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Characterization of polyarylamide fibers by inverse gas chromatography

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Abstract

Two types of commercial polyaramide fibers have been characterized by inverse gas chromatography. Using the fibers as stationary phases, adsorption isotherms for nonane, decane and undecane were obtained. Specific surface areas and isosteric heats of adsorption were also obtained by this method. Experimental results have been discussed as a function of hydrocarbon–fiber interaction and fiber crystallinity.

Keywords: Adsorption isotherms; Polyarylamide fibers; Specific surface area; Heat of adsorption; Nonane; Decane; Undecane

1. Introduction

NOMEX is a polyarylamide fiber [poly(*m*-phenylene-diamine-isophthal)amide, MPD-I] developed by DuPont, and commercialized since 1960. It is widely used for the manufacture of protective wearing apparel (firemen, industrial plant operators), and industrial filters, due to its high thermal and chemical resistance.

The characteristics of the solid surface and the degree of crystallinity are key properties of the fiber that condition their applications. Crystallinity is determined in practice by a dyeing method, which is rather complex and time-consuming, and only gives an indirect measurement of this property. In order to overcome those difficulties two techniques may be used to characterize the MPD-I fibers: inverse gas chromatography (IGC) and differential scanning calorimetry (DSC).

IGC has frequently been applied for surface characterization of industrial, textile and natural fibers [1], as well as to provide useful information on the transition temperatures, crystallinity and on the thermodynamics of fiber–solute interactions [2,3].

Characteristics of solid surfaces are generally determined by adsorption of gases and vapors. The isotherms allow one to obtain information about substrate surface chemistry, adsorbent specific surface area, porosity as well as thermodynamics and kinetics of adsorption [4,5].

In this work IGC was used to determine the adsorption isotherms of several hydrocarbons (nonane, decane and undecane) on MPD-I. In addition, heats of adsorption and specific surface areas of the fibers were measured by this method. The chromatographic data obtained should provide information on the degree of interaction between the

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adsorbate molecules and the fiber and hereby provide some insight into the nature of the surface of the fibers.

2. Theory

2.1. Basics of IGC and adsorption

IGC is a gas chromatographic technique in which the adsorbent is placed in the chromatographic column as stationary phase and known solutes are injected into the carrier gas stream. Retention time and shape of the chromatogram are a function of the interactions between the solute and stationary phase, and can be used to determine several physico–chemical properties of the adsorbate–adsorbent system, such as adsorption properties, heat of adsorption, interaction parameters, and diffusion coefficients [4]. In addition, IGC can be used to determine various properties of the stationary phase, such as transition temperatures, polymer–polymer interaction parameters, solubility parameters, crystallinity, surface tension, and specific surface area.

Numerous methods have been developed to obtain adsorption isotherms from chromatographic peaks. In this work two methods have been used: the elution by characteristic point (ECP) method, and the peak maxima (PM) method.

In the ECP method the isotherm is determined from a single chromatogram. The chromatogram is usually an asymmetric peak with a sharp front and an extended tail, or vice versa, which shows deviations from ideality and the non-linearity of the isotherm. The method gives good results if the front or rear profiles of the peaks (diffuse part) for various sample sizes overlap, which is known as *coincidence phenomenon* [6,7]. Furthermore, the sample size must be small enough to build-up (cover) a monolayer on the surface. This can be noticed if changes in the concentration are followed by changes in the localization of the diffuse side.

The method was proposed by Gluckauf [8–10] and its accuracy has been studied by Miyabe et al. [11]. It relates chromatographic and adsorption parameters by Eq. (1) [6]:

$$a = \frac{m_a S_{ads}}{m S_{peak}} \quad p = \frac{m_a hRT}{F S_{peak}} \tag{1}$$

where a is the adsorption coefficient in μmol/g, m_a is the amount of injected adsorbate in μmol, m is the adsorbent mass in the column in g, S_{ads} is the area bounded by the height between the outflow of the non-adsorbing gas and the diffuse side of the chromatogram in mV min, S_{peak} is the adsorbate peak area in mV min, p is the partial pressure in Pa, h is the chromatogram height in mV, R is the ideal gas constant in J/(K mol), T is the temperature in K, and F is the volumetric flow-rate of carrier gas in the column in ml/min.

The PM is the simplest method to determine the adsorption isotherm when peaks are symmetrical and Gaussian, and it is also useful for peaks showing slight tailing [6,12]. In this case, the tailing of the peak can be replaced by a line connecting several points. Each one of these points corresponds to the maximum height of the peak obtained when several samples sizes are injected. The adsorption surface area, S_{ads}, is determined up to the corrected tailing line of the chromatogram.

In any case, the aforementioned methods are strictly valid only for ideal chromatographic conditions. However, real peaks show peak broadening due to thermodynamic, diffusion and kinetic effects. There are a number of graphical methods of correcting peaks for diffusion. This correction is particularly important when retention times of the solute are short. The Bechtold [13] graphical method assumes that the diffusion of the front profile of the peak is equal to the diffusion of the rear profile. Thus, the non-diffusional profile of the peak can be used as a correction of the broadened profile.

2.2. Isosteric heat of adsorption

Isosteric heat of adsorption, for a given surface coverage, can be determined from adsorption isotherms at different temperatures, by least-squares plots of ln p vs. $1/T$ according to Eq. (2). The slope of this plot is $\Delta H_a/R$:

$$\ln p = -\frac{\Delta H_a}{RT} + C \tag{2}$$

where p is the adsorbate partial pressure (Pa); R is

the gas constant (8.31 J/K mol-g); T is the absolute temperature (K), $-\Delta H_a$ is the heat of adsorption (J/mol-g), and C is constant.

2.3. Specific surface area

The Brunauer, Emmett and Teller (BET) equation for adsorption data given by Eq. (3):

$$\frac{p}{a(p_o - p)} = \frac{1}{a_m c} + \frac{(c-1)p}{a_m c p_o} \quad (3)$$

may be used to determine specific surface areas from retention data. In Eq. (3) a is the amount of adsorbate adsorbed, a_m is the amount of adsorbate required to form a monolayer, c is the BET constant, and p_o is the vapor pressure of the solute at the temperature of operation. A least-squares fitting of the plot $p/a(p_o - p)$ vs. p/p_o enables the estimation of c and a_m. The specific surface area S, is related to the monolayer saturation capacity, a_m, by Eq. (4):

$$S = a_m NA \quad (4)$$

where N is Avogadro's constant, and A is the cross-sectional area of the adsorbate (solute).

3. Experimental

3.1. Chromatographic columns

Two types of polyaramides fibers have been used in the experiments: a non-crystallized fiber (DTF 1.9 T-455), and a crystallized fiber (DTF 1.7 T-451), both supplied by DuPont Ibérica. Fibers are characterized industrially by the *decitex* parameter, defined as the mass in grams, per 10 000 m of filament. Linear densities of the fibers used in this work, as given by the manufacturer, were 2.1 (fiber A), and 1.9 (fiber B).

Fiber columns were prepared by pulling intact fiber bundles through 1/4 in. Supelco Premiun grade 304 stainless steel tubing with passivated inner walls, and an inner diameter of 5.3 mm (1 in. = 2.54 cm). The excess fiber material at both column ends was cut. With this procedure tightly packed IGC columns are produced that contain up to 42 000 individual fiber threads. As the fibers are not chopped, no additional surface is created during column preparation. Table 1 shows the column characteristics.

Table 1
Characteristics of the GC columns used

	Non-crystallized fiber	Crystallized fiber
Fiber denomination	Fiber A	Fiber B
Column length (cm)	112.5	75.9
Polymer mass (g)	10.0010	9.5925
Packing degree (%)	29.2	41.5

3.2. Chemicals

The solvents nonane, decane and undecane purchased from Sigma–Aldrich, were used without further purification.

3.3. Equipment

A commercial gas chromatograph (Shimadzu GC-17) with a flame ionization detection (FID) system was used to determine the adsorption chromatograms. A personal computer was connected to the gas chromatograph to control, acquire and process the chromatographic data. For the data acquisition Shimadzu Class-VP software was used. Each chromatogram used for calculations was repeated several times.

3.4. Procedure

Before each series of experiments, the columns were preconditioned at 170 °C for 24 h in a slow helium stream, in order to remove any remaining solvent from the manufacturing process. Helium was used as carrier gas, and the chromatograph was equipped with an advanced flow controller, that allowed the measurement of the column inlet pressure. It was corrected for the pressure drop of the fittings, which was obtained from measurements using an empty column. Gas flow-rate was corrected by the James–Martin compressibility factor. The outlet pressure was the atmospheric pressure and was measured by a barometer. The detector and injector were maintained at 150 °C.

Column dead time was determined in each experi-

ment by injecting 2.5 ml of methane, using a Hamilton gas syringe.

4. Results and discussion

4.1. Adsorption isotherms

Adsorption isotherms of the three hydrocarbons studied (C_9–C_{11}), were obtained in the temperature range of 40–80 °C. The chromatographic elution peaks are asymmetric displaying an almost sharp front and a diffuse rear profile, as shown in Fig. 1 for *n*-decane, at 50 °C with fiber A and different hydrocarbon sample sizes.

The specific retention volume vs. sample size for the same system is plotted in Fig. 2. The plot shows the usual behavior of decreasing specific retention volume for increasing sample size. At small values of the sample size, kinetic factors are important and partial penetration of the solute molecules into the bulk polymer occurs [3,15]. At moderate values, the specific retention volume is independent of the sample size and at high values, a slight increase in the retention volume, due to multi-layer adsorption [15], can be observed. Adsorption isotherms for the *n*-decane/fiber A system at 50 °C have been obtained in the intermediate region of independent specific retention volume, using the ECP method, neglecting the 10% lower part of the elution peaks, and correcting them by the Bechtold method, and by the PM method. The ECP method is suitable if the front or rear peaks for various sample sizes overlap [6] as happens in this case. Results, shown in Fig. 3, indicate that both methods give similar results, in the range of sample size tested. Adsorption isotherms for *n*-nonane, *n*-decane, and *n*-undecane on fiber A at several temperatures are shown in Figs. 4, 5 and 6, respectively.

The adsorption of *n*-decane in fiber B at 50 °C was

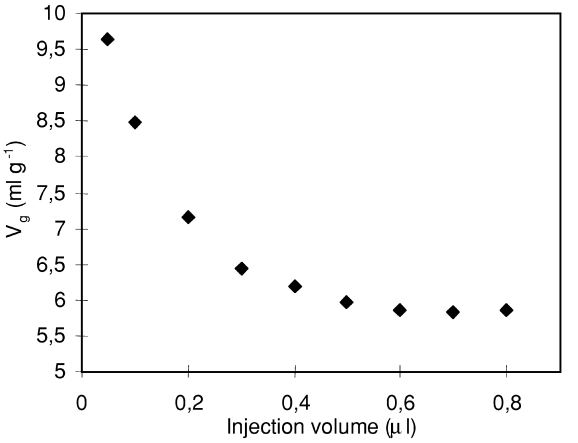


Fig. 2. Specific retention volume vs. injection volume for *n*-decane on fiber A at 50 °C.

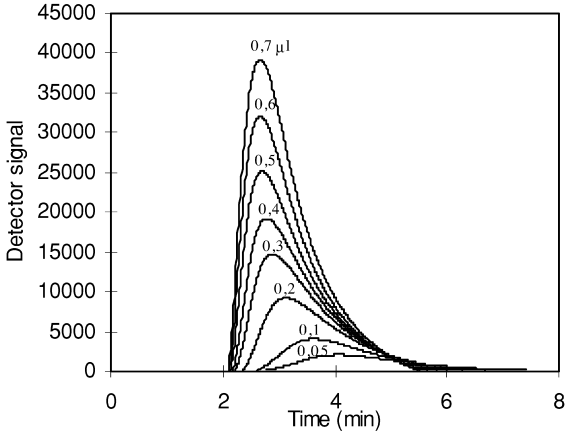


Fig. 1. Chromatographic elution peaks for *n*-decane on fiber A at 50°C, with different injection volumes.

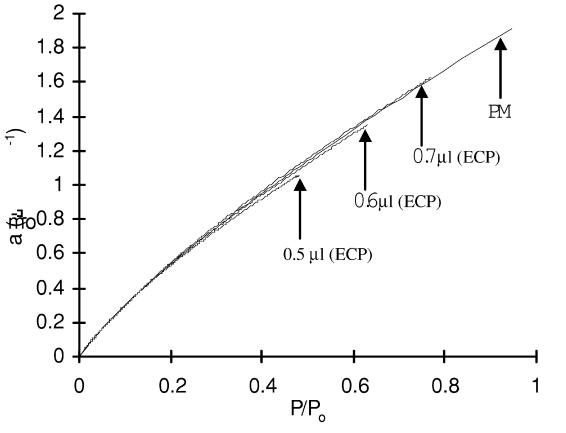


Fig. 3. Adsorption isotherms for *n*-decane on fiber A at 50 °C, obtained by ECP and PM methods.

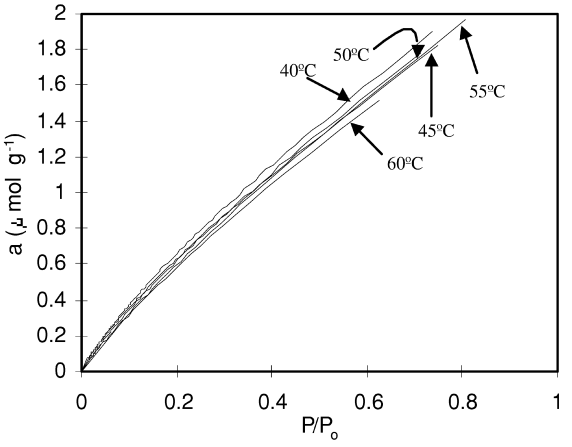


Fig. 4. Adsorption isotherms for *n*-nonane on fiber A at various temperatures, obtained by the PM method.

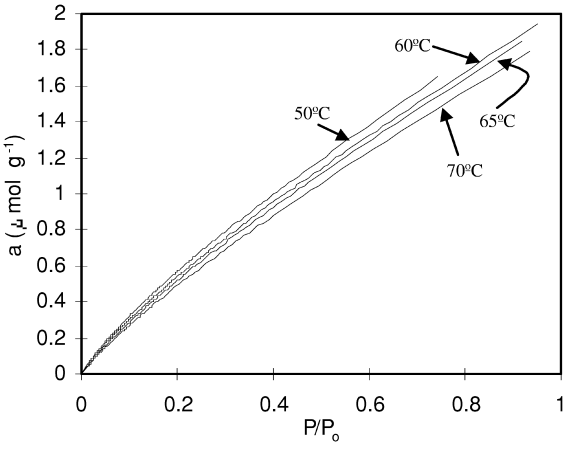


Fig. 6. Adsorption isotherms for *n*-undecane on fiber A at various temperatures, obtained by the PM method.

also studied. For this system, chromatographic peaks were found to be more symmetrical, and the specific retention volumes were almost independent of the sample size. Therefore, the adsorption isotherms determined by the ECP and PM methods overlap as are shown in Fig. 7.

There is not a clear relationship between the adsorbate molecular mass and amount adsorbed. The maximum adsorption corresponded to *n*-nonane. Comparison of results for *n*-decane at 50 °C indicates that the amount adsorbed is higher for the non-crystallized fiber A.

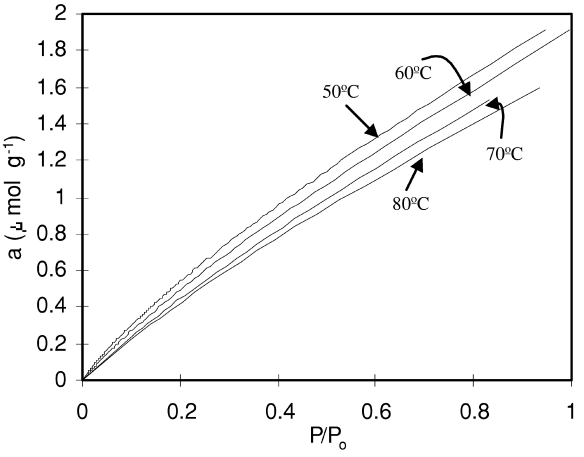


Fig. 5. Adsorption isotherms for *n*-decane on fiber A at various temperatures, obtained by the PM method.

4.2. Heat of adsorption

Isosteric heats of adsorption at different surface coverages have been calculated for *n*-nonane, *n*-decane and *n*-undecane on fiber A from the adsorption isotherms at several temperatures, and using Eq. (2). Results are shown in Fig. 8. The relatively high initial isosteric adsorption heat, which decreases with increasing surface coverage, is characteristic for heterogeneous surfaces. Adsorption heats increase with increasing adsorbate molecular mass; values for high coverage are of the same magnitude, but higher, than the corresponding heats of liquefaction (−46.55, −51.42 and −56.58 kJ/mol for *n*-nonane, *n*-decane and *n*-undecane, respectively [14]).

4.3. Specific surface area

BET parameters, a_m and c, were obtained from the adsorption isotherms of *n*-decane on fibers A and B at 50 °C by a least-squares fitting of the data shown Fig. 9, and their values are given in Table 2. The good linearity of the BET isotherms suggests that the concentration of high-energy sites on the fibers surface is low. This low-energy character of the adsorbent–adsorbate interaction is also reflected by

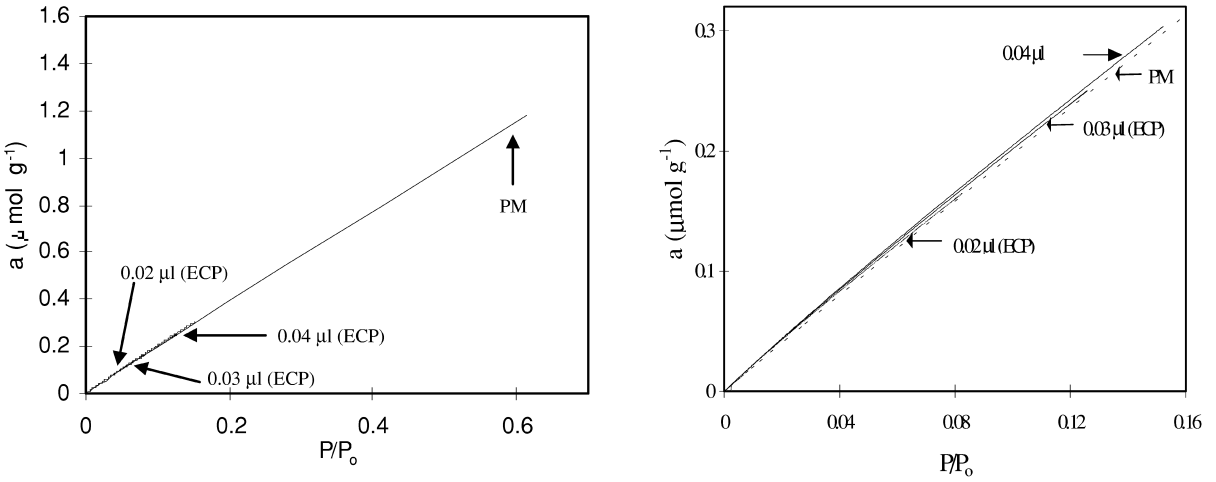


Fig. 7. Adsorption isotherms for *n*-decane on fiber B at 50 °C, obtained by ECP and PM methods.

the low *c* values, although they are slightly higher for the non-crystallized fiber A.

In order to calculate the specific surface area from a_m data, the cross-sectional area of the adsorbed molecules *A* must be known, but it is difficult to estimate as the nature of packing of the adsorbed molecules in a completed monolayer is not known. Assuming a cross-sectional area of 0.68 nm^2 for the *n*-decane molecule, as reported previously [15], the specific surface area S_1 can be calculated and results are given in Table 2.

Some authors propose, as an alternative method, to calculate *A* from the liquid density of the adsorbate [5]. Assuming that the arrangement of the adsorbed molecules on the solid surface is the same as it would be on a plane surface if placed within the bulk of the liquid, without disturbing the pre-existing arrangement, the molecular cross-sectional area can be obtained from:

$$A = f\left(\frac{M}{\rho N}\right)^{2/3} \cdot 10^{14} \quad (5)$$

where *f* is a packing factor, ρ is the liquid density, and *M* the molecular mass. The packing factor depends on the number of nearest neighbor molecules, so that for 12 nearest neighbors in the bulk

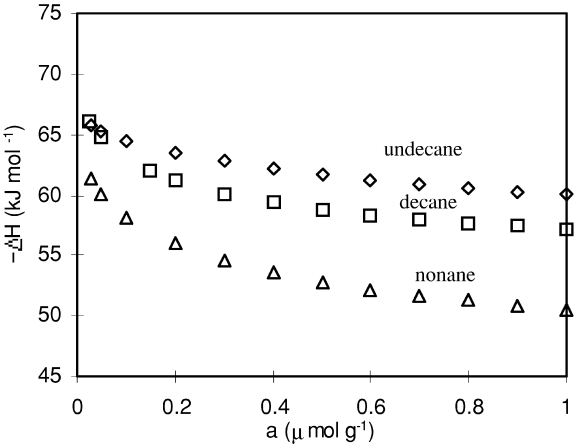


Fig. 8. Heats of adsorption vs. surface coverage for *n*-nonane, *n*-decane and *n*-undecane on fiber A.

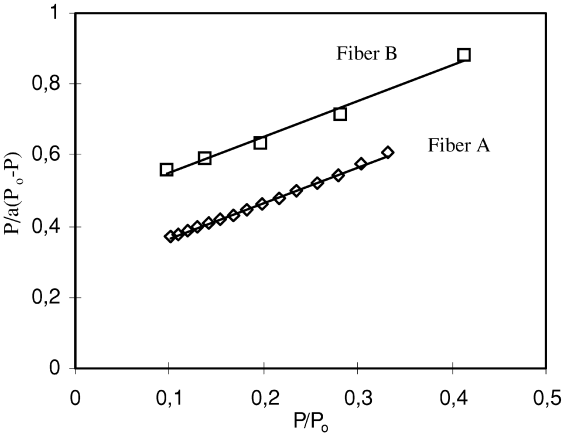


Fig. 9. BET transformed from IGC data for fibers A and B.

Table 2
Superficial parameters obtained for the two samples of MPD-I fibers

Fiber	$a_m \cdot 10^6$ (mol g^{-1})	c	S_1 (m^2/g)	S_2 (m^2/g)	S_{BET} (m^2/g)
A	0.79	4.71	0.32	0.25	0.37
B	0.70	3.04	0.29	0.23	0.31

liquid and six on the plane (a common arrangement) the value of f is 1.091, and a cross-sectional area of 0.53 nm^2 for *n*-decane at 50 °C is obtained. The values of the specific surface area, S_2, calculated by this method, are shown in Table 2.

The specific surface of the fibers has been also measured by the conventional nitrogen adsorption–desorption technique at −196 °C, using a Micromeritics ASAP 2000 apparatus, considering a value of 0.164 nm^2 for the cross-sectional area of the nitrogen molecule. Adsorption isotherms are shown in Fig. 10. Both fibers show type II isotherm shapes, characteristic for heterogeneous surfaces, according to the BDDT classification. Specific surface areas calculated by this method are 0.37 and 0.31 m^2/g for fibers A and B, respectively.

The specific surface area of the fibers can be also calculated from their decitex linear density and the diameter, measured from scanning electron microscopy (SEM) photographs (Fig. 11), assuming that fibers are cylinders with no roughness. Values calculated by this method, that might be called *geometrical specific surface area*, are 0.22 and 0.17 m^2/g for fibers A and B, respectively.

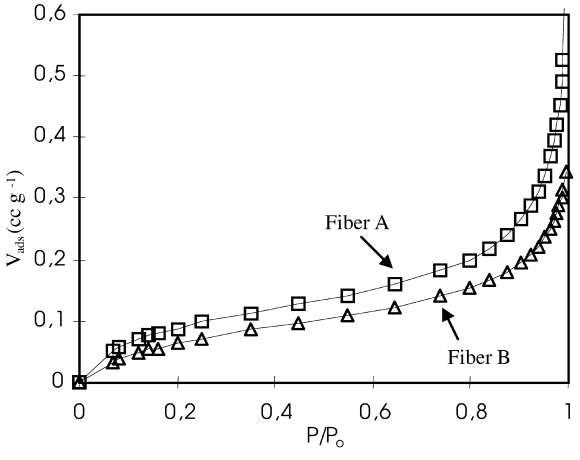
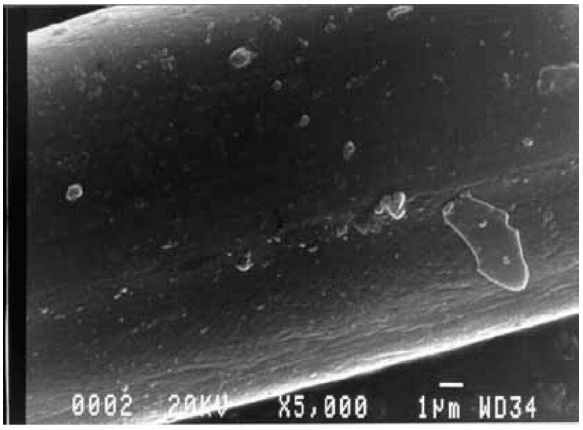
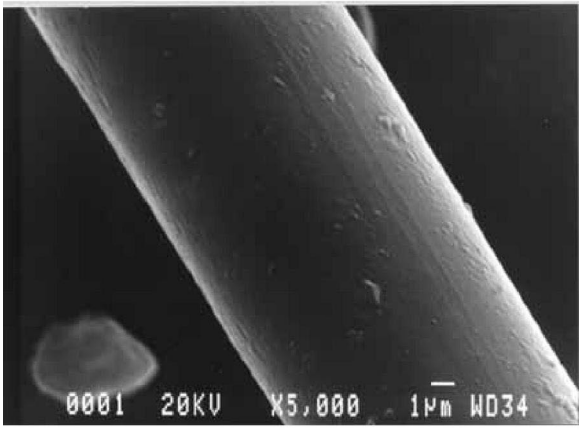


Fig. 10. Nitrogen adsorption isotherms for fibers A and B.

The fibers specific surface area, determined by the different methods described, is always higher for fiber A than for fiber B, although the observed diameter for fiber B is smaller. This can be explained by the lower density of the non-crystallized sample, and by the presence of more irregularities in the fiber



(a) Fiber A



(b) Fiber B

Fig. 11. SEM photographs: (a) fiber A, (b) fiber B.

surface. A comparison between values obtained by IGC indicates that S_1 is always higher than S_2. The S_1 values obtained by IGC are slightly lower than the nitrogen adsorption values, with geometrical values being the lowest. It must be realized that geometrical specific surface area, does not take into account the surface irregularities, and is affected by the inaccuracies in the determination of both the decitex value, and the measurement of the fiber diameter, made from a limited number of SEM observations.

5. Conclusions

Two types of commercial fibers with different crystallinity were characterized by inverse gas chromatography, using C_9–C_{11} hydrocarbons as adsorbates. Specific surface areas obtained by this method are higher than the geometrical specific surface area (estimated from SEM measurements), which can be explained by the surface imperfections presented in the fibers. BET specific surface areas were higher than both IGC and geometrical specific surface areas, but it must be taken into account that the classic BET technique is not very precise for low specific surface areas. The non-crystalline fiber showed consistently higher specific surface area. Isosteric heats of adsorption were calculated for the non-crystallized fiber at different surface coverages. The heat of adsorption increases for increasing adsorbate molecular mass. For high surface coverage the values are close to the heats of liquefaction.

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