JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, 3161-3168 (1975)

An Investigation of the Surface Areas of Dyed and Undyed Secondary Cellulose Acetate by *p*-Nitrophenol Adsorption

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Synopsis

The surface areas of dyed and undyed secondary cellulose acetate fibers were estimated using *p*-nitrophenol adsorption. When values of specific surface area are plotted against dye concentration, there is a marked change in the region corresponding to a theoretical monolayer adsorption of the dye.

INTRODUCTION

Various theories have been proposed to explain the dyeing mechanism of secondary cellulose acetate.[2,3,4] These appear to concentrate mainly on the examination of the dye concentration range in normal use, little notice being taken of examination of the build-up of dye from very small amounts to fairly large concentrations. The purpose of the present work was to examine how the surface area of the fibre varied as the amount of dye was increased.

The surfaces of secondary cellulose acetate have been examined previously. Kartaschoff[5] explained the impermeability of cellulose acetate to water by its very small porosity which Marsden and Urquhart[6] estimated to be 5–10 Å compared with Morton's[7] value of 20–30 Å for viscose rayon.

Studies of the diffusion of gases and liquids in polymers have shown that the diffusion rate is markedly affected by structural changes, but the equilbrium sorption level is considerably less sensitive

Dyeing isotherms obtained by Bird et al.[8] indicated a linear reversible partition over the entire concentration range for normal dyeings. Similar straight-line relationships were obtained by Wahl, Arnould, and Simon[9] and Daruwalla and Turner.[10] These linear isotherms with sharp turning points at the fiber saturation concentration are indicative of a simple solution theory. Bird[1] and Vickerstaff,[4] however, were both cautious of such a simple mechanism and suggested an initial "adsorption" on to the surface of the fiber followed by diffusion in solution through the water-filled network of fiber molecules to become deposited on sites located on the micellar surfaces.

Recent research into the dyeing mechanism of secondary cellulose acetate by disperse dyes has concentrated upon the elucidation of the types of forces employed during the three recognised stages of dyeing, viz., the initial attraction of dye molecules to the fiber surface to form the diffusional boundary

layer, the initial adsorption of dye on to the fiber surface, and finally the penetration of the dye throughout the matrix of the substrate.

In any investigation of the dyeing of fibers, it is useful to examine the surface of the fiber upon which adsorption of dye occurs. The most obvious and simplest technique is to visually examine the surfaces of the fiber by optical microscopy. Such techniques reveal a smooth surface on the synthetic fiber but electron microscopy examination has revealed roughnesses which will give much greater values for their surface areas. Unfortunately, most methods of sample preparation for electron microscopy distort the pore structures and it is difficult to make exact comparisons of pore size by this technique with those calculated from any other method, such as gas adsorption. Merian,[11] however, was able to detect a change in the submicroscopic roughness before and after dyeing cellulose acetate with disperse dye, both samples having been given similar water treatments.

The surface areas of fibers and other materials have been determined by Giles and others using the adsorption of simple phenols from solutions.[12] In these investigations, they found that simple phenols, specifically *p*-nitrophenol, were adsorbed on many solids, including fibers and dyes. *p*-Nitrophenol was employed in dilute solutions, in a nonpenetrating solvent, such as *n*-hexane or *n*-heptane, to determine the surface areas of a number of fibers by plotting short time adsorption isotherms. The adsorption isotherms obtained indicated monolayer formation, so that, using the cross-sectional area of the *p*-nitrophenol molecule, they were able to calculate the specific surface area of the fiber. Using this technique, it was also possible to detect small degrees of mechanical or chemical damage to fibers. The surface areas of dyes on cellulose were also measured. For this investigation, the fact that *p*-nitrophenol does not become adsorbed on cellulose was important, so that a measure of the specific surface area of the dye present was obtainable.

By this method, Giles was able to follow the changes in surface areas of dyes already on the fiber before and after soaping. *p*-Nitrophenol was used because it is readily purified, easily analyzed by spectroscopic techniques, and its volume size is easily measured. It is also fairly stable, although Rao and Ramarkrishna[13] have noted changes in pH and optical density when aqueous solutions were kept for more than 24 hr, believed to be due to transformation from a normal to a quinonoid structure.

In his work, Giles preferred the use of organic solvents when measuring the adsorption of *p*-nitrophenol on fibers, arguing that if water were used, the fibers would be swollen and a surface area, not representative of unswollen fiber, obtained. In the present investigation, water was used as solvent and shorter-period isotherms drawn. The specific surface—time graph thus obtained should give a more realistic picture of the rate of adsorption of the *p*-nitrophenol and thus of a disperse dye from an aqueous dye bath.

EXPERIMENTAL

Secondary cellulose acetate yarn of acetyl content 53.80% and moisture content 6.01% was used throughout. It was purified by Soxhlet extraction for 24 hr with petroleum ether (boiling point 40–60°C), dried, and washed for 24 hr in a stream of distilled water. The surface water was removed by pressing

between filter papers and the yarn dried in an oven at 60°C overnight. Upon removal from the oven, it was allowed to condition in the atmosphere for 24 hr before being used. *trans*-4-Nitro-4′-hydroxy-α-cyanostilbene prepared by the method of Colonge and Frank[14] was used as a model disperse dye.

Adsorption of *p*-Nitrophenol on Undyed Fiber

About 0.3-g samples of the purified secondary cellulose acetate fiber were accurately weighed into 25-ml stoppered, conical flasks. The *p*-nitrophenol solution was then added by pipetting volumes of 0.2–3.0 ml of 3 mmole/l. solution preceded by the volume of water required to standardize the total volume to 5 ml. A blank determination with no *p*-nitrophenol present was also carried out. The samples were each shaken on a laboratory shaker for the specified times, after which 2-ml samples of the solution were removed, two drops of 0.1*M* NaOH added, and made up to 10 ml with distilled water for colorimetric estimation using a Unicam SP 500 spectrophotometer at 400 nm.

Adsorption of *p*-Nitrophenol on Dyed Fiber

Dyeings of the purified secondary cellulose acetate fiber, plus a blank in distilled water, were carried out for 1 hr at at 80°C on a Jeffries Laboratory Dyemaster apparatus. The samples were then removed, washed with cold distilled water, the dye baths discarded, and all samples treated for a further 1 hr in fresh baths of distilled water at 80°C. The samples were again rinsed with cold distilled water and dried overnight in an oven at 80°C. The samples were left for 24 hr to condition before weighing 0.3 g of each into boiling tubes with rubber stoppers. The *p*-nitrophenol solution was then added by pipetting volumes of 1.0–4.0 ml of 3 mmole/l. solution preceded by the volume of water required to standardize the total volume to 5 ml. A blank estimation without *p*-nitrophenol was also carried out.

After five days, a 2-ml sample of each solution was transferred to a 10-ml volumetric flask, two drops of 0.1*M* NaOH were added, and the volume made up to 10 ml with water. The *p*-nitrophenol concentration was determined as described.

RESULTS AND DISCUSSION

Adsorption of *p*-Nitrophenol by Undyed Fiber

Short-time (<10 min) adsorption isotherms were obtained for undyed secondary cellulose acetate. The isotherms are plotted in Figure 1. The small plateaux indicate monolayer formation, and, because of the shortness of the plateaux, the monolayer of adsorbed *p*-nitrophenol molecules exposes a surface which has nearly the same affinity for *p*-nitrophenol as has the substrate itself. A long plateau would indicate that a high energy barrier has to be overcome before additional adsorption of *p*-nitrophenol can occur. The concentration of *p*-nitrophenol on the fiber at which the monolayer occurs can be easisly obtained from the curves in Figure 1 and thus the specific surface of the fiber for each equilibrium time calculated.

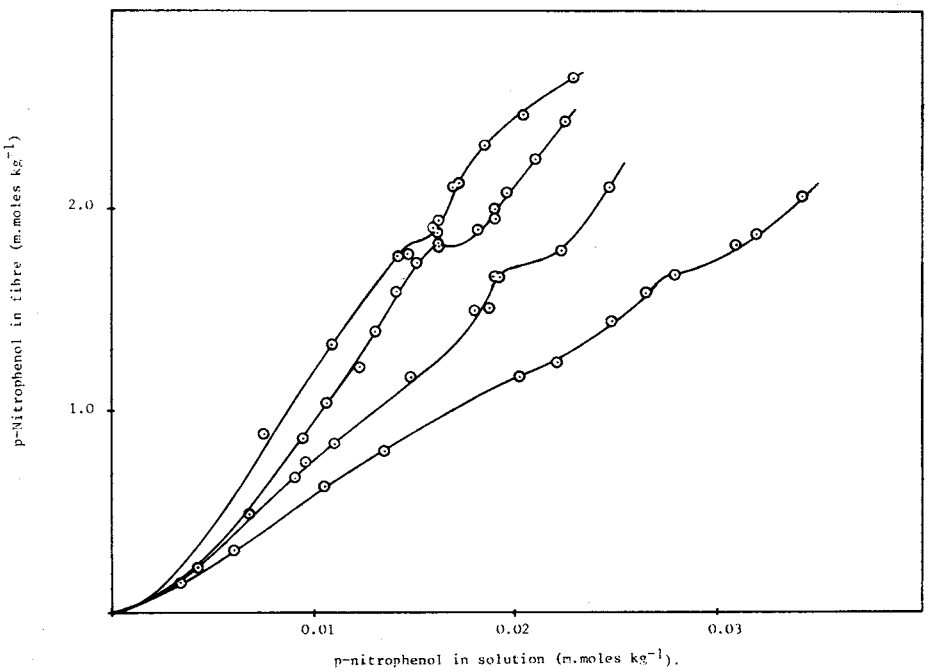

Fig. 1. Adsorption isotherms for *p*-nitrophenol on secondary cellulose acetate at 20°C from water.

TABLE I
Surface Area of Fiber at Different Times of Equilibration

Calculated Specific Surface Area ($m^2/g.$)	Time of Equilibration (mins.)
0.2513	1
0.2618	2
0.2709	3
0.2784	4

The isotherms are of the S-type shape, indicating that the *p*-nitrophenol molecule is adsorbed end-on, in which case a surface area of 25 Å^2 is presented to the adsorbant. These results are shown in Table I and illustrated graphically in Figure 2.

Extrapolation of the straight line to zero time in Figure 2 gives a value of 0.242 m^2/g for the surface area of unswollen secondary cellulose acetate.

The specific surface area obtained from *p*-nitrophenol adsorption is in good agreement with the value of 0.2 m^2/g obtained by the benzene permeability methods.[15] The increased polarity of the adsorbate, therefore, does not appear to have any appreciable effect on the value obtained for the specific surface area.

Adsorption of *p*-Nitrophenol on Dyed Secondary Cellulose Acetate

Giles et al.[16] used *p*-nitrophenol adsorption to investigate the surfaces of dye already present in a cellulose substrate. This is based on the ability of

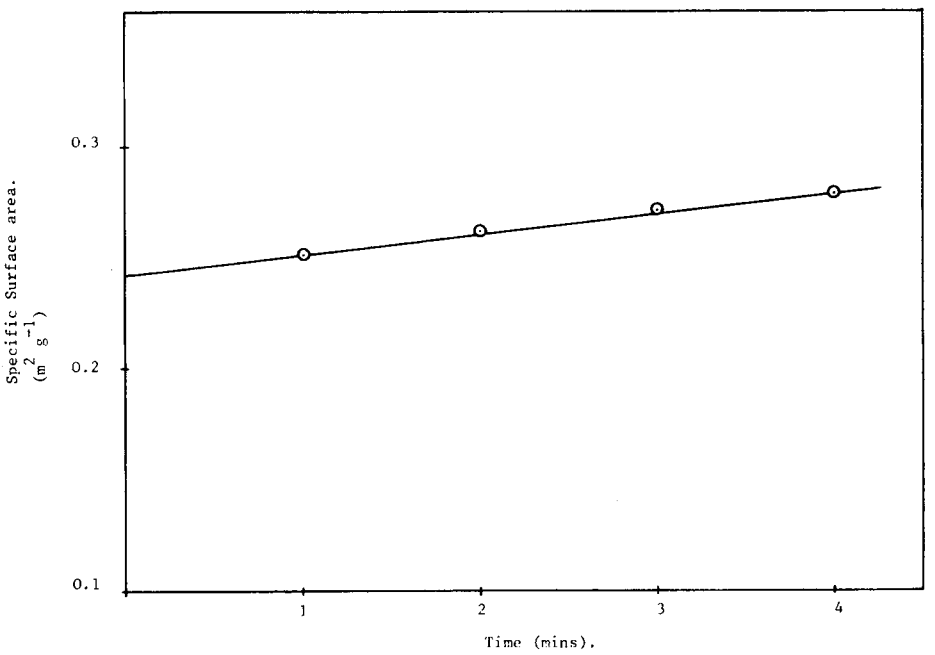

Fig. 2. Change in specific surface area with time of equilibration.

the phenol to become adsorbed on solid dye particles but not on cellulose, and Giles was able to measure changes in the specific surface areas of azoic, vat, reactive, and direct dyes on cellulose before and after soaping.

In preliminary experiments it was found that *p*-nitrophenol is adsorbed on to *trans*-4-nitro-4′-hydroxy-α-cyanostilbene when the stilbene is in a finely divided state. Figure 3 shows adsorption isotherms of *p*-nitrophenol on secondary cellulose acetate (a) undyed and (b) dyed with the stilbene derivative. If the isotherm for the undyed fiber is subtracted from that of the dyed fiber, then an indication of the adsorption of the *p*-nitrophenol on the stilbene is obtained, i.e., the difference at the point of inflexion in Figure 3. Specific surface areas may be calculated using the equation of Giles and Tolia[17]:

$$S = y_m NA \times 10^{-20}\ m^2/\text{g}.$$

From this, the specific surface area of the dye in the secondary cellulose acetate is calculated as 2189.6 m^2/g, and this is fairly close to the theoretical value of 2715.3 m^2/g for molecularly dispersed stilbene uniformly distributed through the fiber.

Samples of secondary cellulose acetate were dyed to different depths with the stilbene derivatives and the surface area of the dye calculated by *p*-nitrophenol adsorption.

The results are given in Table II, and in Figure 4 the dye concentration in the fiber is plotted against calculated specific surface area of the dye. This curve shows a marked change in the region where the dye concentration is 0.5–1.0 mmole/kg coinciding with the theoretical monolayer concentration of the dye, which is 0.67 mmole/kg. Extrapolation of the linear portion of the

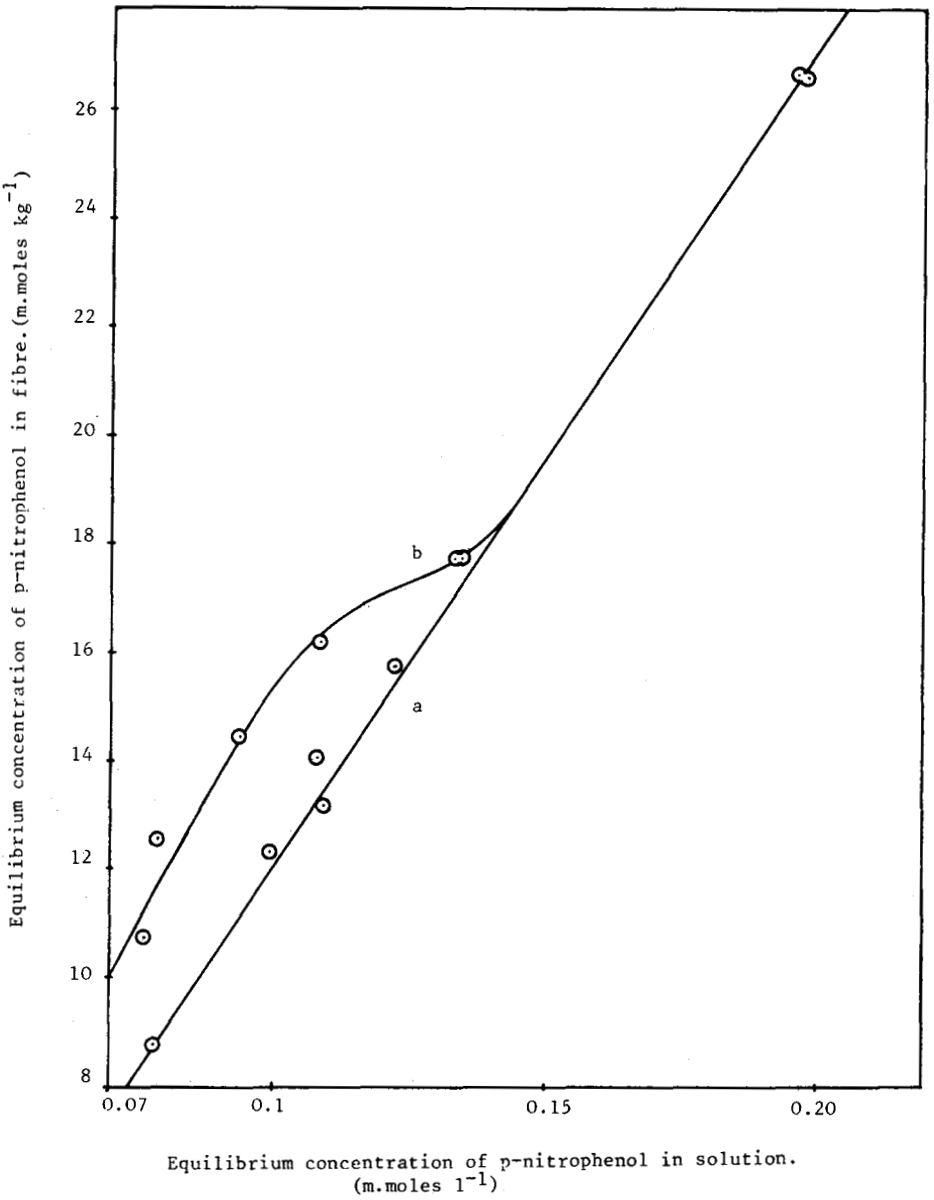

Fig. 3. Adsorption isotherm for *p*-nitrophenol on (a) undyed and (b) dyed secondary cellulose acetate (1.370 mmoles dye/kg).

curve gives a value close to the theoretical figure of 2715.3 m^2/g for the surface area of stilbene. At dye concentration less than about 0.6 mmoles/kg, the calculated surface area of the dye rises very rapidly. This would indicate the presence of two distinct dyeing mechanisms. Initially, a Freundlich adsorption where the polymer structure is open until monolayer coverage is attained. The specific surface area of the dye decreases only slowly as the dye molecules begin to build upon each other, thus blocking the "pores" of the substrate.

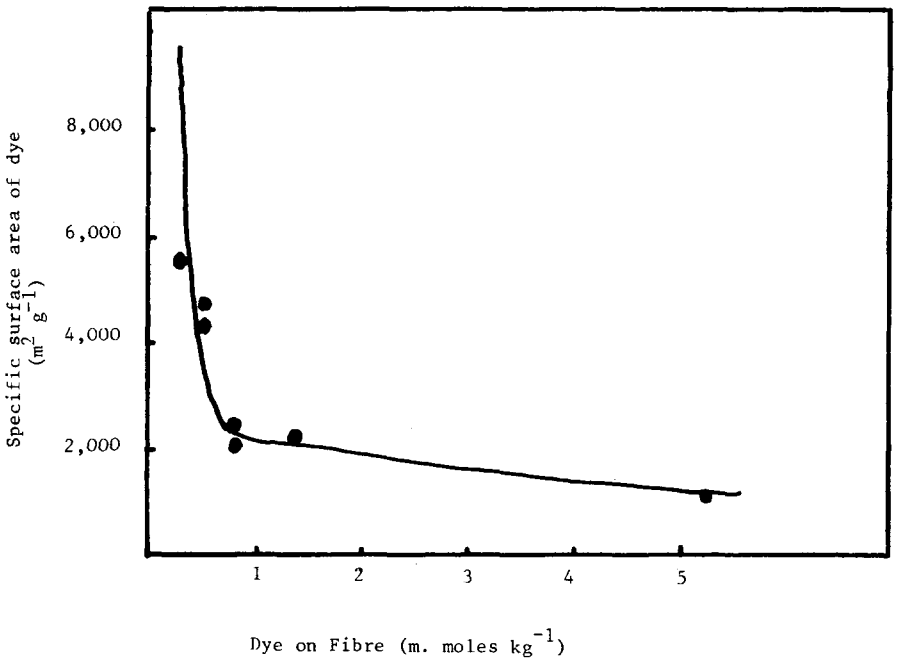

Fig. 4. Plot of surface area of dye against concentration of dye in fiber.

TABLE II
Surface Area of Dyed Fiber at Different Dye Concentration

Dye concentration in fiber, mmoles/kg	Calculated surface area of dye, m^2/g
5.288	1201.8
1.370	2157.2
0.853	2089.0
0.820	2390.4
0.554	4503.2
0.524	5039.6
0.292	5411.0

Preliminary experiments using nitrogen adsorption measurements are in agreement with these results from *p*-nitrophenol adsorption.

The authors thanks the Department of Education of Northern Ireland for a post graduate studentship to M.J.M.

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Received January 27, 1975
Revised April 25, 1975