

The Effect of *o*-Phenyl Phenol on the Dyeing of an Acrylic Fiber with Basic Dyes

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SYNOPSIS

The equilibrium uptake of *o*-phenyl phenol onto Courtelle S at 98°C was found to follow a Nernst adsorption mechanism, indicating that uptake arises by virtue of hydrophobic interaction as well as ion-dipole, dipole-dipole, and dipole-induced dipole forces operating between the fiber and the nonionic carrier. Differential scanning calorimetry was used to demonstrate the plasticizing action of the carrier on Courtelle S yarn. A linear relationship was obtained between the extent of plasticization, as measured by reduction in T_g of the fiber, and concentration of carrier applied to the fiber with the maximum extent of plasticization, showing a close correspondence to the aqueous solubility of *o*-phenyl phenol at 98°C, the temperature at which the fiber was treated with the carrier. The relationship between the extent of enhancement of uptake of C. I. Basic Green 4 and C. I. Basic Red 13 onto Courtelle S yarn at 98°C and concentration of the carrier in the dyebath was also examined: The concentration of *o*-phenyl phenol that gave maximum enhancement of dye uptake coincided with the aqueous solubility of the carrier at 98°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The glass transition temperature (T_g) is of major significance in relation to the dyeing of acrylic fibers with basic dyes, since it is responsible not only for the characteristic excellent wet fastness of the resultant dyeings, but also for the marked temperature sensitivity of the basic dye-acrylic fiber system. Owing to the virtual absence of segmental mobility of the macromolecular chains within the substrate at temperatures below T_g , little, if any, diffusion of basic dye occurs at such temperatures. At or above the T_g of the fiber, however, the rate of dye uptake increases markedly owing to the onset of segmental mobility and concomitant increase in free volume within the substrate. Since T_g of the fiber constitutes the major barrier to basic dye diffusion, much work has attended the reduction of this parameter in order to expedite dyeing.

Many workers, using several techniques, have examined the effects of various carriers on the dyeing of acrylic fibers using basic dyes¹⁻¹⁶; of the various compounds examined in this context, benzyl alcohol has been most extensively used. Among the numerous explanations given, over many years, on the effects of carriers on the dyeing of acrylic and other hydrophobic fibers, only one has been widely accepted, namely, that carriers plasticize or reduce the T_g of the fiber.

The aim of this work was to use differential scanning calorimetry (DSC) to determine the effect of *o*-phenyl phenol, a widely used carrier for the dyeing of polyester fiber using disperse dyes, on the T_g of acrylic fiber and to examine the relationship between this parameter and dyeability with two basic dyes.

EXPERIMENTAL

Fiber

A commercial sample of 3 denier, staple Courtelle S yarn, kindly supplied by Courtaulds Fibres Plc,

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was used. The yarn was scoured in a weakly alkaline aqueous solution of a nonionic dispersing agent containing 1% o.w.f (i.e., on the weight of fiber) Sandozin NIE (Sandoz) and 1% o.w.f 25% aqueous ammonium hydroxide solution for 30 min at 55°C using a liquor-to-goods ratio of 100 : 1. The scoured yarn was then rinsed using water and, after centrifuging, dried in an oven at 60°C.

Dyes and Chemicals

The two basic dyes used, namely, C. I. Basic Green 4 and C. I. Basic Red 13, were generously supplied by Bayer. C. I. Basic Green 4 was purified by dissolving 50 g of the commercial dye in 400 cm³ of hot (90°C) water and filtering the ensuing dye solution under vacuum using a preheated Buchner funnel. The filtrate was cooled to room temperature, and the recrystallized dye was filtered and dried in an oven at 60°C for 48 h. This process was repeated two further times and dye purity was checked by comparison of the molar extinction coefficient ($\epsilon = 96,428 \text{ L mol}^{-1} \text{ cm}^{-1}$, at 620 nm) of the purified dye with that ($\epsilon = 104,000$) of 100% pure dye in glacial acetic acid¹⁷; the purity was found to be 92.7%. C. I. Basic Red 13 was purified by extracting 40 g of the commercial dye using 200 cm³ of warm (50°C) ethanol; the ensuing solution was filtered and the solvent was removed, and the remaining dye was dried in an oven at 60°C for 48 h. Thirty grams of the dry, purified dye was then dissolved in 120 cm³ of hot (90°C) water and the solution was filtered. The filtrate was cooled to room temperature and the recrystallized dye was filtered and dried in an oven at 60°C. The molar extinction coefficient (ϵ) of the purified dye in water was 45,256 L mol⁻¹ cm⁻¹ at 520 nm.

Analytical grade of *o*-phenyl phenol was used. All other reagents used in the experiments were of laboratory grade.

Determination of the Partition Coefficient of *o*-Phenyl Phenol between Water and Courtelle S

Four baths, containing 0.5, 1, 1.5, and 2 g L⁻¹ *o*-phenyl phenol were prepared in 80 cm³ capacity stainless-steel dyepots with 50 cm³ of distilled water. Each sealed dyepot was housed in a laboratory-scale rotary dyeing machine set at 98°C and rotated at this temperature for 60 min to make a carrier solution. One gram of Courtelle S yarn was then placed in the dyepot and treatment was continued for 2 h.

After the treatment, the absorbance of the exhausted solution was measured at 245 nm using a Pye-Unicam PU 8600 UV/visible spectrophotometer (Philips, U.K.) and the amount of carrier remaining in the solution was determined. Subtraction of this residual carrier concentration from the original was taken as the amount of *o*-phenyl phenol adsorbed by the fiber. A plot of concentration of carrier in the fiber vs. that in the exhausted bath gave a straight line passing through the origin (Fig. 1); the partition coefficient of the carrier between the fiber and water was obtained from the slope of the straight line.

Dyeing of Courtelle S in the Presence and Absence of *o*-Phenyl Phenol

(i) Determination of the Rate of Uptake of C. I. Basic Green 4 at 98°C

A 300 cm³ aqueous dyebath containing 0.12 g of the dye, 0.06 g of glacial acetic acid, 0.18 g of sodium acetate, and an appropriate amount (0.5, 1, 1.7 g L⁻¹) of *o*-phenyl phenol was prepared in a 500 cm³ reaction flask, fitted with stirrer and condenser, and immersed in a water bath of 98°C. A 6 g sample of Courtelle S was added to the dyebath and dyed for 120 min, during which time 1 cm³ aliquots of the dyebath were removed in a sequence of time intervals for the absorbance measurement and calculation of the amount of dye diffused into the fiber. A graph was constructed of the quantity of dye adsorbed by the fiber vs. time of dyeing (Fig. 2).

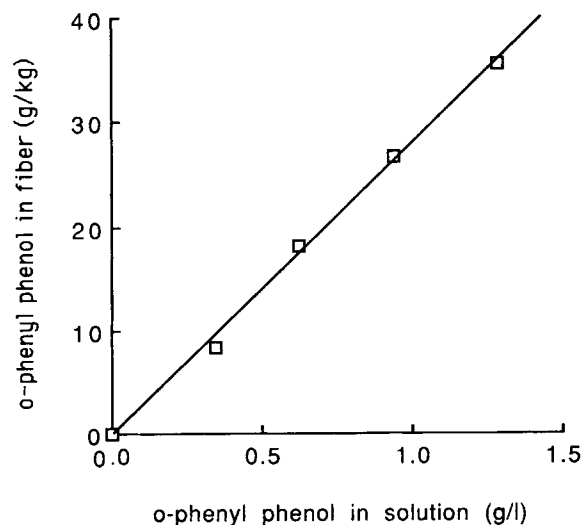


Figure 1 Equilibrium partition of *o*-phenyl phenol between Courtelle S and water at 98°C.

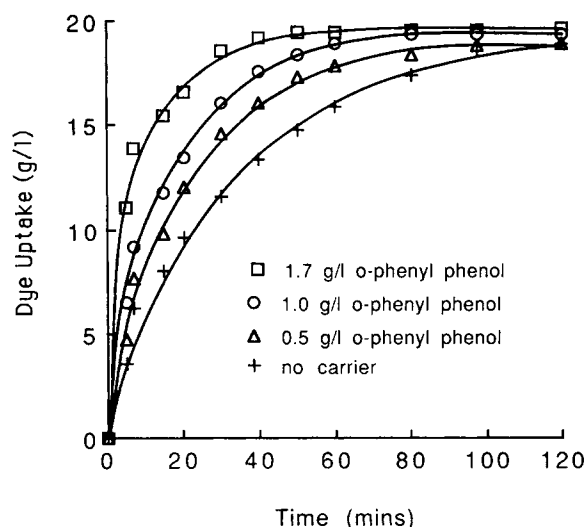


Figure 2 Effect of *o*-phenyl phenol on dyeing rate of C. I. Basic Green 4.

(ii) Determination of the Dyeing Transition Temperature (T_d) of C. I. Basic Green 4

Aqueous dyebaths, 50 cm³, containing 0.02 g of the dye, 0.02 g of acetic acid, 0.06 g of sodium acetate, and an appropriate quantity (1, 1.5, 2 g L⁻¹) of *o*-phenyl phenol were prepared in stainless-steel dye-pots. The dyebath was adjusted to the required dyeing temperature, and after thermal equilibrium had been achieved, a 1 g sample of Courtelle S yarn was added to the dyebath and dyed for 30 min. The dyed sample was then removed, rinsed with water and acetone, and dried in an oven at 60°C. The dry, dyed yarn, 0.02 g, was dissolved in 8 cm³ of DMF at room temperature, to which was then added 2 cm³ of glacial acetic acid. The ensuing solution was centrifuged and absorbance of the solution was measured at 628 nm to calculate the concentration of dye in the fiber. A graph was constructed of the concentration of dye in the fiber vs. dyeing temperature for each of the concentrations of *o*-phenyl phenol used. The T_d of the dye, in both the absence and presence of the carrier, was obtained as the intercept on the abscissa of the contact line representing dye uptake of 1 g kg⁻¹ per 1°C increase in dyeing temperature (Fig. 3); a plot of T_d against carrier concentration in the dyebath was constructed (Fig. 4).

(iii) Determination of the Effect of *o*-Phenyl Phenol on the Extent of Uptake of C. I. Basic Green 4 and C. I. Basic Red 13 at 98°C

The equipment and procedure described in Subsection (ii) were used, except that 0.04 g of each dye

was employed and dyeing was carried out for 30 min at 98°C. In the case of C. I. Basic Red 13, DMF alone was used to dissolve the dyed sample and to dilute the solution; the absorbance of the diluted dye solution was measured at 532 nm. In the cases of both C. I. Basic Green 4 and C. I. Basic Red 13, a graph was constructed of the quantity of dye absorbed by the fiber vs. concentration of *o*-phenyl phenol present in the dyebath (Fig. 6).

Determination of the Effect of *o*-Phenyl Phenol on the T_g of Courtelle S

One gram samples of Courtelle S yarn were treated in *o*-phenyl phenol solutions of appropriate concentration as explained in the section on partition coefficient determination. The treatment was carried out at 98°C for 90 min, after which time the treated fiber was removed, rinsed in warm (40°C) distilled water, and dried in an oven at 40°C. DSC of *o*-phenyl phenol-treated fiber was carried out using a DuPont 1090 thermal analyzer. The T_g of the fiber was determined using the DuPont General Analysis Program. A graph was made of the T_g of the fiber vs. concentration of *o*-phenyl phenol applied to the substrate (Fig. 5).

Determination of the Aqueous Solubility of *o*-Phenyl Phenol

An excess amount of *o*-phenyl phenol was placed in an 80 cm³ capacity stainless-steel dye-pot, to which was then added 70 cm³ of distilled water. The re-

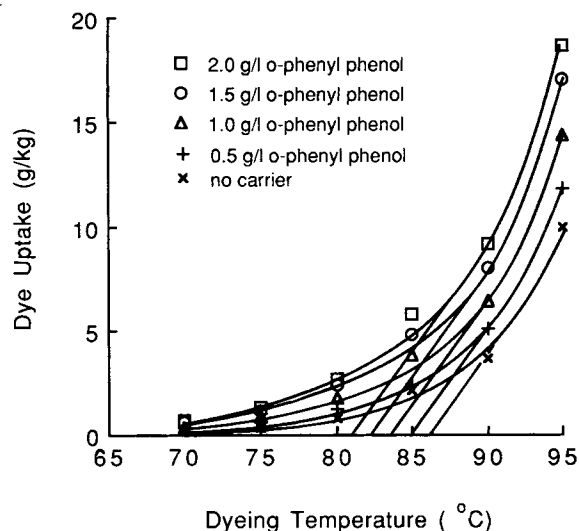


Figure 3 Effect of *o*-phenyl phenol on the uptake of C. I. Basic Green 4 and determination of the T_d of the dye.

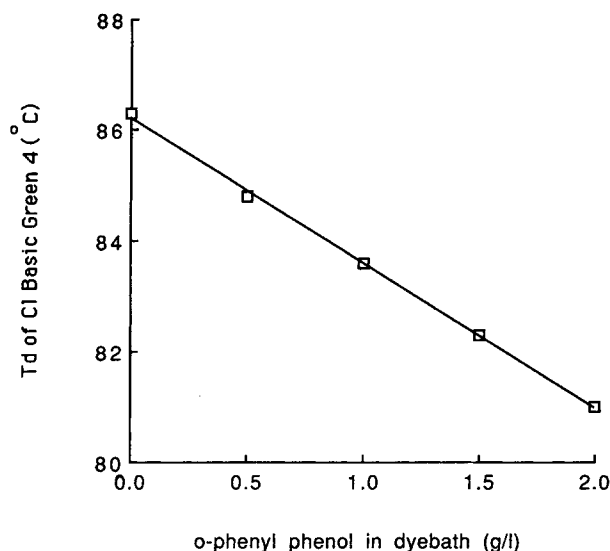


Figure 4 Effect of *o*-phenyl phenol on T_d reduction.

sulting dispersion in the sealed dyepot was housed in a laboratory-scale rotary dyeing machine set at 98°C and the dyepot agitated for 2 h at this temperature, after which time the contents of the dyepot were quickly transferred to a 100 cm³ conical flask that was suspended in a preheated water bath set at 98°C. The dispersion was allowed to settle for 120 min; a 1 cm³ aliquot was then removed using a preheated pipette and diluted using distilled water. The absorbance of the resulting solution at 245 nm was measured, and by reference to the calibration curve, the aqueous solubility of the carrier at 98°C was determined.

RESULTS AND DISCUSSION

Figure 1 shows that absorption of *o*-phenyl phenol onto Courttelle S at 98°C followed a Nernst mechanism; this finding concurs with that of Jin and Cates¹⁸ who found a linear partition for *o*-phenyl phenol between water and polyester fiber and therefore suggests that absorption of the nonionic carrier onto acrylic fiber occurs by virtue of similar forces of interaction that operate between the carrier and polyester fiber, e.g., dipole-dipole, dipole-induced dipole, and ion-dipole forces as well as hydrophobic interaction. The high partition coefficient obtained for the carrier between water and Courttelle S (27.5 g kg⁻¹/g L⁻¹) demonstrates, as might be anticipated, that the hydrophobic carrier has considerably greater substantivity toward the hydrophobic fiber phase than toward the aqueous phase.

It is well known that carriers, such as *o*-phenyl phenol, which are mostly used in the dyeing of polyester and cellulose triacetate fibers with disperse dyes, increase the rate of dyeing, thereby enabling commercially acceptable dyeing rates to be achieved at the boil rather than at the elevated temperatures (such as 130°C in the case of polyester and 120°C for triacetate) that are necessary when dyeing is affected in the absence of a carrier. Figures 2 and 3 show that *o*-phenyl phenol increased the rate and extent of uptake of C. I. Basic Green 4 on Courttelle S and that this enhancement of dye uptake increased with increasing concentration of the carrier present in the dyebath. Figure 3 shows that the uptake of C. I. Basic Green 4 onto Courttelle S increased sharply over a relatively narrow temperature range; the inflection point of such dyeing rate curves is commonly referred to as the dyeing transition temperature T_d ¹⁹ and this value is often used as an indicator of T_g of a fiber. From Figure 3, the T_d of C. I. Basic Green 4 on Courttelle S in the absence of *o*-phenyl phenol was found to be 86.3°C.

The T_g of the Courttelle S yarn used in this work, at 0% R.H., was found, using DSC, to be 104.3°C, which is 18°C higher than the T_g of the fiber, inferred from the value of T_d obtained from Figure 3, under aqueous dyeing conditions and, therefore, indicates the marked plasticizing action of water on the acrylic fiber. This finding concurs with those of other workers who have demonstrated, using various techniques, the plasticizing action of water on acrylic fibers.^{6,9,20-23}

From Figure 3, the values of T_d of C. I. Basic Green 4 on Courttelle S at each concentration of *o*-phenyl phenol used were determined and these values, together with the T_d of the dye in the absence of carrier, were plotted as a function of carrier applied to the substrate to yield Figure 4. As previously discussed, it is generally considered that carriers plasticize the fiber, causing a reduction in the T_g of the fiber. In essence, a plasticizer reduces the T_g of a polymer by functioning as a diluent, its presence disturbing the packing of the polymer chains, as a result of which segmental mobility is increased by means of a reduction in interchain bonding; consequently, the extent of plasticization will increase with increasing concentration of plasticizer in the substrate. Since the T_d of a particular dye in a given fiber is closely related to the T_g of that fiber, it can be argued that a carrier will also reduce the T_d and that the extent of this reduction in the T_d will increase with increasing concentration of carrier in the fiber. It can be proposed that in view of the linear partition of *o*-phenyl phenol (Fig. 1), the amount

of *o*-phenyl phenol adsorbed by the fiber will increase with increasing concentration of the carrier applied to the fiber over the particular concentration range used to obtain the results displayed in Figures 3 and 4 (i.e., below the aqueous solubility of the carrier, which was determined as 3.02 g L^{-1} at 98°C). The results shown in Figure 4 support the view that the carrier plasticizes the fiber; the extent of reduction in the T_d of C. I. Basic Green 4 decreased linearly with increasing concentration of *o*-phenyl phenol in the dyebath, which, by inference, implies that the T_d decreased linearly with increasing concentration of *o*-phenyl phenol in the fiber over the particular concentration range used.

Figure 5 clearly demonstrates the marked plasticizing action of *o*-phenyl phenol on the fiber (at 0% R.H.) as evidenced by the reduction in the T_g of the substrate. This finding concurs with that of Peters and Wang¹⁰ who demonstrated, using dynamic mechanical analysis, the plasticizing action of *o*-phenyl phenol on "Acrilan" acrylic fiber. The values obtained for the T_g of the fiber at 0% R.H. are higher than those values of T_g , inferred from T_d values, obtained under aqueous dyeing conditions (Fig. 4); as discussed previously, this difference can be attributed to the plasticizing action of water on Courttelle S. Figure 5 also shows that a linear relationship was obtained between the T_g and the concentration of *o*-phenyl phenol applied to the fiber in that the T_g initially decreased linearly with increasing carrier concentration before reaching a minimum value at an applied carrier concentration of about 3.2 g L^{-1} , after which the T_g remained constant with further

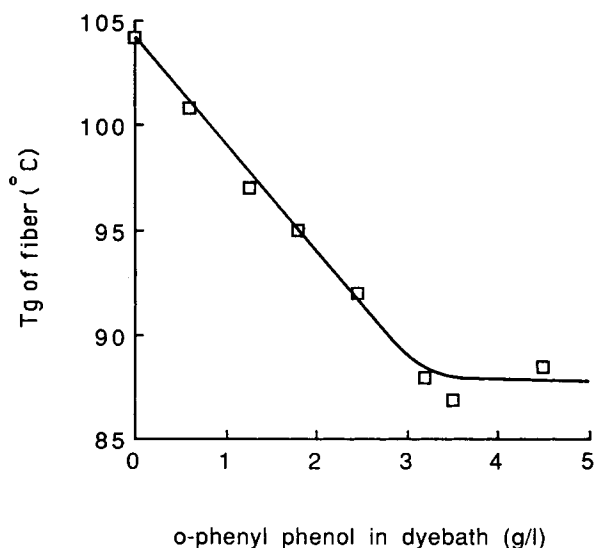


Figure 5 Effect of *o*-phenyl phenol on T_g reduction.

increase in applied *o*-phenyl phenol. Aitken et al.,¹⁶ using a modified DMA technique, demonstrated that the reduction in T_g of wet Courttelle S imparted by benzyl alcohol was related to the amount of the carrier absorbed by the fiber, with the maximum extent of T_g reduction (plasticization) coinciding with the maximum concentration of benzyl alcohol absorbed by the fiber, which, in turn, corresponded to the aqueous solubility of benzyl alcohol at the particular application temperature (80°C) employed. The results displayed in Figure 5 support the findings of Aitken et al.¹⁶ that the maximum extent of plasticization (T_g reduction) obtained when *o*-phenyl phenol had been applied to Courttelle S at 98°C occurred at a concentration of the carrier that approximately corresponded to the aqueous solubility of the carrier at 98°C . Consequently, it is proposed that the observed linear reduction in the T_g that accompanied an increase in concentration of *o*-phenyl phenol applied to the fiber up to about 3.2 g L^{-1} is due to a corresponding increase in concentration of the carrier absorbed by the substrate. The maximum reduction in the T_g that occurred at 3.2 g L^{-1} *o*-phenyl phenol corresponded to the maximum amount of carrier absorbed by the fiber, which, in turn, shows a reasonable correspondence to the aqueous solubility of *o*-phenyl phenol at 98°C . The results shown in Figures 4 and 5 therefore demonstrate that *o*-phenyl phenol acts as a diluent of the Courttelle S, the extent of plasticization (T_g reduction) of the substrate being dependent upon the concentration of the carrier in the substrate.

Figure 6 shows the effect of various concentrations of *o*-phenyl phenol on the uptake of C. I. Basic Green 4 and C. I. Basic Red 13 at 98°C , from which it is evident that the enhancement of uptake of both dyes furnished by the carrier reached a maximum value that corresponded to a concentration of 3 g L^{-1} *o*-phenyl phenol; this particular concentration corresponds very closely to the aqueous solubility of the carrier at 98°C , namely, 3.02 g L^{-1} . Aitken et al.^{15,16} demonstrated that the extent of enhancement of uptake of C. I. Basic Blue 45 and C. I. Basic Blue 3 onto Courttelle S at 80°C imparted by benzyl alcohol was related to the amount of the carrier present in the dyebath; the maximum extent of dye uptake coincided with the aqueous solubility of benzyl alcohol, which, in turn, corresponded to the maximum concentration of benzyl alcohol absorbed by the fiber¹⁶ under the particular application temperature employed in their work. Thus, in view of the results shown in Figures 5 and 6, the observed increase in uptake of these two particular dyes that occurred in the presence of up to 3 g L^{-1} *o*-phenyl

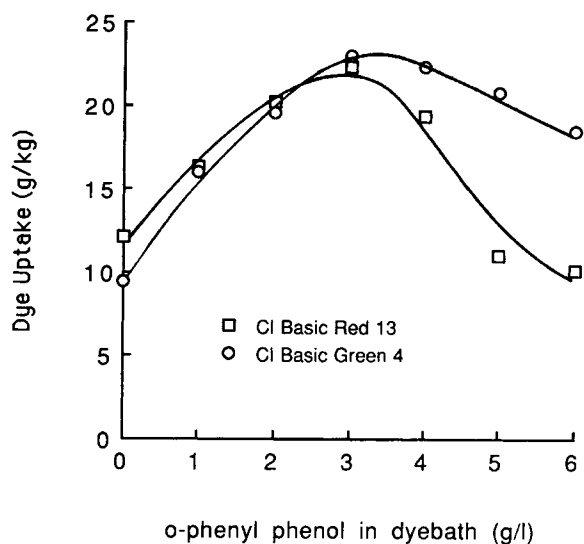


Figure 6 Effect of dyebath *o*-phenyl phenol concentration on dye uptake.

phenol (Fig. 6) can be attributed to an increase in plasticization of the fiber caused by an increase in concentration of the carrier absorbed by the fiber. The maximum value of dye uptake that occurred at 3 g L⁻¹ *o*-phenyl phenol corresponds to the maximum aqueous solubility of the carrier at 98°C, which, as shown in Figure 5, approximates to the maximum reduction in T_g of the fiber. The observed decrease in uptake of C. I. Basic Green 4 and C. I. Basic Red 13, found for concentrations of *o*-phenyl phenol in excess of 3 g L⁻¹, can be attributed to the higher solubilities of the dyes in the undissolved carrier phase in the dyebath. The finding that maximum enhancement of uptake of both C. I. Basic Green 4 and C. I. Basic Red 13 corresponded to the maximum solubility of *o*-phenyl phenol at the dyeing temperature used agrees with those of Aitken et al.^{15,16} for the absorption of C. I. Basic Blue 45 and C. I. Basic Blue 3 onto Courtelle S in the presence of benzyl alcohol.

CONCLUSIONS

The absorption of *o*-phenyl phenol onto Courtelle S was found to follow a Nernst mechanism; the carrier was shown, using differential scanning calorimetry, to reduce the T_g of the fiber, the maximum extent of reduction in T_g (i.e., plasticization) showing a close correspondence to the aqueous solubility of *o*-phenyl phenol at 98°C. The maximum extent of enhancement of uptake of C. I. Basic Green 4 and C. I. Basic Red 13 imparted by *o*-phenyl phenol coincided with the aqueous solubility of the carrier at

98°C, which, in turn, corresponded approximately to the maximum extent of plasticization of the fiber. The results clearly demonstrate that *o*-phenyl phenol functions as a diluent of the fiber, facilitating dye diffusion by disruption of the structure of the fiber.

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