Journal of the Korean Society of Dyers and Finishers
Vol. 3, No. 4, pp. 13~16 (1991. 12)

〈研究論文(學術)〉

셀루로오즈에서 C.I. Reactive Blue 19의 반응과 확산에 Dimer의 기여

金仁會 · 森田全三

東京農工大學, 日本

(1991. 11. 15 접수)

Contribution of Dimer to Reaction and Diffusion of C.I. Reactive Blue 19 in Cellulose

In Hoi Kim, Hiromi Motomura and Zenzo Morita

School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

(Received November 10, 1991)

Abstract—C.I. Reactive Blue 19에 대한 hydroxylethylsulfonyl type의 수용액에서의 용해성과 안정성을 조사한 결과 이온강력 0.15, pH 5.8과 9.2에서 초기의 용해도를 4시간 동안 유지했으며, 이온강력을 증가시키면 용해도의 안정성이 감소했다. 그러나 용액을 교반하면 안정성이 증가하여 이온강력 0.30에서 초기용해도가 하루 동안 유지되었다. 셀로판 필름을 원주형태의 롤로 만들어 확산과 흡착 거동을 조사한 결과 hydroxylethylsulfonyl type의 용액 농도가 증가하면 표면농도, C_0가 증가했으나 확산계수, D는 일정한 값을 유지했다. Bis(arylsulfonylethyl)ether type의 셀룰로우스와의 반응성은 vinylsulfonyl type에 대해 겉보기 반응속도가 1/6 정도였다.

1. Introduction

Vinylsulfonyl (VS) dyes have grown into the largest dye group of reactive dyes. Rys and Stamm[1] investigated the hydrolysis mechanism of C.I. Reactive Yellow 17 and Blue 19 and proved the formation of bis(arylsulfonylethyl) ether (E) as a by-product. We estimated the rate constant k for the formation and decomposition of the E type for C.I. Reactive Yellow 17, Orange 16, and Blue 19 (k for the formation : Blue 19$\gg$Yellow 17$>$ Orange 16).[2] Blue 19 has excellent wet and light fastness in VS dyes and also some deficiencies in the dyeing properties. However, the essential reason of the deficiency has not been quantitatively elucidated. A low solubility of the hydroxyethylsulfonyl (Hy) type and an easy formation of the E type with high affinity have been known.

In the present study, the solubility and stability of the Hy and E types for Blue 19 in an aqueous solution are examined, and their diffusion and adsorption behaviors are studied by the method of cylindrical film roll. The reactivity of E type with cellulose is also estimated.

2. Experimental

2.1 Film and Reactive Dye

Cellophane film was cut into pieces of 5 cm wide and 60 cm long and then scoured in boiling water for 2 h. The cylindrical cellophane film roll was made by a usual method.[3]

The commercial dye sample of Blue 19 and the sample containing no dispersing agent, which were supplied by Sumitomo Chemical Co. Ltd., were purified with organic solvent.[4] The dimer of Blue 19 was made by the reaction between VS type and Hy type. The components of dye were analyzed by HPLC.[5]

2.2 Solubility and Stability

The pH of the dyebath was adjusted by Kolthoff's buffer solution. Their ionic strength was adjusted by the addition of sodium sulfate. A dye sample was dissolved in water at 100°C and then each dye solution was kept at 50°C without stirring. After suitable time, an aliquot of the solution was pipetted out and was analyzed spectrophotometrically and by HPLC if necessary.

2.3 Diffusion and Adsorption

The experimental method was same as before.[6] The diffusion of the Hy and E types was examined by the method of cylindrical film roll.

3. Results and Discussion

3.1 Solubility of Hy type

Fig. 1 and 2 show the variation in the solubility of Hy type and that of a mixture of Hy and E types with time in an aqueous solution of various ionic strengths (I) at 50°C. The initial solubility of Hy type was kept for 4 h at I=0.15 and pH 5.8 and 9.2. An increase in the ionic strength decreased the stability in the solubility of Hy type. Stirring the solution increased the stability and kept the initial solubility of Hy type constant for at least one day at I=0.30.

The absorption spectra of a mixture of the Hy and E types were not varied with the change in the molar ratio, if the total concentration of a mixture was kept constant in the monomer unit. The total concentration of a mixture of Hy and E types was kept constant for at lease three days at I=0.15 and 50°C, and an increase in the ionic strength decreased the stability, as shown in Fig. 2. Within the experimental time, the composition or the molar ratio of Hy and E typess was confirmed to be constant by HPLC. The E type seemed to increase the stability in the solubility of Hy type. In practice, some dispersing agents are used to prevent the precipitation of Hy type in the dyebath. From the results of the present study, an experimental condition (I=0.15 and pH 5.8) was adopted.

3.2 Diffusion and Adsorption of Hy and E types

When a cellophane roll is immersed in a solution of Hy and E types, the Hy and E types are adsorbed on the surface of the substrate and dif-

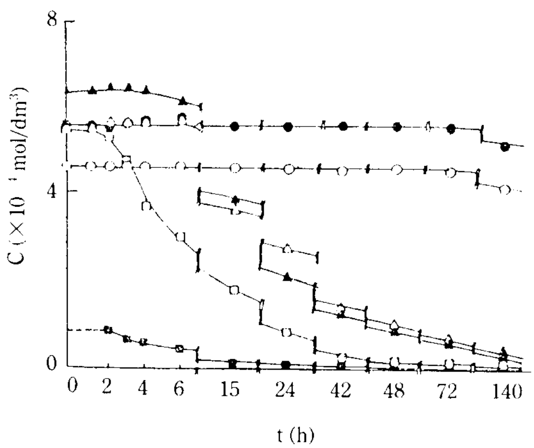

Fig. 1. Variation of solubility of the Hy type for C.I. Reactive Blue 19 at 50°C and at various I's. (● : I=0.03 ; and ○ : I=0 ; △ : I=0.15 at pH 5.8 ; ▲ : I=0.15 at pH 9.2 ; □ : I=0.30 at pH 5.8 ; ■ : I=0.30 at pH 9.2).

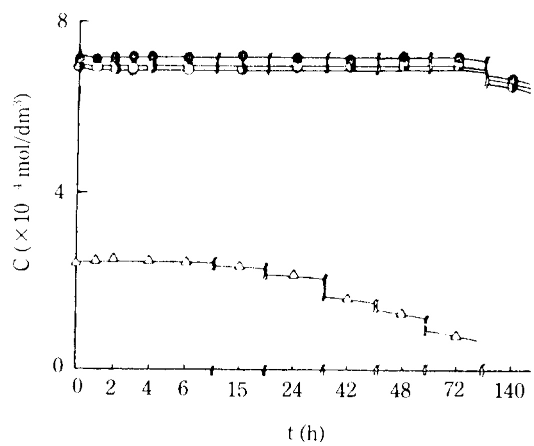

Fig. 2. Stability of solution of the mixture (E : Hy = 70.2 : 29.8 monomer mol% for C.I. Reactive Blue 19 at 50°C and various I's. (○ : I=0 ; ◐ : I=0.15 at pH 9.2 ; ● : I=0.15 at pH 5.8 ; △ : I=0.30 at pH 5.8).

fuse into it. The film roll may be regarded to be a semi-infinite medium. The diffusion profiles of Hy type and a mixture of Hy and E types in cellulose obtained are shown in Fig. 3. If plots of the concentration vs. $x/2\sqrt{t}$ were made, a diffusion profile was obtained, which showed a constant surface concentration, C_0 (mol/kg), and a diffusion coefficient obeying Fick's law, D (cm^2/min). With an increase in the solution concentration of Hy type, the values of C_0 for Hy type were increased but those of D were kept constant ($D=2.1\times10^{-6}$ cm^2/min).

The diffusion profile obtained from the solution of a mixture of Hy and E types is also shown in Fig. 3. When it is compared with that of the Hy type, the E type seems to diffuse independently. Since an extrapolation of the profiles to the surface gives the surface concentration, the adsorption isotherms for Hy and E types were obtained. The subtraction of the corresponding profile of Hy type from the total one gives the profile for E type. The value of C_0 for E type was kept constant during diffusion experiment and the value of D for the E type was estimated to be 0.85×10^{-6} cm^2/min. The affinities for VS, E and Hy types were nearly equal to one another. The E type is adsorbed on cellulose and diffuses into the substrate, if it is formed in the dyebath.

3.3 Reaction of E type with Cellulose

After a mixture of the Hy and E types was adsorbed on cellophane, the film was rolled on a glass tube and then new cellophane film was further rolled on the cellophane roll. The film roll thus made was immersed in an aqueous solution of sodium carbona (0.05 mol/dm^3) at 50℃. By adsorbing the VS type on cellophane, a similar experiments was carried out. The concentration profiles of fixed and unfixed species after the immersion for 4 h are shown in Fig. 4. The E type reacted more slowly with cellulose than the VS type did. The apparent rate of reaction with cellulose for the E type was estimated to be about one sixth of the VS type. The variation in the molar ratio of Hy and E types adsorbed gave no effect on the apparent reactivity of E type. The completion of reaction of E type with cellulose in this experiment required about 3 days under these conditions.

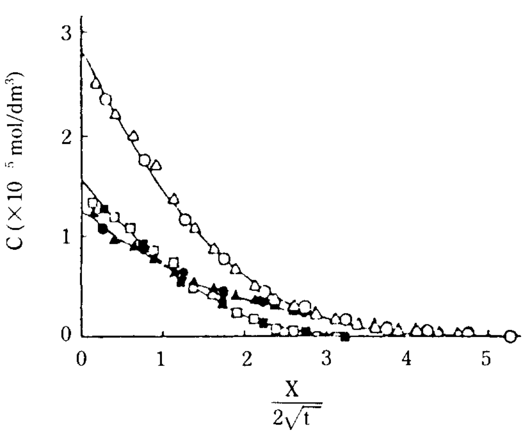

Fig. 3. Diffusion profiless of the mixture (E : Hy= 70.2 : 29.8 monomer mol %, ○ : 1 h, △ : 4 h), Hy type (● : 1 h, ▲ : 4 h) and E type (for C.I. ■ : 1 h, □ : 4 h) Reactive Blue 19 in cellulose at 50°C, pH 5.8, and at I=0.15 (Conc. of the E type=1.49×10^{-3} monomer mol/dm^3, that for Hy type=5.90×10^{-4} monomer mol /dm^3).

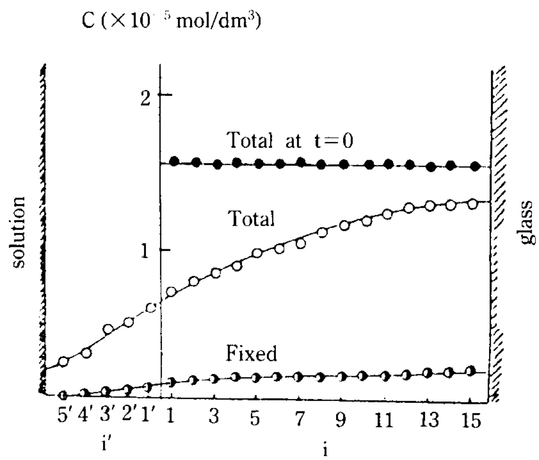

Fig. 4. Concentration profiles of the mixture (E : Hy=70.2 : 29.8 monomer mol%) for C.I. Reactive Blue 19 after the reaction with cellulose and water in substrate in Na_2CO_3 (0.05 M) soln. at 50°C, I=0.15, and for 4 h.
(● : total at t=0 ; ○ : total ; ◑ : fixed)
i : No. of layers, i' : No. of layers of undyed film

References

1. P. Rys and O.A. Stamm, *Helv. Acta*, **49**, 2287 (1966).
2. I.-H. Kim, H. Motomura and Z. Morita, Preprint of the 30th Sympossium on Dyeing Chemistry, The Chemical Society of Japan and the Society of Fiber Science and Technology, Japan, Osaka, July, 1988, p. 58.
3. H. Motomura and Z. Morita, Sen'i Gakkaishi, **41**, T-390 (1985).
4. H.U. Mehta, M.R. Ravikrishnan, and A.G. Chitale, *J. Soc. Dyers Colour.*, **78**, 552 (1962).
5. I.-H. Kim, H. Motomura and Z. Morita, *Sen'i Gakkaishi*, **45**, 167 (1989).
6. H. Motomura and Z. Morita, *J. Appl. Polym. Sci.*, **24**, 1747 (1979).