

# Surface Characterization of Intact Fibers by Inverse Gas Chromatography

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## Synopsis

Inverse gas chromatography (IGC) was used to determine adsorption isotherms and isosteric heats of adsorption for several normal alkanes on a number of intact textile fibers and to determine the specific surface areas of these fibers. Surface areas obtained by IGC were in excellent agreement (except for cotton) with those calculated from the geometric dimensions of circular cross-section fibers and with those obtained by the adsorption of krypton. Heats of adsorption were found to be only slightly higher than the corresponding heats of liquefaction of the probes. The effect of fiber surface purity on adsorption behavior as well as computerized data reduction are briefly discussed.

## INTRODUCTION

The surface morphology of fibers strongly affects many of their properties critical for ease of processing and end-use performance. In this context knowledge of fiber surface area and any modification of it is of considerable importance. Adsorption of various gases and vapors has long been used to determine surface area and other surface properties of solids; however, measurements of adsorption of organic adsorbates on polymeric substrates, which generally belong to a class of low surface area and low surface energy materials, are difficult because these adsorbates diffuse slowly into the noncrystalline regions of the polymer and because extremely small amounts of vapor are adsorbed.<sup>1,2</sup>

Inverse gas chromatography (IGC), on the other hand, has successfully been used in the past decade to study various polymer-solvent interactions as well as bulk polymer properties.<sup>3-7</sup> In particular, Gray et al. have used the elution of characteristic point method<sup>8</sup> to characterize the surface of cellulose,<sup>9-12</sup> cellophane,<sup>13</sup> and poly(ethylene terephthalate) (PET) film.<sup>14</sup> Recently, this method has been used to study surface properties of short glass fibers<sup>15</sup> and of wool.<sup>16</sup> An attempt has also been made<sup>17</sup> to characterize changes in the morphology of solvent-crystallized PET fibers by measuring the retention times of a series of *n*-alkanes above the glass transition temperature of PET. It would appear, however, that the preparation technique used in this latter case (the fibers were ground in a Wiley mill) may have seriously changed the morphology of the fiber surface. Similar data have been published for polypropylene and nylon 66 fibers.<sup>18</sup>

The surface morphology and adsorption properties of intact fibers are of particular interest in a number of fields. A simple technique which permits packing a skein of intact fibers into a gas chromatographic column developed by Miller et al. of this laboratory<sup>19</sup> has been used to prepare the columns investigated here. The purpose of the present work was to deter-

TABLE I  
 Characteristics of Commercial Yarns and Experimental Fibers Studied by Inverse Gas Chromatography

Sample	Polymer	Manufacturer	Characteristics
PET feed (Dacron T56)	Poly(ethylene terephthalate)	DuPont	150 den/yarn, 34 fils, twist 10R
PET textured (Dacron T56)	Poly(ethylene terephthalate)	DuPont	150 den/yarn, 34 fils, twist 10R
Nylon 6	Poly( $\epsilon$ -caprolactam)	Allied Corp.	1206 den/yarn, 70 fils, draw ratio 3
Rayon	Regenerated cellulose	Avtex Fibers, Inc.	1650 den/yarn, 720 fils, low tenacity
Carbon fiber (Celiox 10WC)	Preoxidized poly(acrylonitrile)	Celanese Fibers Co.	800 den/yarn, without binders
Aramid (Kevlar 49)	Poly( <i>p</i> -phenylene <i>p</i> -terephthalamide)	DuPont	1420 den/yarn, 1000 fils
Cotton	Cellulose	—	1530 den/yarn, peroxide-bleached
PET D	Poly(ethylene terephthalate)	Allied Fibers & Plastics Co.	80 den/monofilament, draw ratio 4.5 at 100°C

mine adsorption isotherms for a series of normal alkanes on various intact commercial fibers by the elution of characteristic point technique, and from these to determine specific surface areas of the fibers and heats of adsorption of the alkanes at "infinite" dilution. A comparison of the IGC surface areas with data obtained by the classical BET method (adsorption of krypton) and from fiber geometric dimensions is also presented.

## EXPERIMENTAL

### Materials

All solvents used for fiber purification and all solutes were chromatography or reagent grade and were used without further purification.

The characteristics of the various commercial and experimental polymeric multifilament yarns or fibers studied in this work are shown in Table I. Sample PET D was prepared in this laboratory from a single filament of amorphous PET (363 denier, Allied Fibers and Plastics Co.) by low-speed drawing (3.8 m/min) at 100°C to a draw ratio (DR) of 4.5.

### Columns

A 109 cm long, 2.1 mm i.d. stainless steel column packed with a parallel skein of yarns to a packing density of 0.2–0.4 was used throughout this work, though essentially the same results were obtained by using a 55.5 cm long, 2.1 mm i.d. column. The fibers packed into the column were purified by passing Freon 1165(1,1,2-trichloro-1,2,2-trifluoroethane), methanol, and then acetone (except in the case of rayon), for ~20 min each through the column under respirator vacuum. The column was then dried by pulling air through it, and, finally, a stream of dry helium at 105°C was passed through the column in the gas chromatograph until a constant base line was obtained. It was found that this purification procedure rendered a preliminary washing of commercial fibers in an aqueous scouring solution unnecessary. The weight of fibers was determined by weighing the sample after the GC experiments. Characteristics of the columns used are given in Table II.

TABLE II  
Characteristics of Columns<sup>a</sup> Packed with Various Textile Fibers

Sample no.	Fiber	No. of yarns	No. of fils	Sample weight (g)	Polymer density (g/cm <sup>3</sup> )	Packing factor	Pressure drop, $p_i/p_0$
1	PET feed	140	4760	2.3478	1.38	0.451	1.082
2	PET tex. <sup>b</sup>	80	2720	1.5273	1.38	0.288	—
3	Nylon 6	10	700	1.4105	1.15	0.325	1.033
4	Rayon <sup>b</sup>	8	5760	1.4741	1.52	0.257	1.055
5	Carbon <sup>b</sup>	20	—	1.9398	1.75–2.0 <sup>c</sup>	0.30–0.26	1.31
6	Aramid	10	1000	1.7600	1.44	0.324	1.411
7	Cotton <sup>b</sup>	50	—	0.9855	1.48	0.176	1.147

<sup>a</sup> 109 cm long, 2.1 mm i.d. stainless steel column.

<sup>b</sup> Filaments with irregular cross section.

<sup>c</sup> True value unknown.

### Instrumentation

Inverse gas chromatography (IGC) experiments were carried out with a minicomputer-controlled programmable Hewlett-Packard 5880A Gas Chromatograph equipped with a high sensitivity single-filament thermal conductivity detector. Carrier gas (Linde Zero Grade helium) flow rates ( $\sim 30$  cm<sup>3</sup>/min) were measured with a soap bubble flow meter and were corrected for the temperature of the gas in the flow meter, water vapor pressure at flow meter temperature, and pressure drop in the column. The latter was measured by connecting an open-end mercury manometer to the injection port of the gas chromatograph with one end of the column open. Injections of probes as a saturated vapor or liquid were made with 1- $\mu$ L Unimetrics or 10- $\mu$ L Hamilton syringes. The net retention times of injected probes were determined electronically from the peak maxima for the probe at "infinite" dilution (amount of probe  $< \sim 10^{-10}$  mol/g) and an air peak. The columns were heated for 30 min at 80°C after each injection of liquid probe to remove trace amounts of probe absorbed in the bulk polymer.

Krypton adsorption measurements were carried out by Quantachrome Corp., Syosett, NY, using krypton in helium as the adsorbate.

### Calculations

In order to obtain adsorption isotherms from the shape of a single gas chromatographic peak covering a region of higher relative vapor pressures of the adsorbate ( $p/p_0$  up to 0.5–0.6), finite concentration GC techniques were used.<sup>6</sup> As a rule, partition isotherms are nonlinear within this region, causing distortion of the gas chromatographic peak. Langmuir-type isotherms (type I according to Brunauer's classification<sup>20</sup>) give rise to peaks with a self-sharpening front and a diffuse rear boundary (peak A, Fig. 3), whereas anti-Langmuir-type isotherms (type III) characteristic of multilayer adsorption lead to peaks having a diffuse front and self-sharpening rear boundary (peak B, Fig. 3).<sup>6</sup> In both cases, however, each point on the diffuse boundary is related to a point on the isotherm through the retention volume  $V_N$  at this point and the partial pressure of the adsorbate,  $p$ :

$$V_N = w_s RT \left( \frac{\partial q}{\partial p} \right)_T \quad (1)$$

where  $q$  is the number of moles of adsorbate per gram of adsorbent and  $w_s$  is the mass of adsorbent. After integration, one obtains

$$q = \frac{1}{w_s RT} \int_0^p V_N dp \quad (2)$$

which, when plotted against  $p$  for increasing values of  $V_N$ , gives the adsorption isotherm. It should be noted that in eq. (2) all effects of gas phase nonideality and of sorption have been neglected, but in this case the assumptions seemed justified because of the very low partial pressures of adsorbates used.<sup>6</sup>

The specific retention volume  $V_g^0$  ( $\text{cm}^3/\text{g STP}$ ) and the net retention volume  $V_N$  ( $\text{cm}^3$ ) in the "infinite" dilution region were calculated from the following relationships<sup>6</sup>:

$$V_g^0 = \frac{273 V_N}{w_s T} \quad (3)$$

and

$$V_N = t'_R \cdot J_2^3 \cdot F_M \left(1 - \frac{p_w}{p_{at}}\right) \cdot \frac{T}{T_F} \quad (4)$$

where  $t'_R$  is the net retention time of the probe,  $J_2^3$  is a correction factor for gas compressibility,  $F_M$  is the carrier gas flow rate at flow meter temperature  $T_F$ ,  $T$  is the column temperature,  $p_w$  is saturated water vapor pressure at the flow meter temperature, and  $p_{at}$  is the atmospheric pressure.

Assuming that the peak height  $h$  is proportional to the partial pressure of the adsorbate  $p$ , the latter can be calculated for a given detector response by a simple calibration procedure<sup>9</sup>:

$$p = \frac{m \cdot R \cdot T_0}{S_{cal} \cdot M \cdot V_g^0 \cdot w_s} h = K_p \cdot h \quad (5)$$

where  $m$  is the mass of probe injected,  $T_0 = 273.2\text{K}$ ,  $M$  = molecular weight of probe, and  $S_{cal}$  is the area under the calibration peak resulting from injection of  $m$  grams of adsorbate. Similarly, the amount of probe adsorbed can be calculated from the following equation<sup>9</sup>:

$$q = \frac{m_{cal}}{S_{cal} \cdot M \cdot w_s} S_{ads} = K_a \cdot S_{ads} \quad (6)$$

where  $S_{ads}$  is the area on the chart defined by the gas holdup time, the base line, the diffuse front of the peak whose other boundary is self-sharpening, and a given detector response.

In practice, calibration data were obtained by injecting  $5.0 \mu\text{L}$  of a liquid probe at a given column temperature and electronic integration of the area under the resulting peak. The very low but long tail, found for all probes studied, particularly *n*-decane, was probably caused by slow diffusion of the hydrocarbons into the bulk polymers, which can occur when larger amounts of the probe are injected and the corresponding retention times are longer.<sup>21</sup> Therefore, the adsorption isotherms were determined by using smaller amounts of liquid probe ( $0.5\text{--}2 \mu\text{L}$ ) and with the integrator in the slice area mode. In this mode, the built-in computer divides the peak into vertical slices of preprogrammed width ( $\geq 0.01$  min) whose areas are printed out along with their respective retention times, and which are stored in the computer memory. These data are used to calculate  $p$ ,  $q$ ,  $p/p_0$ , and their BET transform,  $p/p_0/[q(1 - p/p_0)]$ , using eqs. (3)–(6) and a program written

in BASIC. The data are plotted by the line printer according to the standard BET equation:

$$\frac{p/p_0}{q(1 - p/p_0)} = \frac{1}{q_m \cdot C} + \frac{C - 1}{q_m \cdot C} \cdot \frac{p}{p_0} \quad (7)$$

where  $q_m$  is the amount of probe adsorbed at monolayer coverage and  $C$  is a constant related to the heat of adsorption. Both the monolayer coverage  $q_m$  and the constant  $C$  were calculated on-line by the least-squares method using the experimental points within the usual region of applicability of the BET theory, i.e., for  $0.07 < p/p_0 < 0.35$ .

The specific surface area of the fiber was calculated using the formula<sup>9</sup>

$$S_{\text{IGC}} = q_m \cdot a_m \cdot N/w_s \quad (8)$$

where  $a_m$  is the area occupied by a probe molecule in the surface layer and  $N$  is Avogadro's number. A value of  $0.52 \text{ nm}^2$  was assumed for  $a_m$  for *n*-decane; it was calculated by assuming that the molecules are spherical and arranged on the adsorbent surface in the same way as on a planar surface placed within the corresponding bulk liquid.<sup>9,10</sup>

Heats of adsorption in the "infinite" dilution region (isosteric heats of adsorption) were calculated from the slope of the plot  $\ln(V_N/T)$  vs.  $1/T$ , using  $0.02\text{--}2 \mu\text{L}$  of hydrocarbon vapor within the temperature range  $35\text{--}60^\circ\text{C}$ , since

$$\left( \frac{\partial \ln p}{\partial (1/T)} \right)_v = \frac{\Delta H_{\text{st}}}{R} \quad (9)$$

where  $\Delta H_{\text{st}}$  is the isosteric heat of adsorption, i.e., the heat developed when 1 mol of adsorbate is adsorbed by an infinite amount of solid without change in the fraction of surface covered by the adsorbate.<sup>6</sup>

## RESULTS AND DISCUSSION

### Purification of Fibers

Adsorption processes are very sensitive to the chemical composition, homogeneity, and, thus, the purity of the surface under consideration. It is therefore necessary to remove all processing aids, such as spin finishes, binders, etc., from the fiber surface. The choice of organic solvents for finish removal is, however, critical, since some solvents interact with the fiber-forming polymers giving rise to changes in the fiber surface and bulk polymer morphology via solvent-induced crystallization, partial extraction of oligomers or low molecular weight fractions, or crack formation.<sup>22,23</sup>

Preliminary experiments showed that retention times of normal alkanes in the "infinite" dilution region and the shapes of chromatographic peaks in the finite concentration region depend markedly on the kind of solvent purification procedure to which the fiber was subjected. In general, elution

peaks obtained for insufficiently purified samples had markedly more diffuse front boundaries, leading to BET plots which were curved upward with decreasing values of  $p/p_0$  and had negative slopes ( $C < 1$ ). Surface areas obtained from straight-line sections of such plots were unreasonably high. A typical example is shown in Figure 1(A). Extensive experimentation has shown that reproducible values of specific surface area and, to a lesser degree, of the  $C$  constant can be obtained when the purification procedures outlined in the experimental section and below are followed.

The fibers are usually washed with Freon 1165 (1,1,2-trichloro-1,2,2-trifluoroethane), then with methanol, and acetone, for 20 min each at ambient temperature. However, in the case of undrawn (unoriented) polyester and some other fibers (e.g., polycarbonate, rayon, and some other cellulose derivatives), acetone cannot be used since it causes solvent-induced crystallization, swelling, or dissolution of the fiber material. On the other hand, fully drawn (oriented) PET and nylon 6 fibers can be washed with dimethylformamide (DMF) followed by methanol without meaningful change in specific surface area of the fiber; graphite and aramid fibers require strongly polar solvents such as DMF followed by methanol or acetone to remove the resin finishes with which these fibers are coated.<sup>24</sup> Higher values of  $C$  have been obtained for fibers washed with stronger interacting solvents, which

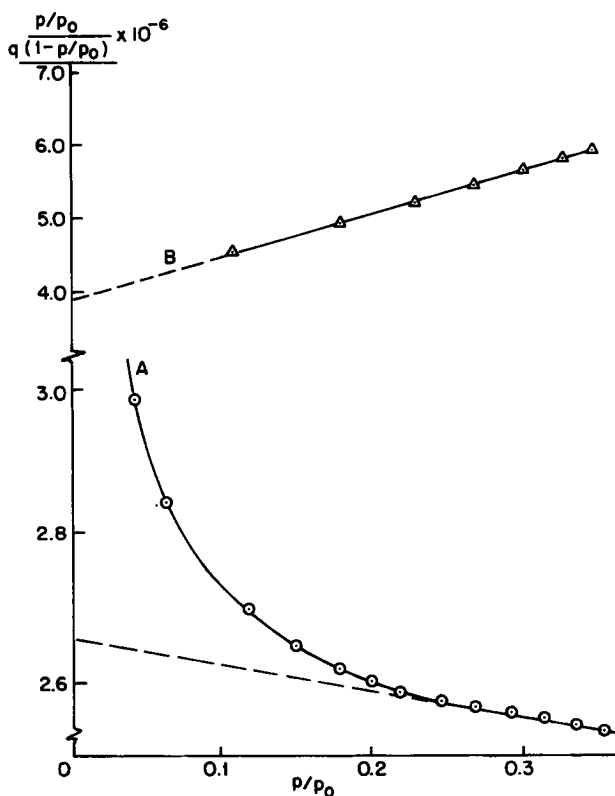


Fig. 1. The effect of fiber sample purity on BET plots (*n*-decane at 40°C on sample 12, Table III): (A) unwashed sample,  $C = 0.88$ ,  $S_{IGC} = 0.168$  m<sup>2</sup>/g, (B) sample washed with acetone,  $C = 2.54$ ,  $S_{IGC} = 0.0327$  m<sup>2</sup>/g,  $S_{geom} = 0.0324$  m<sup>2</sup>/g.

may indicate either a purer surface or increased interactions with solvent pockets occluded in the surface layer of the fiber.

### Peak Shapes and Adsorption Isotherms

If an adsorption isotherm is to be derived from the shape of a single gas chromatographic peak, several conditions have to be met.<sup>6</sup> (1) The isotherm should not have a point of inflection; otherwise, at least two peaks are needed to construct the isotherm: a low pressure peak having a self-sharpening front and diffuse rear boundary, and a high pressure peak (i.e., covering a higher range of  $p/p_0$  values) having a diffuse front and a self-sharpening rear boundary. (2) The so-called "coincidence phenomenon" has to occur, namely, all diffuse boundaries of the peaks obtained by injecting varying amounts of the probe have to be superimposable. The often reported method using multiple injections and the resulting peak maxima to define an isotherm<sup>10,12</sup> has recently been criticized by Conder and Young<sup>6</sup> on theoretical grounds as representing a case of nonideality too complex to deal with at the present stage of development of GC theory.

In the case of the polymeric fibers studied in this work, the adsorption isotherms for *n*-decane at 40°C (Fig. 2) were either of the anti-Langmuir type within almost the whole range of  $p/p_0$  values studied with only a very weak knee (PET, nylon 6, carbon, rayon, cotton washed with solvents of intermediate polarity), or they had a sigmoidal shape and a pronounced knee (aramid, cotton washed with DMF). The diffuse front boundaries of the peaks of varying height were superimposable for a majority of samples (except for those exhibiting the sigmoidal shape) down to peak heights corresponding to  $p/p_0 \sim 0.03$ – $0.05$  for *n*-decane at 40°C. For the aramid fiber, the diffuse rear boundaries were superimposable up to effective peak heights corresponding to  $p/p_0 \sim 0.07$  (peak A, Fig. 3), where their self-sharpening

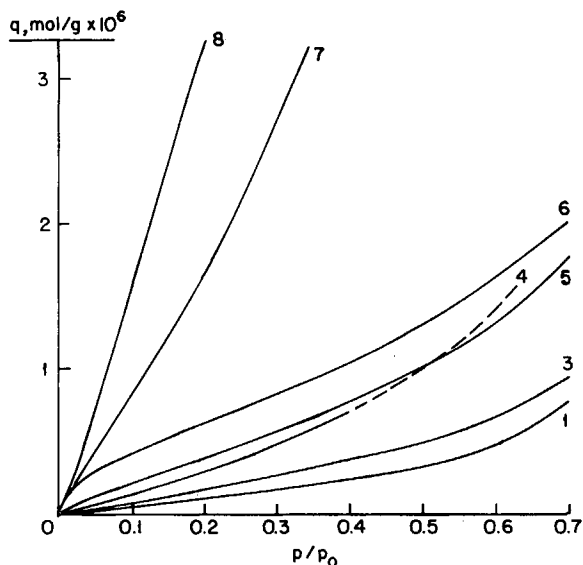


Fig. 2. Adsorption isotherms for *n*-decane on various commercial fibers (sample numbers given in Table III) at 40°C determined by inverse gas chromatography.



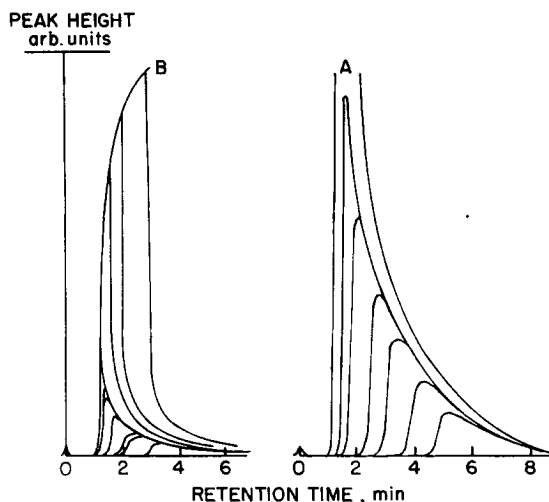


Fig. 3. Gas chromatographic peak shapes for *n*-decane at 40°C (0.01–2.0  $\mu$ L) on Kevlar 49 fibers (sample 6, Table II).

front boundary became almost superimposable with the lower part of the diffuse front boundary of a high pressure peak (peak B, Fig. 3). The peaks of *n*-decane on DMF-washed cotton cellulose had reproducible, superimposable front boundaries if the peak height exceeded the value corresponding to  $p/p_0 \sim 0.05$ –0.1. For lower peak heights, however, neither the self-sharpening front nor the diffuse rear boundaries were superimposable, as reported by Tremaine and Gray.<sup>10</sup> This suggests some degree of nonideal behavior of the columns at lower vapor pressures of *n*-decane.

It has been found that for GC columns filled with high tenacity polypropylene fibers or polyfluorocarbon fibers (Teflon) the gas chromatographic peaks resulting from injections of *n*-decane ( $\sim 5 \mu$ L) were extremely diffuse, thus indicating strong retention of the hydrocarbon in the bulk polymer. This finding is in agreement with earlier reports that polytetrafluoroethylene is relatively easily penetrated by lower hydrocarbons<sup>25</sup> and that surface adsorption measurements by IGC on polyethylene were unsuccessful when using *n*-decane at 23°C.<sup>4</sup> Therefore, further studies of these two fibers were discontinued, although an attempt to use much lower temperatures and more volatile probes might be successful.

It should be noted that the adsorption data (Fig. 2 and Table III) are given in mol/g rather than in mol/m<sup>2</sup>, since the surface area of fibers was not known *a priori*. However, if the values of adsorption in mol/g for different fibers at a given relative vapor pressure are divided by the corresponding surface area values obtained by the IGC or krypton adsorption method, the amounts of *n*-decane adsorbed at  $p/p_0 = 0.3$  and 40°C in mol/m<sup>2</sup>  $\times 10^6$  obtained for the various samples are very similar: PET 2.1; nylon 6 2.3; carbon 2.8; aramid 3.5; rayon 1.9; cotton 2.1. The increased adsorption on aramid and carbon fibers reflects their stronger interaction with the adsorbate at low surface coverages. Both these adsorbents contain aromatic structures which can give rise to increased interactions through dispersive London forces.<sup>11</sup>

TABLE III  
Comparison of Specific Surface Areas of Intact Fibers Determined by Various Methods

Sample no.	Fiber <sup>a</sup>	C ±0.2	$q_m$ ( $\mu\text{mol}/\text{g}$ )	$S_{\text{IGC}}^b$ ( $\text{m}^2/\text{g}$ )	$S_{\text{geom}}^c$ ( $\text{m}^2/\text{g}$ )	$S_{\text{BET}}^d$ ( $\text{m}^2/\text{g}$ )
1	PET feed yarn	2.1	0.444	0.139	0.135	0.13
2	PET text.	2.5	0.476	0.146	— <sup>e</sup>	0.14
3	Nylon 6	2.4	0.242	0.076	0.078	0.070
4	Rayon	1.6	0.836	0.262	— <sup>e</sup>	0.27
5	Carbon	3.8	0.657	0.206	— <sup>e</sup>	0.21
6	Aramid	11(±2)	0.746	0.234	0.234	0.23
7	Cotton	2.0	4.16	1.30	— <sup>e</sup>	0.66
8	Cotton (DMF)	3.4	5.75	1.80	— <sup>e</sup>	—
9	PET feed (DMF)	3.0	0.460	0.144	0.135	—
10	Nylon 6 (DMF)	2.8	0.249	0.077	0.078	—
11	Rayon (acetone)	3.3	1.07	0.336	— <sup>e</sup>	—
12	PET D	2.5	0.106	0.0332	0.0324	0.028

<sup>a</sup> Samples 1–7 and 12 are the same as in Table I.

<sup>b</sup> Determined using *n*-decane at 40.0°C ( $a_m = 0.52 \text{ nm}^2$ ).

<sup>c</sup> Calculated using Eq. (10).

<sup>d</sup> Determined by adsorption of krypton ( $a_m = 0.205 \text{ nm}^2$ ).

<sup>e</sup> Not calculated because of surface irregularities.

### Specific Surface Areas

Calculation of monolayer capacity  $q_m$  and specific surface area  $S$  of an adsorbent by the widely used BET approach involves making several assumptions,<sup>20</sup> which, although often criticized,<sup>26</sup> generally lead to satisfactory or good agreement with the expected or otherwise calculated values of  $S$ . For several of the fiber samples studied in this work, such comparisons could be made with their geometric surface areas, since the monofilaments had smooth surfaces with very few irregularities and regular, circular cross sections, as confirmed by light and scanning electron microscopy (Fig. 4). The geometric specific surface area  $S_g$  of such a sample can be calculated from the simple formula:

$$S_g = \sqrt{4\pi L/md} \quad (10)$$

where  $L$  is the total length of the filaments,  $m$  is the weight of the sample, and  $d$  is polymer density. The calculated values are included in Table III, except for carbon fiber, rayon, and cotton, which all have either irregular cross sections or unknown numbers of filaments per yarn. Since some of the samples contained filaments of low denier (aramid, rayon, carbon), their calculated or expected specific surface areas  $S_g$  fall within a region (0.2–0.3  $\text{m}^2/\text{g}$ ) where the krypton adsorption method gives quite accurate and reproducible results. Thus, the direct comparison of specific surface areas obtained by three independent methods, i.e., geometric, krypton adsorption, and IGC, was possible for fibers made of a variety of polymers.

BET plots for the fibers calculated from IGC data are shown in Figure 5. In order to calculate specific surface areas from the adsorption isotherms by the BET method, one has to know the saturated vapor pressure  $p_0$  of

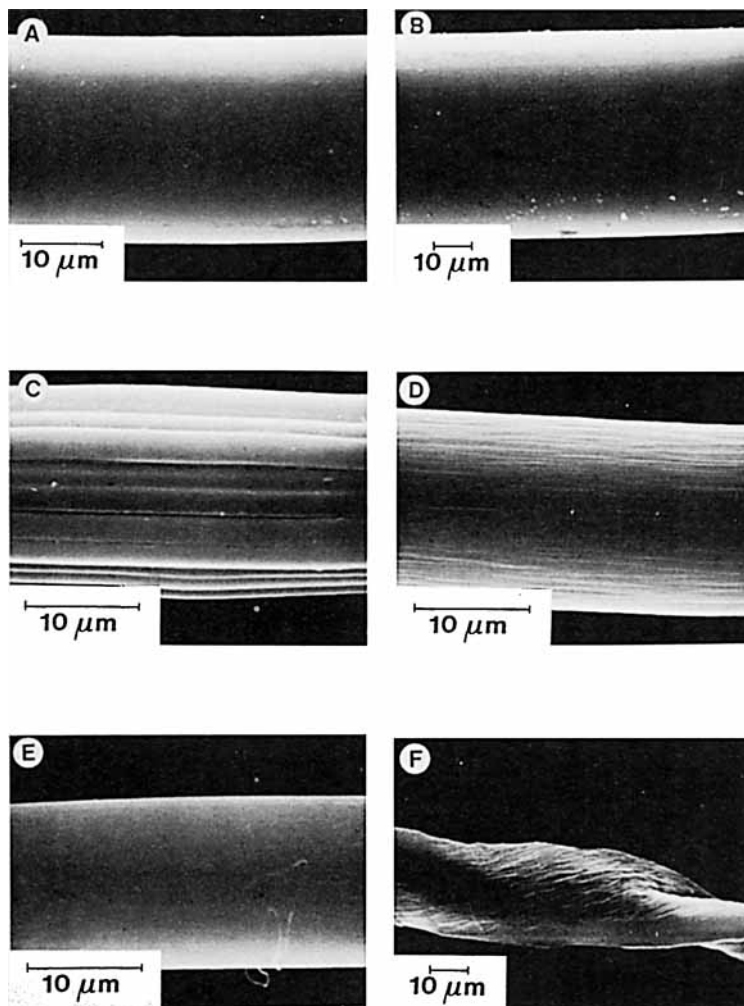


Fig. 4. Scanning electron microphotographs of commercial fibers studied (samples 1, 3-7, Table III): (A) PET; (B) nylon 6; (C) rayon; (D) carbon; (E) aramid; (F) cotton.

the adsorbate at the column temperature and the area  $a_m$  occupied by each molecule in the adsorption layer. The literature sources cite, however, a whole range of values for saturated vapor pressures of *n*-decane at a given temperature. To avoid confusion and to obtain comparable data, it was decided to carry out all experiments under similar conditions, i.e., by using *n*-decane at 40°C and the value of  $p_0 = 3.86$  mm Hg for its saturated vapor pressure, taken from Jordan.<sup>27</sup>

Similar difficulties were encountered when choosing the value of the molecular area of the *n*-decane molecule, since the values cited by different authors vary from 0.52 nm<sup>2</sup>/molecule calculated from the hard sphere model to more than 0.70 nm<sup>2</sup>/molecule.<sup>4,9-11,15</sup> The choice was made after establishing which of these values gave the best fit to the specific surface area determined by krypton adsorption and geometrical calculations. Since the krypton adsorption method gave results almost identical to those calculated

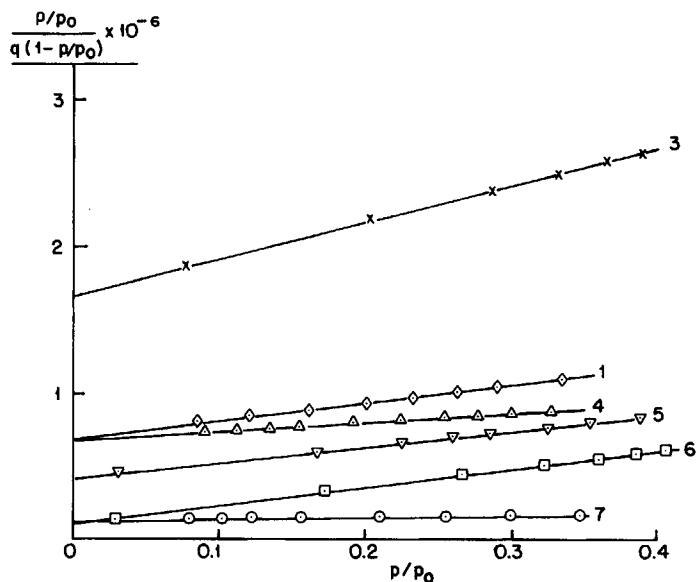


Fig. 5. BET plots for adsorption of *n*-decane at 40°C on commercial fibers (samples 1, 3-7, Table III) determined by inverse gas chromatography.

from eq. (10) for circular cross section filaments, these values were used as an independent check to calculate  $\alpha_m$ . On all the fibers except cotton, this value was found to be  $\sim 0.52 \text{ nm}^2$ , which is equal to that derived from the hard sphere model and used previously in some papers by Gray et al.<sup>9,10</sup> This result is remarkable and rather surprising, since it indicates that the molecular area of *n*-decane is almost independent of the chemical structure of the adsorbing fiber, which seems to be contrary to previous suggestions.<sup>11,28</sup> However, all the samples for which this calculation was made can be characterized as low surface energy and low surface area adsorbents; thus this conclusion is limited to similar cases.

The various parameters derived from the BET plots for the adsorption of *n*-decane on the group of fiber samples (Fig. 5), i.e., the BET constant  $C$ , the monolayer coverage  $q_m$ , and the specific surface area  $S_{\text{IGC}}$ , are listed in Table III. The reproducibility was high; for seven determinations of  $S_{\text{IGC}}$  on the same packing of the PET feed yarn (sample 1), the standard deviation was  $0.003 \text{ m}^2/\text{g}$  from a mean of  $0.1385$ . When *n*-nonane was used as a probe ( $p_0$  at 40°C = 11.1 mm Hg,  $\alpha_m = 0.492 \text{ nm}^2$ ),<sup>11,27</sup> similar specific surface areas were obtained; e.g., for C fiber,  $C = 2.9$ ,  $q_m = 0.697 \mu\text{mol}/\text{g}$ ,  $S_{\text{IGC}} = 0.207 \text{ m}^2/\text{g}$ . The  $S_{\text{IGC}}$  values are compared in Table III with specific surface areas determined by krypton adsorption and those calculated from geometric dimensions, and excellent agreement is found between the three methods except for cotton.

The large discrepancy between surface area of cotton cellulose obtained by the krypton adsorption method ( $0.66 \text{ m}^2/\text{g}$ ) and the IGC method ( $1.30 \text{ m}^2/\text{g}$ ) cannot be explained at this point. IGC experiments with cotton were repeated several times using newly prepared columns and different probes (*n*-octane, *n*-nonane and *n*-decane) at different temperatures, but similar results were always obtained. It may be noted, however, that the IGC value

shown in Table III is closer to that reported by Gray et al.<sup>10,11</sup> for paper cellulose (0.9–1.9 m<sup>2</sup>/g) than to the value obtained by a single krypton adsorption experiment.

It is also noteworthy that the IGC method gave reproducible results in the case of sample 12, PET D, Table III, a very low surface area, high denier PET sample for which the krypton adsorption method ( $S_{\text{BET}}$ ) gave too low values. This sample was obtained by slow drawing of a 363 denier amorphous PET monofilament at 100°C at DR = 4.5 to give an oriented, smooth 80 denier monofilament with a geometric surface area  $S_g = 0.0324$  m<sup>2</sup>/g. This value seems to be near the lower limit of the modern krypton adsorption method, since the  $S_{\text{BET}}$  result (0.028 m<sup>2</sup>/g) is ~16% lower than that obtained from geometric calculations, and the points on the corresponding BET plot are markedly scattered. On the other hand, Table IV shows that the IGC method gave surface areas for this sample very close to the calculated one within the temperature range from 30°C to 50°C. It appears that 60°C is too close to the  $T_g$  of PET (69°C), so that the slow bulk diffusion of *n*-decane begins to have an effect on the calculated specific surface area.

### Heats of Adsorption

Heats of adsorption (isosteric or at a given surface coverage) are often used to characterize adsorption properties of polymer surfaces and polymer-organic adsorbate interactions.<sup>4,14</sup> In the BET theory, the heat of adsorption is related to the constant  $C$  by the following expression<sup>9</sup>:

$$E_1 - H_L \propto RT \ln C \quad (11)$$

where  $E_1$  is the heat of adsorption of the first layer of the adsorbate and  $H_L$  is the heat of liquefaction of the adsorbate. However, because of the approximate nature of this expression as well as the sensitivity of the constant  $C$  to experimental parameters, particularly when its value is close to 2, it is of little use in the determination of the heat of adsorption.<sup>10</sup> Therefore, a more direct approach was used involving the temperature dependence of the net retention volume  $V_N$  of a given adsorbate at "infinite" dilution [eq. (9)]. This was achieved by plotting  $\ln(V_N/T)$  as a function of  $1/T$ .<sup>6</sup> for all the fiber samples studied with the exception of DMF-washed cotton. It was extremely difficult to locate the peak maximum for cotton because at "infinite" dilution the peaks were so broad that they became almost indistinguishable from the baseline. This again seems to suggest the

TABLE IV  
Specific Surface Area of Drawn PET Fiber (80 denier) by IGC at Various Temperatures<sup>a</sup>

Column temp. (°C)	$C$	$q_m \times 10^6$ (mol/g)	$S_{\text{IGC}}$ (m <sup>2</sup> /g)
60	1.5	0.135	0.0422
50	1.9	0.107	0.0335
40	2.5	0.105	0.0327
30	2.4	0.110	0.0343

<sup>a</sup>  $S_{\text{geom}} = 0.0324$  m<sup>2</sup>/g;  $S_{\text{BET}} = 0.028$  m<sup>2</sup>/g. Probe *n*-decane,  $a_m = 0.52$  nm<sup>2</sup>.

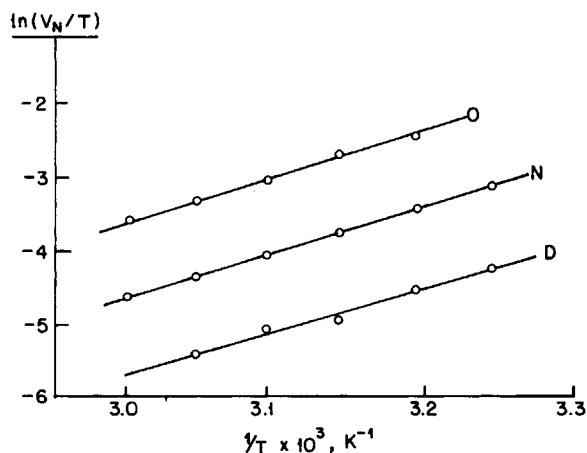


Fig. 6. Relationship between  $\ln(V_N/T)$  and reciprocal temperature for *n*-octane (O), *n*-nonane (N), and *n*-decane (D) on PET fiber (Dacron T56, sample 1, Table III) at "infinite" dilution.

existence of specific adsorption sites or of some other stronger retention mechanism.

The Arrhenius plot for Dacron T56 is shown in Figure 6 as a typical example for these relationships, and the calculated values of the isosteric heats of adsorption are shown in Table V. The plots were linear even at temperatures close to the glass transition temperature of some of the polymers (69°C for PET, 40–52°C for nylon 6),<sup>29</sup> probably because the diffusion of the adsorbates into the bulk polymers was very slow. In general, the heats of adsorption increase in the order *n*-octane < *n*-nonane < *n*-decane, which is in agreement with literature data.<sup>4,12,14</sup> In most cases the values were found to be only slightly higher than the heats of liquefaction (by ~4–6 kJ/mol), which indicates that very weak interactions exist between these polymeric fibers and aliphatic hydrocarbons. Somewhat higher differences were found for the carbon and aramid fibers (~8–14 kJ/mol), suggesting that the aromatic structures present in these polymers might be responsible for increased interactions.

## CONCLUSIONS

Inverse gas chromatography was successfully applied to determine the specific surface area of a number of intact textile fibers as well as the heats

TABLE V  
Isosteric Heat of Adsorption of *n*-Alkanes on Fibers as Determined by IGC

Fiber	$-\Delta H_{st} [\text{kJ/mol} (\pm 1 \text{ kJ/mol})]$		
	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane
PET feed	48.2	51.1	53.7
Nylon 6	45.9	51.9	57.1
Rayon	48.1	52.5	55.1
Carbon	48.4	55.0	60.7
Aramid	51.8	54.6	58.4
Cotton	44.4	50.5	55.9

of adsorption of several normal alkanes on these fibers. The results obtained are in very good agreement with the values obtained on the basis of fiber geometry and with those obtained by the krypton adsorption technique. It has been found that the fiber surface purification procedure is one of the critical steps in the successful application of this technique. The method is relatively uncomplicated, and the data reduction can be easily carried out by a moderate-size minicomputer when a gas chromatograph having peak-slicing capability is used. The IGC method could not be used, however, to study polypropylene and polyfluorocarbon fibers because of significant diffusion of the probe molecules into the bulk polymer.

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