{60} and C_{70} , respectively. This represents a relatively small volume change by comparison to the value measured with some peptides (bradykinin and kallidin $\Delta V = 35 \text{ mL/mol}$ [15]) or proteins (insulin variants, $\Delta V = 90 \text{ mL/mol}$ [16]). Reported to the molecular scale, the volume of one molecule of fullerene increases by 20.5 \AA^3 during its transfer from the liquid to the solid phase. If the diameter of C_{60} is 7.00 \AA in the mobile phase, its final diameter when adsorbed on the TPP-bonded silica increases by about 0.5% to 7.03 \AA . This effect might be ascribed to the interactions of the fullerene molecule with the phenyl groups of the TPP ligands. However, since the effects are similar for the two compounds, no improvements in the selectivity were measured ($\alpha = 3.50$).

5. Conclusion

The phase system of TPP-bonded silica as the stationary phase and solutions of toluene and 1-methylnaphthalene as the mobile phase affords the extraction/purification of significant amounts of the fullerenes (C_{60} and C_{70}) in preparative chromatography. The classical tools previously developed, the measurement of isotherm data by FA, the calculation of the adsorption energy distributions show that the adsorption mechanism of these compounds is explained by a heterogeneous two-sites surface, modeled by the classical bi-Langmuir isotherm. At column saturation, one molecule of fullerene seems to be in contact with two TPP ligands (60 mmol of C_{60} for 120 mmol of TPP ligands per liter of adsorbent). Because of the low bonding density of TPP (0.3 $\mu\text{mol/L}$), the fullerenes encounter a heterogeneous surface environment. Their molecules may adsorb between two or three TPP ligands on the most numerous low-energy sites (99% of the total surface area) or even on the high-energy sites (1%). The separation of C_{70} and C_{60} is based on the much stronger adsorption constant of C_{70} on the low- and the high-energy sites, despite a more limited access to the surface.

The band profiles recorded upon the injection of fullerenes mixture carried out at different loadings demonstrate that competition for adsorption takes place on both types of sites. A competitive bi-Langmuir isotherm model was successfully used to account for the overloaded band profiles of binary mixtures of C_{60} and C_{70} . This model combined with the simple equilibrium-dispersive model of chromatography provides an accurate tool for the optimization of purification processes of fullerenes. Since the soot obtained by electrical discharge contains numerous fullerene molecules, the generalization of the adsorption model derived to other fullerenes, e.g., C_{84} should be useful to a degree [19]. This could allow the accurate prediction of band profiles of mixtures containing numerous fullerenes based on the competitive multi-component bi-Langmuir adsorption isotherm. However, the higher fullerenes may be too dilute for much competition to take place.

Acknowledgement

This work was supported in part by grant CHE-02-44693 of the National Science Foundation, by Grant DE-FG05-88-ER-13869 of the US Department of Energy, and by the cooperative agreement between the University of Tennessee and the Oak Ridge National Laboratory.

References

- [1] M.P. Gasper, D.W. Armstrong, J. Liq. Chromatogr. 18 (1995) 1047.
- [2] J. Theobald, M. Perrut, J. Weber, E. Millon, J. Muller, Sep. Sci. Technol. 30 (1995) 2783.

- [3] M. Kele, R.N. Compton, G. Guiochon, *J. Chromatogr. A* 786 (1997) 31.
- [4] D. Graham, *J. Phys. Chem.* 57 (1953) 665.
- [5] M. Jaroniec, R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam, 1988.
- [6] A. Felinger, A. Cavazzini, G. Guiochon, *J. Chromatogr. A* 986 (2003) 207.
- [7] G. Guiochon, S. Golshan-Shirazi, A.M. Katti, *Fundamentals of Preparative and Nonlinear Chromatography*, Academic Press, Boston, MA, 1994.
- [8] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [9] M. Suzuki, *Adsorption Engineering*, Elsevier, Amsterdam, 1990.
- [10] P.W. Danckwerts, *Chem. Eng. Sci.* 2 (1953) 1.
- [11] P. Rouchon, P. Valentin, M. Schönauer, C. Vidal-Madjar, G. Guiochon, *J. Phys. Chem.* 88 (1985) 2709.
- [12] P. Rouchon, M. Schonauer, P. Valentin, G. Guiochon, *Sep. Sci. Technol.* 22 (1987) 1793.
- [13] G. Guiochon, S. Golshan-Shirazi, A. Jaulmes, *Anal. Chem.* 60 (1988) 1856.
- [14] F. Gritti, G. Guiochon, *J. Colloid Interface Sci.* 264 (2003) 43.
- [15] D. Zhou, X. Liu, K. Kaczmariski, A. Felinger, G. Guiochon, *Biotechnol. Prog.* 19 (2003) 945.
- [16] X. Liu, D. Zhou, P. Szabelski, G. Guiochon, *Anal. Chem.* 75 (2003) 3999.
- [17] V.L. Guffin, C.E. Evans, *J. Microcolumn Sep.* 3 (1991) 513.
- [18] G. Guiochon, M.J. Sepaniak, *J. Chromatogr.* 606 (1992) 148.
- [19] M. Diack, R.L. Hettich, R.N. Compton, G. Guiochon, *Anal. Chem.* 64 (1992) 2143.