Measurement of External Specific Surface Area of Fibers by Solution Adsorption

INTRODUCTION

A method for measuring the external specific surface area of fibers has been developed by Giles et al.[1-3] The fibers are immersed in dilute solutions of p-nitrophenol, preferably in n-hexane or n-heptane, for short periods in which adsorption is confined mainly to the external surface of the fibers. Spectrophotometric analysis of the solutions enables the adsorption isotherms to be determined for each equilibration time. The point on the curves corresponding to completion of the first monolayer is then located and the apparent external specific surface area calculated. The values increase with the time of equilibration because the solution slowly diffuses into the fibers; however, the surface area can be obtained by extrapolating the apparent values to zero time.

In this note, we show that diffusion of p-nitrophenol into fibers occurs only when the fibers are hydrated and that the extrapolated surface area can be determined from a single isotherm provided the fibers are dried before being equilibrated with the p-nitrophenol solution.

EXPERIMENTAL

Wool fibers (22 μm diam.) and nylon monofilament (43 μm diam.) were Soxhlet extracted with methylene chloride and then stored in air at ambient relative humidity for at least 24 hr prior to use. Solutions for adsorption runs were prepared from spectroscopy-grade n-hexane and p-nitrophenol that had been recrystallized from water.

The samples (0.3–0.5 g) of wool or nylon were immersed in aliquots of solution, usually 10 ml, contained in U-tubes as shown in Figure 1. One arm of each tube was connected to a manifold, which in turn was connected to an air displacement pump operating at 20 cycles per min. This apparatus enabled the p-nitrophenol solution to be forced back and forth between the fibers so that rapid equilibration occurred; also, it allowed a low solution/fiber ratio to be used when necessary.

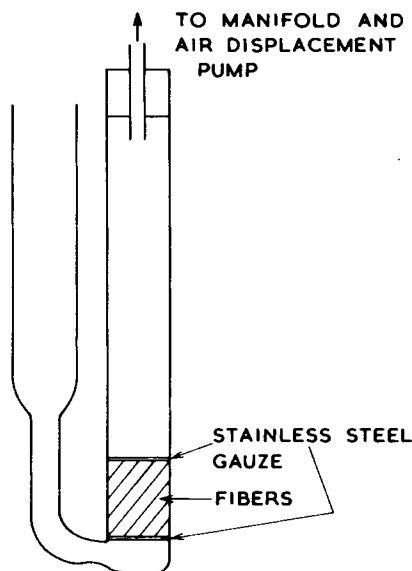The solutions were analysed spectrophotometrically as described by Giles et al.[3]

TO MANIFOLD AND AIR DISPLACEMENT PUMP

STAINLESS STEEL GAUZE

FIBERS
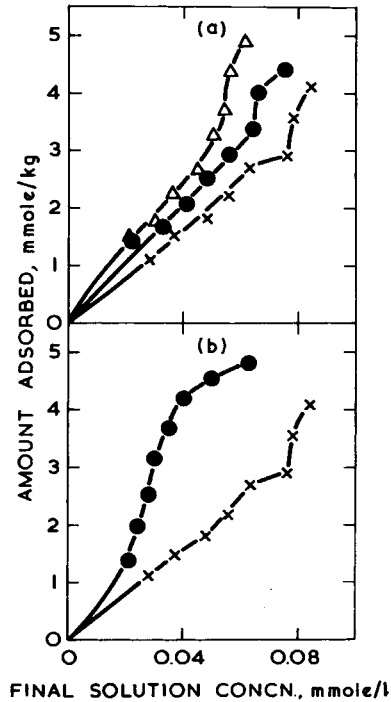
Fig. 1. Adsorption apparatus.

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Fig. 2. Short-period isotherms for PNP adsorption from n-hexane at 20°C. Fibers at ambient regain. (a) Nylon 5 (X), 10 (●), and 15 (△) min, respectively; (b) nylon, 5 min: 53% (X) and 69% (●) R.H., respectively.
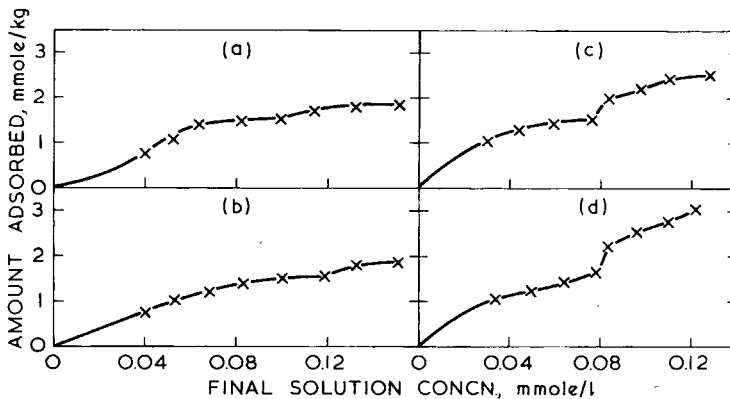

Fig. 3. Short-period isotherms for PNP adsorption from n-hexane at 20°C. Fibers dried for 1 hr at 105°C before adsorption: (a) wool, 2 min; (b) wool, 10 min; (c) nylon, 10 min; (d) nylon, 20 min.

RESULTS AND DISCUSSION

Preliminary experiments showed that with undried fibers the rate of uptake of p-nitrophenol increased not only with the equilibration time, as reported previously,[1-3] but also with the ambient relative humidity (see, for example, Fig. 2). As the equilibrium water content of both wool and nylon increases with relative humidity, it seemed likely that diffusion of p-nitrophenol into the fibers might be facilitated by water adsorbed on hydrophilic sites within the fibers. Under practical conditions, wool and nylon contain considerable quantities of water, 14.7% and 3.7% by weight, respectively,
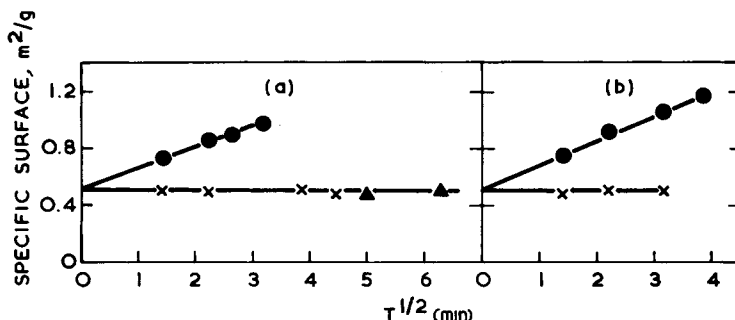
Fig. 4. Specific surface–time graphs for PNP adsorption from n-hexane at 20°C. (a) Wool: 0.3 g, 53% R.H. (●); 0.3 g, dry (×); 0.5 g, dry (▲). (b) Nylon: 0.3 g, 53% R.H. (●); 0.3 g, dry (×).

at 60% relative humidity.[4] The absorption of such quantities of water is known to cause swelling,[5] and, with wool, it is also known that higher aliphatic alcohols diffuse more rapidly into hydrated fibers than dry fibers.[6-8]

These observations suggested that diffusion of p-nitrophenol into the fibers, a complicating factor in surface area measurements, might be eliminated simply by drying the fibers. Results in Figure 3 show this to be the case. With dry fibers, the amount of p-nitrophenol adsorbed is reduced and the isotherms are invariant with respect to the equilibration time for both wool and nylon. Also, if the apparent specific surface area is plotted against the square root of the equilibration time, there is excellent agreement between the extrapolated value obtained with hydrated fibers and the constant value obtained with dry fibers (Fig. 4). This means that the specific surface area of these and, presumably, other fibers can be obtained from a single isotherm, provided they are dried beforehand.

A further advantage in using dry fibers lies in the fact that the inflection on the isotherm marking the completion of the first monolayer is very easy to locate because of the long plateau region. With hydrated fibers, especially nylon, the plateau region is short and the point at which the monolayer is completed is not easily identified.

Since dehydration of the fibers would tend to make their internal structure inaccessible, this method gives the external surface area of the fibers. The values obtained are small, typically 0.5 m^2/g, and are comparable with those obtained by air permeability[2,9] and optical microscopy.[2] By contrast, techniques involving adsorption of vapor[10,11] at low temperature give the total (internal + external) surface area of the substrate and consequently reveal finer details of morphology. For example, the fibrillar structure of acrylic fibers[12,13] generated during wet and dry spinning has been studied by this method. Generally, the external surface area of fibers is too small to be measured accurately by gas adsorption methods, and adsorption of p-nitrophenol from solution provides a satisfactory alternative.

Interestingly, Giles et al.[2] found that the adsorption isotherm of phenol on nylon could be changed from the type shown in Figure 2 to that shown in Figure 3 by rigorously drying the solvent. The effect was attributed to a reduction in the polarity of the solute molecules on the surface when the last hydrogen-bonded water molecules were removed.[2] In view of the results of the present work, a more likely explanation would be that, on immersing the fibers at equilibrium with atmospheric moisture in the dry solution, water is transferred from them to the solution until equilibrium is established; if the solution/fiber ratio is sufficiently high, the fibers will be significantly dehydrated and diffusion of the solute into them reduced. A much smaller uptake of solute would then be observed in accordance with the results of the present work.

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Received February 18, 1976
Revised April 22, 1976