

The Dyeing of Secondary Cellulose Acetate. Investigation of the Surfaces of Dyed Fibers by Low- Temperature Nitrogen Adsorption

HAL S. BLAIR and MERVYN J. McELROY, *Department of Industrial Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland*

Synopsis

The surface areas of dyed and undyed secondary cellulose acetate fibers have been determined using low-temperature nitrogen gas adsorption by the method of Brunauer, Emmett, and Teller. The results confirmed earlier work using *p*-nitrophenol, in which it was shown that there is a marked change of surface area of dyed fiber in the region corresponding to a theoretical monolayer adsorption of the dye.

INTRODUCTION

The surface areas of fibers and other materials have been determined by Giles using the technique of adsorption of simple phenols from solution,¹ and in a recent paper,² investigation of the surface areas of dyed and undyed secondary cellulose acetate using *p*-nitrophenol adsorption was described. However, several other techniques have been used for the measurement of fiber surface areas, and in most cases the value obtained depends on the method used. Permeability techniques, in which the viscous flow of fluid under hydrostatic pressure through a bed of fiber have been used to determine the specific surface areas of cellulose acetate fibers,³ using benzene as the fluid, a value of 0.2 m²/g was obtained.

Rowen and Blaine⁴ compared the adsorption of nitrogen and water vapor on purified textile fibers of six different types, and found that all the fibers had a relatively low capacity for the adsorption of nitrogen compared with their capacity for the adsorption of water vapor. This they attributed to the fact that the surface area as measured by nitrogen adsorption was an external surface measurement, while the water vapor, because of its smaller diameter and greater polarity, was able to penetrate the interior of the fibers. Thus, for cellulose acetate an area of 58.8 m²/g was available to the water molecules at 25°C, while an area of only 0.38 m²/g was available to nitrogen molecules at -195°C. In the present work, the surface areas of undyed and dyed secondary cellulose acetate were measured using nitrogen adsorption.

EXPERIMENTAL

The secondary cellulose acetate, undyed and dyed, and *trans*-4-nitro-4'-hydroxy- α -cyanostilbene were prepared as described previously.²

The surface area determinations were made by the method of Brunauer, Emmett, and Teller.⁵ The apparatus used was similar to that developed by Jones and Ross.⁶

Samples were outgassed by surrounding the sample tube with water at 80°C while under vacuum. The outgassed sample was surrounded by a Dewar flask of liquid nitrogen, the level of which was maintained at a glass hook on the sample tube. This level was checked before each dose of nitrogen was admitted and before each equilibrium position was measured. The volume of gas adsorbed was measured using a gas buret surrounded by a water jacket to maintain the gas temperature at 20° ± 0.05°C. The connecting gas tubing from the feed system to the sample was of narrow bore to keep "dead spaces" minimal.

The isotherms were obtained by admitting successive doses of nitrogen to the sample after it had equilibrated from the preceding dose. An equilibrium time of 20 min was found to be satisfactory. The method may not be called an absolute one, since there are probably pores in the substrate into which the nitrogen molecule, with a radius of 3.2 Å, will not penetrate. Relative nitrogen surface areas, however, can be determined with a good degree of reproducibility.

RESULTS AND DISCUSSION

The results are summarized graphically in Figures 1 and 2, and from these isotherms were obtained graphs of $p/V(p_0 - p)$ against relative pressure p/p_0 , as shown in Figures 3 and 4, where V is the volume of gas adsorbed at equilibrium pressure and p_0 is the saturation vapor pressure of adsorbate.

The surface areas available to nitrogen were calculated from the values obtained for V_m , the volume of gas contained in the monolayer. These are collected in Table I.

As expected, the undyed, air-dried sample has a higher specific surface area than the undyed, oven-dried sample. This phenomenon may be due to some of the water freezing in the secondary cellulose acetate structure under the experimental conditions, thus presenting a solid ice surface for adsorption. The freezing may also open the pore structure to present a greater surface to the nitrogen molecules. (The removal of the last traces of water has been shown to be very difficult, and for this reason all the results were obtained using fiber conditioned under standard conditions. Accurate determination of moisture content would be very difficult, and the conditions required might possibly change the character of the sample.)

With the introduction of a very small amount of dye, the surface area initially falls considerably, but quickly rises to a maximum before decreasing as larger amounts of dye build up in the fiber. It is interesting to note that the maximum of this curve falls at a dye concentration between 0.5 and 1 mmole/kg. From *p*-nitrophenol adsorption studies,² a surface area of 0.242 m²/g was obtained for the undyed fiber, and if we take the dimensions of the 4-nitro-

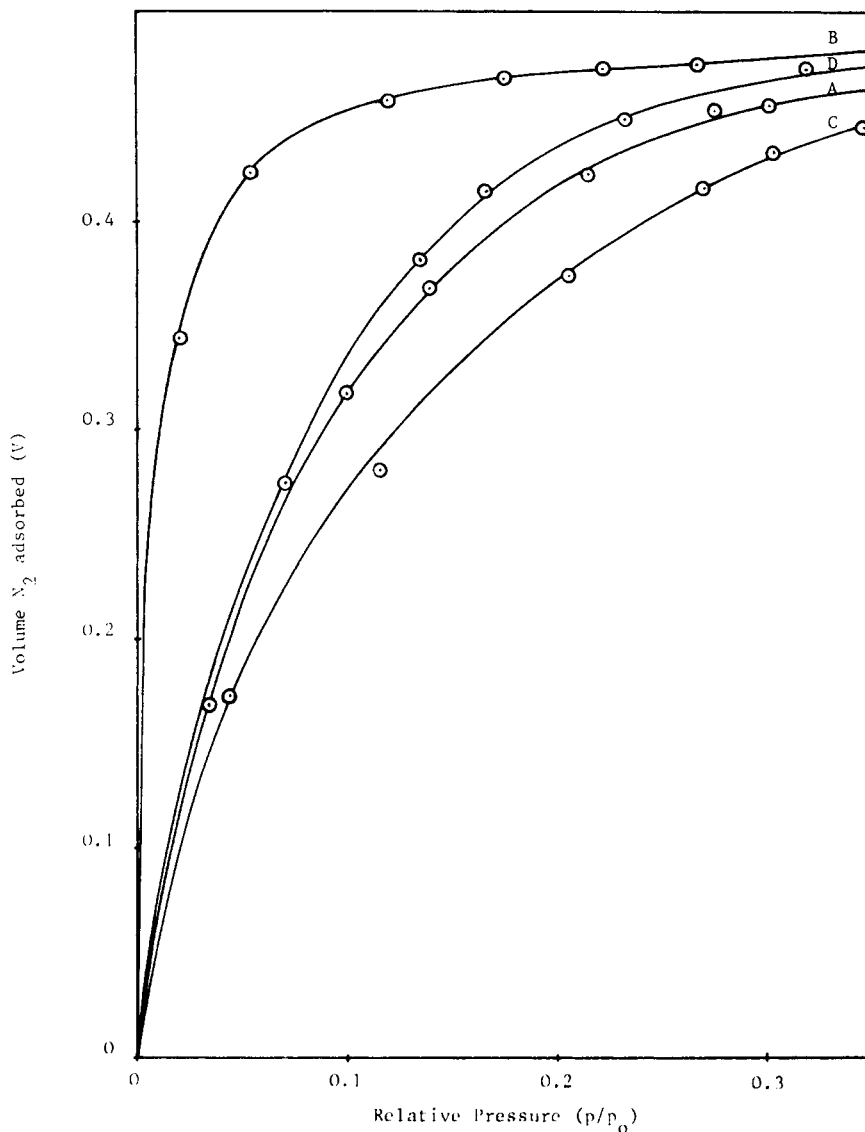


Fig. 1. Nitrogen adsorption isotherms for secondary cellulose acetate: (A) undyed oven-dried; (B) undyed air-dried; (C) 0.17 mmole/kg of dye I; (D) 0.55 mmole/kg of dye I.

4'-hydroxy- α -cyanostilbene molecule to be⁷ approximately 10 Å by 6 Å, then the concentration of stilbene necessary to form a monolayer on the acetate fiber will be

$$\begin{aligned}
 &= \frac{0.242 \times 10^{20}}{60} \times \frac{1}{6.019 \times 10^{23}} \times 10^6 \text{ mmole/kg} \\
 &= 0.67 \text{ mmole/kg.}
 \end{aligned}$$

The maximum surface area would thus appear to be at a dye concentration corresponding to the theoretical monolayer coverage.

From these results, the buildup of dye on the fiber may be explained as fol-

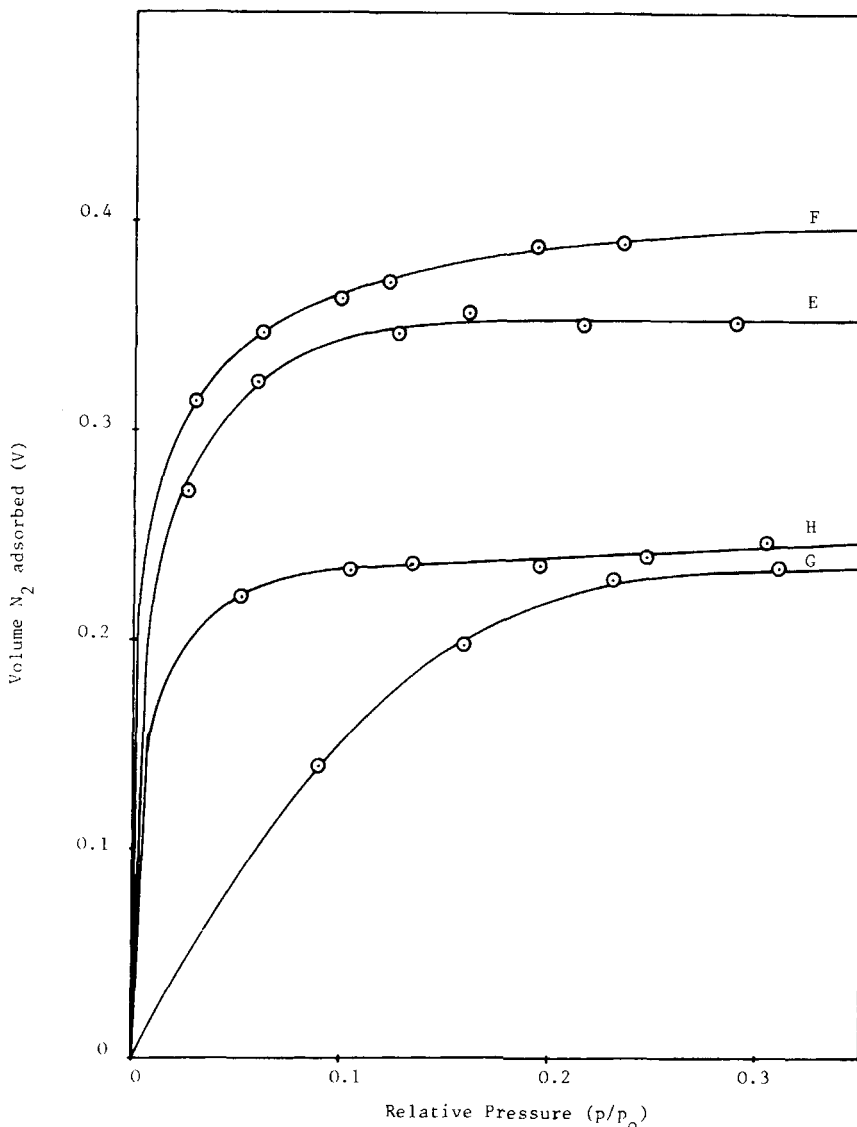


Fig. 2. Nitrogen adsorption isotherms for dye I on secondary cellulose acetate: (E) 0.06 mmole/kg; (F) 2.63 mmoles/kg; (G) 10.0 mmoles/kg; (H) 13.8 mmoles/kg.

At very low dye concentrations, the dye molecules do not penetrate the fiber pores but build up near the surface, and only as more dye is applied will the penetration increase to a maximum at a concentration corresponding to a monolayer of dye on the fiber surface. This would support a Freundlich adsorption theory over this concentration range where the number of sites for adsorption remains constant. Each dye molecule adsorbed breaks open a little more of the substrate structure exposing a fresh site on which the next molecule may be adsorbed. Beyond this concentration, the pores begin to fill, resulting in a corresponding decrease in specific surface area as dye molecules build up by intermolecular bonds between them. The surface is, therefore, no longer available for nitrogen adsorption. Langmuir adsorption oc-

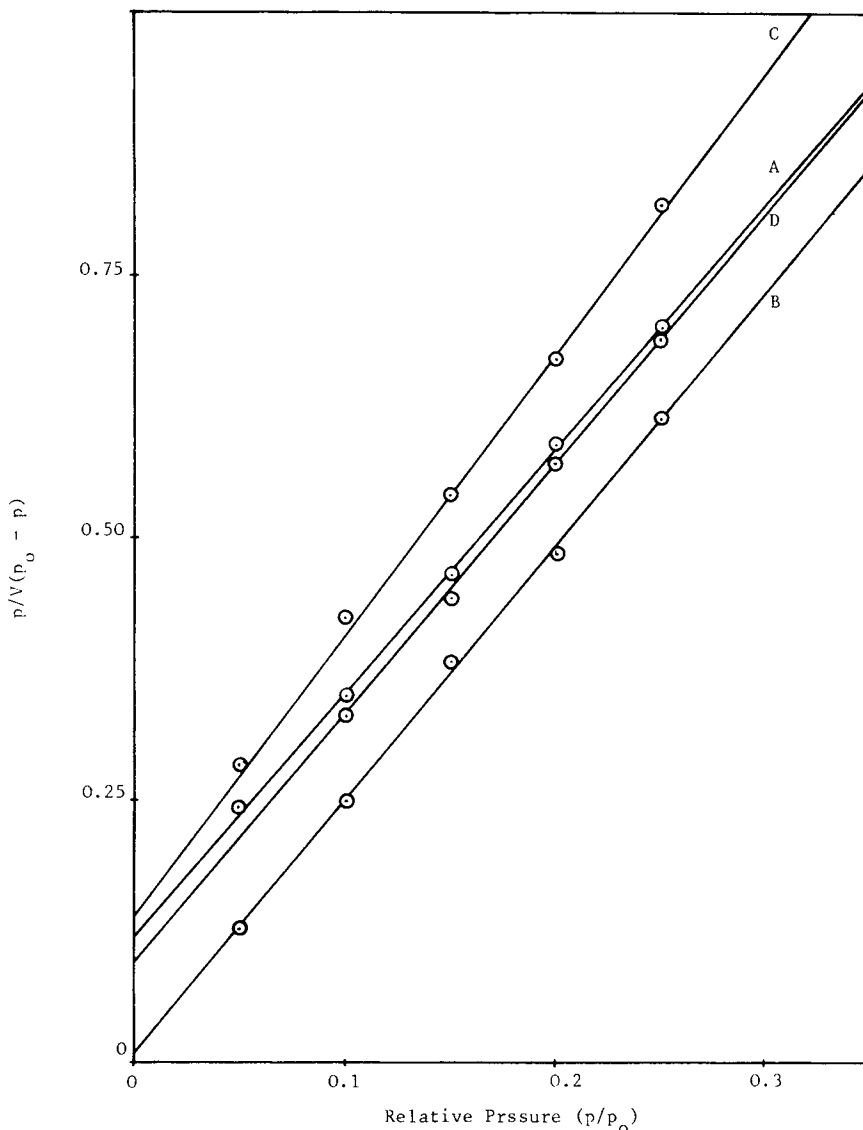


Fig. 3. B.E.T. plots for secondary cellulose acetate: (A) undyed oven-dried; (B) undyed air-dried; (C) 0.17 mmole/kg of dye I; (D) 0.55 mmole/kg of dye I.

curs where the dye sorption takes place on specific sites in the fiber. In this case, when a dye molecule occupies a site, that site is saturated and incapable of further adsorption. Thus, a steady decrease in surface area would be expected because all possible sites would be equally available to the dye molecules.

Rowen and Blaine⁴ gave a value of 0.38 m²/g for undyed secondary cellulose acetate fiber. In their preparation of the fiber for adsorption of nitrogen, they used samples between 20 and 50 g which were evacuated for 16 to 20 hr at room temperature (about 25°C). It is doubtful, however, if the water was completely removed from the fiber under these conditions since Merchant⁸ found that when cotton was freeze-dried, the adsorbed water was not

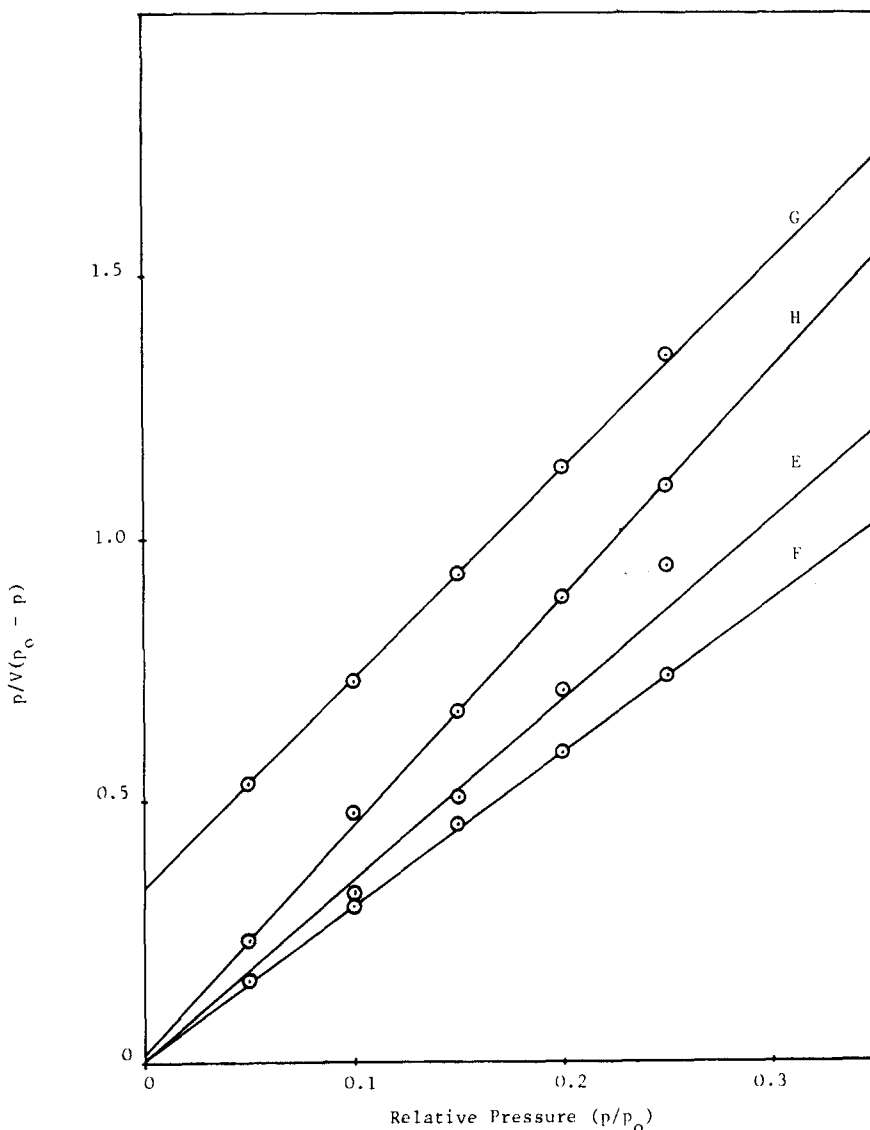


Fig. 4. B.E.T. plots for secondary cellulose acetate: (E) 0.06 mmole/kg of dye I; (F) 2.63 mmole/kg of dye I; (G) 10.0 mmole/kg of dye I; (H) 13.8 mmole/kg of dye I.

frozen since the surface area increased as freezing and thus drying temperatures were lowered. Frommer and Lancet⁹ have studied the freezing and un-freezing of water in cellulose acetate, and they also concluded that since all the water did not freeze, some type of strong bonding between the water molecules and the fiber was present. This prevented freezing of the water, since for freezing to occur, these strong, possibly hydrogen, bonds must be broken to allow the water molecules to reorientate themselves in an ice structure.

It would appear that, in order to remove as much water as possible and thus present the maximum surface to adsorbing nitrogen molecules, since any remaining water will tend to block off smaller pores, more stringent conditions than those used by Rowen and Blaine are necessary. For this reason,

TABLE I
Surface Areas Available to Nitrogen of Undyed and Dyed Cellulose Acetate

Description	Surface area, m ² /g
Undyed, oven dried	1.612
Undyed, air dried	1.782
Dyed, 0.06 mmoles/kg	1.432
Dyed, 0.17 mmoles/kg	1.601
Dyed, 0.55 mmoles/kg	1.711
Dyed, 2.63 mmoles/kg	1.503
Dyed, 10.00 mmoles/kg	0.941
Dyed, 13.80 mmoles/kg	0.766

evacuation in our investigation was carried out at 80°C, and thus the greater value for the specific surface area obtained.

CONCLUSIONS

The variation in surface area, as measured by nitrogen gas adsorption, of secondary cellulose acetate with the amount of stilbene dye applied to it indicates a maximum at a dye concentration of about 0.5 mmoles/kg. Calculations indicate that this maximum surface area coincides with a dye concentration corresponding to the theoretical monolayer coverage.

The variation in surface area of secondary cellulose acetate with its processing history indicates that undyed, air-dried fiber has a higher surface area than a similar fiber which has been thoroughly dried at a higher temperature.

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