Effect of dimer of C.I. Reactive Blue 19 on the reaction with cellulose

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1. Introduction

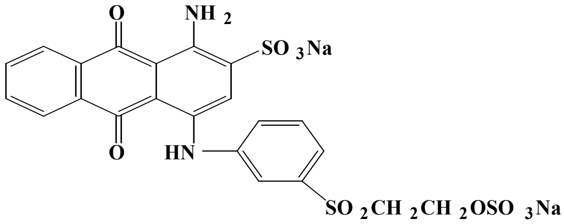
Reactive dyes have become one of the most typical and conventional coloring matters for cellulose, since they have good color-fastness, bright hues, and good cost performance. The frequently occurring hydrolysis of VS type, dimer(D) formation and reverse hydrolysis of the anchored dye at an alkaline pH yielding the hydroxyethylsulfonyl(Hy) type are all wasteful reactions as the Hy type is completely inactive for dyeing. The conclusions that emerge from previous kinetic and mechanistic studies on hydrolysis and the reaction of reactive dyes with cellulose have important technological implications for devising methods that enable reactive dyes to be applied to cellulose fabrics as efficiently and economically as possible, and in designing new dyes possessing desirable application properties.

This study examines the hydrolysis reaction of Blue 19, which forms an ether type dimer. The rate constants of various reactions for Blue 19 dye are estimated and the solubilities of the D and Hy types for Blue 19 are investigated. The diffusion and adsorption behavior of the D and Hy types on cellulose are studied using the cylindrical film-roll method.

2. Experimental

2-1 Reactive dye and Film

The chemical structure of Blue 19 is given in Fig. 1. The D type of Blue 19 was made by the reaction of the VS type with the Hy type. The dye concentrations in aqueous solutions were spectroscopically determined at the wavelength(λ_{max}) of the maximum absorption. The components of the dye during hydrolysis were analyzed by high perfomance liquid chromatography(HPLC). Cellophane film was cut into pieces 5 cm wide and 25 cm long and then scoured in boiling water for 2 h.The cylindrical cellophane-film-roll was made by the usual method. Other chemicals of reagent grade were used as received



Flg. 1 Chemical structure of C.I. Reactive Blue 19

2-2 Solubility and Stability

The pH of the dye solution was adjusted using Kolthoff's buffer. The ionic strength of the dye solution was adjusted by sodium sulfate. A dye sample was dissolved in water at 100℃ and each dye solution with a given composition was kept at 50℃ without stirring. After a suitable time, an aliquot of the solution was pipetted out and analyzed spectrophotometrically and by HPLC, if necessary.

2-3 Diffusion and Adsorption

The cylindrical film-roll method was used for the diffusion and adsorption experiments. The film-roll was immersed in a dyebath at 50℃. After dyeing, the film-roll was quickly washed by distilled water. Then, after unrolling, the dyed film was dried naturally by placing it between leaves of papers. The optical densities of every layer were measured by a spectrophotometer at the wavelength of the maximum absorption.

3. Results and discussion

3-1 Solubility of Hy and D types

The solubilities of the Hy and D types were measured at two pH's and three ionic strengths(I) at 50℃. Figs. 2 and 3 show the variation in the solubilities of the Hy type and a mixture of Hy and D types relative to time in an aqueous solution of various I's, respectively. The initial solubility of the Hy type was maintained for 4h at I=0.15 and at pH 5.8 and 9.2. An increase in the ionic strength and pH decreased the stability of the solubility of the Hy type. The total solubility of the mixture of Hy and D types remained constant for at least three days at I=0.15 and 50℃, plus an increase in the ionic strength decreased the stability of the solubility of a mixture, as shown in Fig. 3. Within the experimental time, the composition or the molar ratio of the Hy and D types was confirmed to be constant by HPLC. The D type seemed to increase the stability of the solubility of the Hy type. The experimental conditions for the diffusion experiments(I=0.15 and pH 5.8) were then e mployed based on the results.

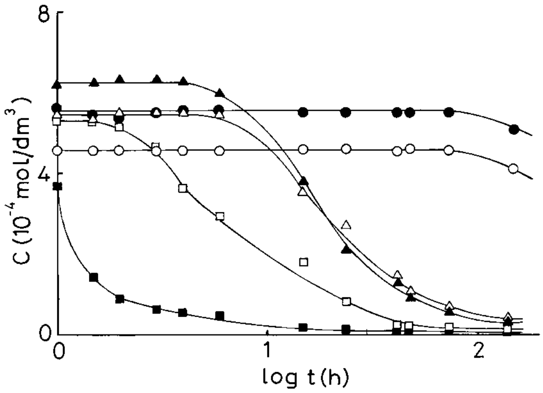


Fig.2. Variation in solubilities for Hy type of Blue 19 relative to time at 50℃ and at various I's.

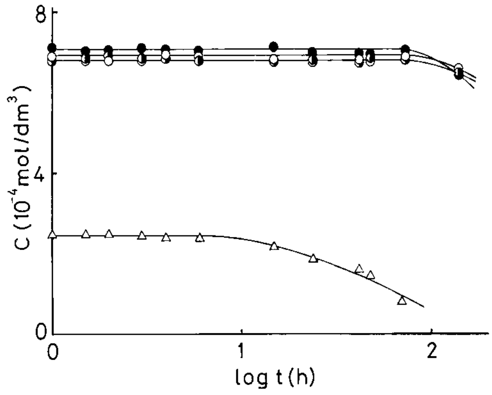


Fig.3. Variation in solubilities for mixture of D and Hy types of Blue 19 in aqueous solutions at 50℃ and at various I's.

3-2 Diffusion and Adsorption of Hy and D types

The diffusion profile of the Hy type and that of a mixture of Hy and D types in cellulose obtained using cylindrical film-roll method are shown in Fig. 4. Based on plots of the concentration vs. $x/2\sqrt{t}$, a diffusion profile was obtained, which showed a constant surface concentration, C_0(mol/kg), and diffusion coefficient obeying Fick's law(cm^2/min). With an increase in the solution concentration of the Hy type below the solubility, the value of C_0 for the Hy type increased. The value of the diffusion coefficient for the Hy type was estimated to be $2.1x10^{-6}$ cm^2/min.

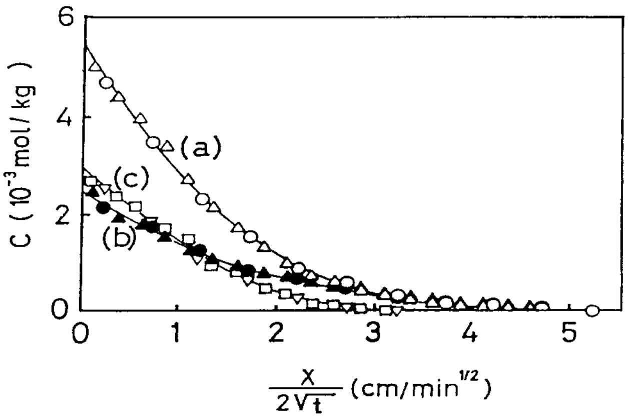


Fig.4. (a) Experimental diffusion profile of mixture(○: 1h, △: 4h) for Blue 19 in cellulose at 50℃, pH 5.8. and I=0.15. (b) That of Hy type(●: 1h, ▲: 4h). (c) Diffusion profile for D type(▽: 1h, □: 4h) estimated from difference between profiles (a) and (b).

The diffusion profile of the D type is also shown in Fig. 4. The subtraction of the corresponding profile of the Hy type from that of the mixture of Hy and D types provided the profile for the D type. When the diffusion profile of the D type was compared with that of the Hy type, the D type seemed to diffuse independently within the experimental time. The value of C_0 for the D type remained constant during the diffusion experiment and the value of the diffusion coefficient for the D type was estimated to be 0.85 x 10^{-6} cm^2/min. The affinities of the D and Hy types were nearly equal to that of the VS type. Since the D type has a high affinity to cellulose, it was adsorbed on cellulose and diffused into the substrate when it was formed in the dyebath.

3-3 Reaction of D Type with Cellulose

After a mixture of Hy and D types was adsorbed on a strip of cellophane, the film was rolled on glass tube, then a new cellophane film was further rolled on the cellophane roll.

This film roll was then immersed in an aqueous solution of sodium carbonate(0.05 mol/dm^3) at 50℃. A similar experiment was carried out by adsorbing the VS type on a film,. The concentration profiles of the fixed and unfixed species in the roll of cellophane, on which the D and Hy types were adsorbed, after the immersion for 4 h and 72 h are shown in Fig. 5. The D type was deproportionated to give the VS and Hy types in an alkaline solution, then the re-formed VS type either reacted with cellulose or was hydrolyzed to give the Hy type. The rate of the reverse reaction of the D type varied with the dye, while the D type of Blue 19 was slowly decomposed. The D type reacted much more slowly with cellulose than the VS type did. The apparent rate of reaction with cellulose for the D type was estimated to be about one sixth of the VS type over 4 h.

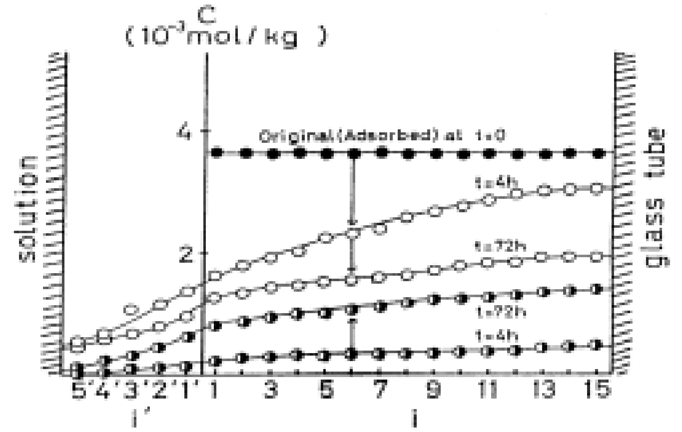


Fig. 5. Concentration profiles of mixture adsorbed on cellophane roll after dipping in Na_2CO_3(0.05M) solution at 50℃, I=0.15, for 4h and 72h(●: original at t=0, ○: total ◑: fixed).

i : No. of layers of dyed film

i': No. of layers of new film

This also decreased with time and was estimated to be about one tenth of the VS type over 72 h. The variation in the molar ratio for the Hy and D types adsorbed produced no effect on the apparent reactivity of the D type. The completion of the reaction of the D type with cellulose in this experiment required about 3 days.

4. Conclusions

The solubilities of the Hy and D types were measured at two pH's and three ionic strengths at 50℃. An increase in the ionic strength and pH decreased the stability of the solubility of the Hy type. The D type seemed to increase the stability of the solubility of the Hy type. The diffusion and adsorption of the Hy and D types in cellulose were measured by using the cylindrical film roll method. The affinities of the Hy and D types were nearly equal to that of the VS type. The D type reacted much more slowly with cellulose than the VS type did.