

# Fundamental Studies on Solvent Dyeing with Tetrachloroethylene. III. Effect of Water Added to the Solvent Dyebath on the Diffusion of Disperse Dyes in Poly(ethylene Terephthalate)

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## Synopsis

The diffusion and adsorption of disperse dyes on poly(ethylene terephthalate) (PET) from the tetrachloroethylene (TCE) dyebath were investigated by the method of cylindrical film roll when water was added to the TCE dyebath. The diffusion coefficients of three disperse dyes were increased with an increase in the addition of water to the TCE dyebath, and that of C.I. Disperse Violet 8 showed a peak. The solubilities of water in TCE in the absence and presence of disperse dye were measured at 90°C by Karl Fischer titration. The solubilities in TCE were 0.040 in the absence of dye and 0.041–0.045 g H<sub>2</sub>O/100 g TCE in the presence of disperse dye. In the presence of Violet 8, the solubilities showed a peak with increasing addition of water. The effect of water addition on the diffusion coefficients was attributed to the dissolution of water in the TCE dyebath. The water dissolved in TCE brought about an additional swelling of PET swollen previously by TCE. No marked influence on the surface concentration of dye was observed by the water addition to TCE.

## INTRODUCTION

The effect of water added to the tetrachloroethylene (TCE) dyebath on the dyeing behavior of disperse dyes has become of major interest since Gebert's reports.<sup>1,2</sup> The addition of water gives rise to an increase in the color yield and diffusion coefficient of disperse dyes. Gebert has also reported that the color yield was considerably increased when water was added to the ligroin dyebath and that the addition of solvent-soluble emulsifiers to the TCE dyebath has no effect on the dyeing results.<sup>1,2</sup> A similar effect of water has already been reported by Schuler and recently by the present authors in the solvent dyeing with iso-octane.<sup>3,4</sup> In previous papers, the authors have reported the addition effect of water on the diffusion of C.I. Disperse Violet 1 in nylon from the TCE dyebath and no effect of water on that of C.I. Disperse Orange 3 in poly(ethylene terephthalate) (PET) from the trichloroethylene dyebath.<sup>4,5</sup> The booster solvents added to the TCE dyebath are expected to bring about a similar effect as water.<sup>1,2,6</sup> This addition effect has been contributed to the attainment of a new distribution equilibrium, the interaction between dye molecule and water, the carrier action of water, or a new swelling equilibrium. Experiments have not yet been performed to prove these causes.

In the present study, the solubility of water in TCE and that in the TCE dyebath containing disperse dyes is investigated at 90°C. The adsorption and

diffusion of some disperse dyes from the TCE dyebath containing water are also studied at 90° and 130°C. The interrelation between the effect of water added to the TCE dyebath on the diffusion coefficient and adsorption of disperse dyes and the solubilities of water in the dyebath are discussed.

## EXPERIMENTAL

### Materials and Chemicals

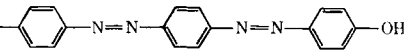
PET films (Mylar C-25, du Pont) treated with water at 160°C for 1 hr, C.I. Disperse Violet 8, the TCE (Toa Gosei Kagaku Kogyo Ltd.) were used as before.<sup>7</sup> C.I. Disperse Red 15 (E. Merck-Schuchardt Preparation for Synthesis), Disperse Yellow 42 (recrystallized with ethanol from the concentrated cake supplied by Mitsubishi Chemical Industries Ltd.), and 1,4-bis(4-hydroxyphenylazo)benzene (synthesized from *N*-acetyl-*p*-phenylenediamine via 4-hydroxy-4'-acetaminoazobenzene<sup>8</sup> and recrystallized with ethanol) were also used as penetrants. The absence of impurities in these dyes was checked by thin-layer chromatography. The other chemicals used were reagent grade.

### Diffusion and Adsorption

Dyeing was carried out by means of the method of cylindrical film roll. As the vapor pressure of the TCE dyebath containing water at 90°C exceeded the atmospheric pressure, a stainless steel high-pressure dyeing bottle or a tightly glass-stoppered diffusion bottle was used. In the latter case, a film roll prepared by the previous method was immersed for a prescribed time in the diffusion bottle containing 100 cm<sup>3</sup> TCE to which a given amount of water and dye was added.<sup>5,7</sup> The time for dissolving the water and dye was 5 or 14 hr. In the case of the stainless steel bottle, the diffusion experiments were carried out by the previous method.<sup>5</sup> Dyeing conditions are shown in Table I. In order to keep the surface concentration constant, i.e., an infinite dyebath condition throughout the diffusion experiments, excess amounts of dye beyond solubility were usually added to the dyebath.

After dyeing and drying, the optical densities of respective layers were measured by means of a Shimadzu MPS-50L recording spectrophotometer. The

TABLE I  
Dyeing Conditions

Dye no.	Dye (dyebath concentration)	Diffusion bottle	Dissolution time of water and dye, hr	Diffusion time, hr
1	C.I. Disperse Yellow 42 (0.75 g/100 cm <sup>3</sup> TCE)	steel	5	15
2	C.I. Disperse Red 15 (0.2 g/100 cm <sup>3</sup> TCE)	glass	14	5
3	 (0.05 g/100 cm <sup>3</sup> TCE)	steel	14	8
4	C.I. Disperse Violet 8 (0.3 g/100 cm <sup>3</sup> TCE)	steel	5	10 or 20

optical density of all the dyes on film was confirmed to obey Beer's law. The diffusion coefficients and surface concentrations were calculated by the Sekido-Matsui method.<sup>7</sup>

### Solubility of Water in the TCE Dyebath

A given amount of water was added to a tightly glass-stoppered bottle to which 100 cm<sup>3</sup> TCE (TCE of reagent grade was also used) was added. It was kept at 90°C in a thermostat for 5, 14, or 96 hr. A known amount of the TCE solution was taken out, and the water contents in the solution were determined by a Karl Fischer Model KFD-S electric titrator (Tsutsui Rikagaku Kikai Ltd.). Chemicals for the titration were Karl Fischer reagents manufactured by Mitsubishi Chemical Industries Ltd.

## RESULTS AND DISCUSSION

### Diffusion and Adsorption

The effect of water added to the TCE dyebath on the diffusion and adsorption of disperse dyes at 90°C are shown in Figures 1 to 4, and those at 130°C, in Figure 5. The diffusion coefficients of C.I. Disperse Yellow 42 (dye 1), Red 15 (dye 2), and synthesized yellow dye (dye 3) were increased with increase in water added to the TCE dyebath, while that of C.I. Disperse Violet 8 (dye 4) showed a peak upon addition of 1–2 g H<sub>2</sub>O/100 g TCE, as shown in Figure 4 and 5. The diffusion coefficients of dyes 2 and 4 from the TCE dyebath were about two to three times that without addition of excess water, and those of dyes 1 and 3 were about four to six times larger. Small differences were also found in the rate of increase of diffusion coefficients upon addition of water to the TCE dyebath containing the

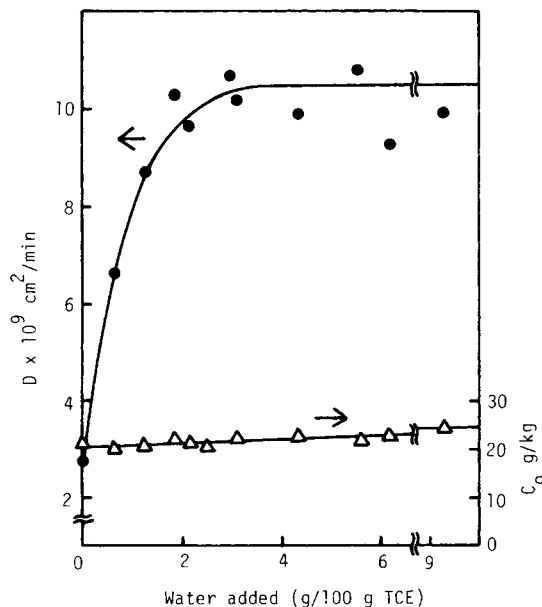


Fig. 1. Effect of water added to the TCE dyebath on the diffusion coefficient  $D$  and surface concentration  $C_0$  of C.I. Disperse Yellow 42 at 90°C (0.75 g dye/100 cm<sup>3</sup> TCE).

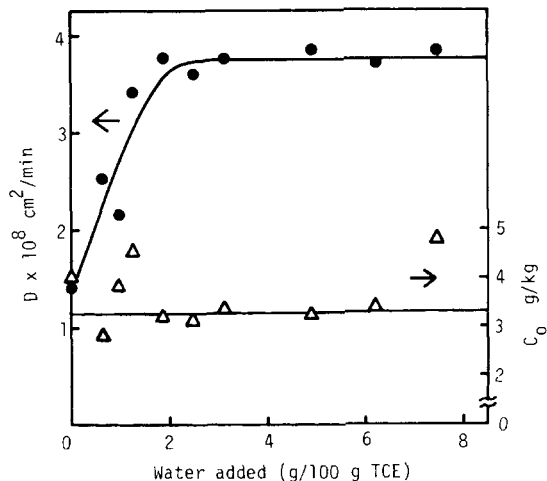


Fig. 2. Effect of water added to the TCE dyebath on  $D$  and  $C_0$  of C.I. Disperse Red 15 at 90°C (0.20 g dye/100 cm<sup>3</sup> TCE).

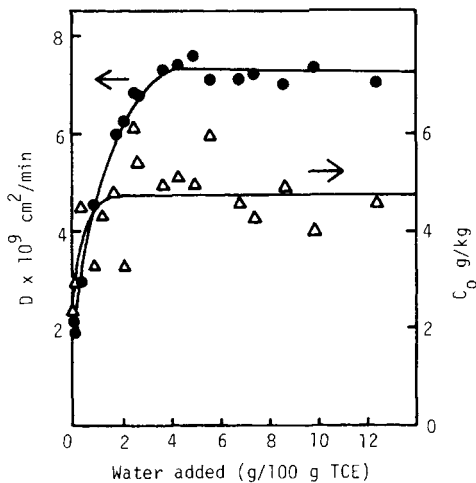


Fig. 3. Effect of water added to the TCE dyebath on  $D$  and  $C_0$  of dye 3 at 90°C (0.050 g dye/100 cm<sup>3</sup> TCE).

four kinds of dyes. Points where the value of diffusion coefficient arrived at the saturated value were observed in the following order: dye 2  $\approx$  dye 1 < dye 3. These facts show that the acceleration effect on the diffusion may be dependent not only upon the amount of water added but also upon the structure of the dyes. As will be mentioned later, the acceleration effect is due to the water dissolved in the TCE dyebath but not to the total amount of water added to the dyebath.

The surface concentrations  $C_0$  of these dyes showed a small increasing tendency with increase in the addition of water, though the values of  $C_0$  showed some scatters. No peak was observed in the  $C_0$  of dye 4, unlike the case of diffusion. These results show that the effects of water added to the TCE dyebath on the adsorption of disperse dyes were relatively small. Gebert has considered the establishment of new distribution equilibria for the dye between the fiber and the dyebath phases as the cause of marked increase in the color yield, i.e., the

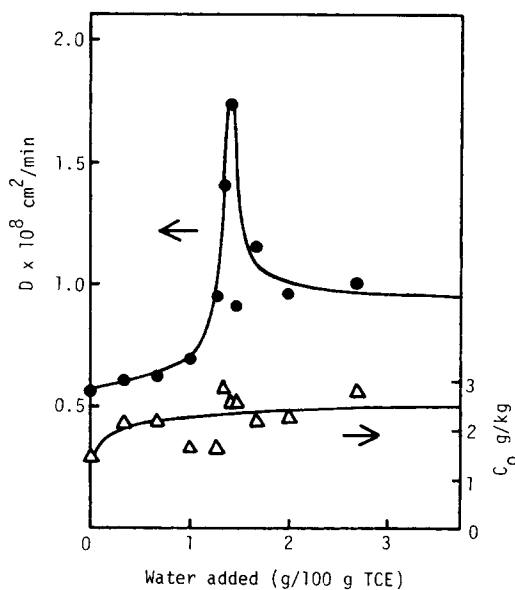


Fig. 4. Effect of water added to the TCE dyebath on  $D$  and  $C_0$  of C.I. Disperse Violet 8 at  $90^\circ\text{C}$  (0.30 g dye/100  $\text{cm}^3$  TCE).

change in distribution coefficient of dye by the addition of water. From the results of the present study, the differences in solubility of the dye in the various phases of the fiber-TCE-water system was considered to be rather small because the solubility of water in TCE was too small to influence that of disperse dye in the dyebath (see the section on the solubility of water in TCE). The cause of the marked increase in color yield in the solvent dyeing with TCE may be attributed to the profound increase in the diffusion coefficient of disperse dyes due to the additional swelling of TCE-swollen PET by water dissolved in the TCE dyebath.

We have also observed a profound increase in the diffusion coefficient and a marked decrease in the surface concentration of disperse dyes when TCE was added to the aqueous dyebath.<sup>9</sup> In this case, the decrease in surface concentration and the increase in diffusion coefficient may also be attributed to the adsorption of TCE on PET.

Some comparisons between the diffusion coefficients of disperse dye from the aqueous and solvent dyebath are summarized in Table II. Usually, diffusion from the solvent dyebath is accelerated by water added to the dyebath, as expected, while diffusion from the pure solvent dyebath is slower than that from the aqueous one. TCE is a special and unique solvent which is different in this respect.

### Solubility of Water in TCE

In order to elucidate the effect of water which accelerated the diffusion of disperse dye from the solvent dyebath when water was added to the dyebath, the solubilities of water in pure TCE and those in the TCE in which disperse dye was dissolved were measured at  $90^\circ\text{C}$ . The results are shown in Figures 6 and 7. The solubility in pure TCE was measured to be 0.040 g  $\text{H}_2\text{O}/100 \text{ g TCE}$  and was smaller than the value obtained by the extrapolation of McGovern's data.<sup>10</sup>

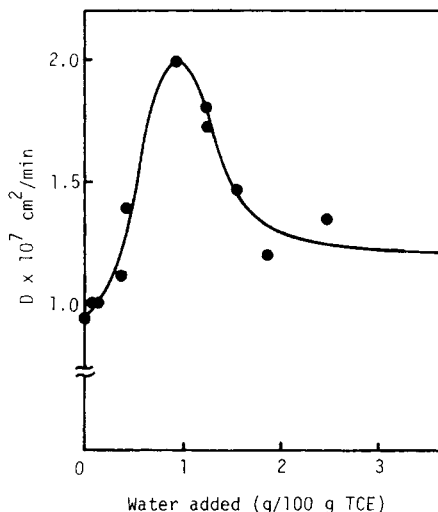


Fig. 5. Effect of water added to the TCE dyebath on  $D$  of C.I. Disperse Violet 8 at  $130^\circ\text{C}$  (0.30 g dye/100  $\text{cm}^3$  TCE).

The Karl Fischer reagent used was calibrated with the standard water methanol solution for Karl Fischer reagent (Mitsubishi Chemical Industries Ltd.) and with sodium tartrate of reagent grade crystallized from water,<sup>11</sup> and the results from both methods were the same. The temperature dependence of aqueous solubility was similar to McGovern's result.<sup>10</sup>

The saturated solubility was attained at a water addition of about 1.2 g  $\text{H}_2\text{O}/100$  g TCE. No effect on the solubility was noted by occasional shaking of the solution. The solubilities measured after 5, 14, and 96 hr were similar to each other, and dissolution was attained after a relatively short time. While all the water added was not dissolved in TCE below the solubility, there were remaining water droplets on the surface of TCE and water vapor on the inner surface of the glass bottle. Only about 3.3% water added was dissolved in TCE when saturated solubility was observed. Thus, a saturated solution was obtained for the first time by a large excess addition of water. These phenomena were also observed at the dissolution of water in TCE at a temperature below  $90^\circ\text{C}$  and at the dissolution in trichloroethylene and isooctane at various temperatures.<sup>12</sup>

On the other hand, the dissolution behavior of water observed has a good correspondence to the addition effect of water on the diffusion of disperse dyes from the TCE dyebath. The fact that the acceleration effect of water on the diffusion from the TCE dyebath in spite of the low solubility of water in TCE

TABLE II  
Comparison of Diffusion Coefficients of Disperse Dye from Various Dyebaths

Substrate	Solvent	Comparison between aqueous and solvent dyeing	Effect of water added	Reference
PET	isooctane	$D_w > D_s$	$D_s < D_{sw}$	3, 5
PET	ligroin	$D_w > D_s$	$D_s < D_{sw}$	1
PET	trichloroethylene	$D_w < D_s$	$D_s \approx D_{sw}$	5
nylon	TCE	$D_w > D_s$	$D_s < D_{sw}$	4
PET	TCE	$D_w < D_s$	$D_s < D_{sw}$	

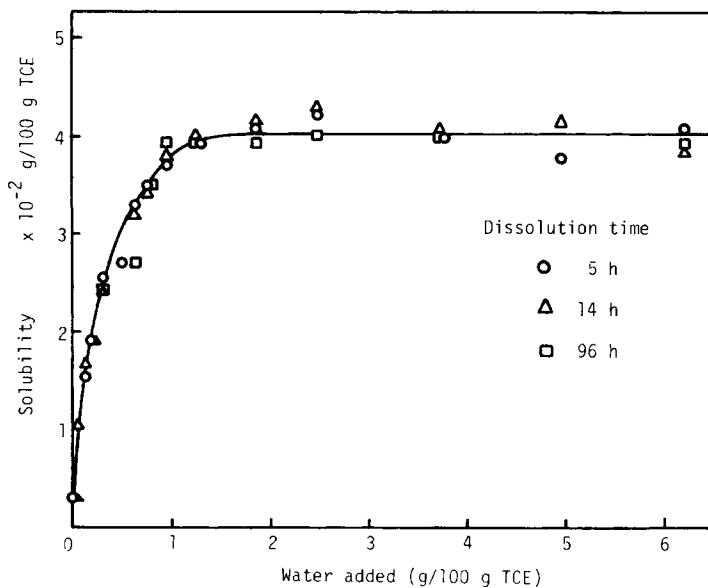


Fig. 6. Solubilities of water in TCE at 90°C.

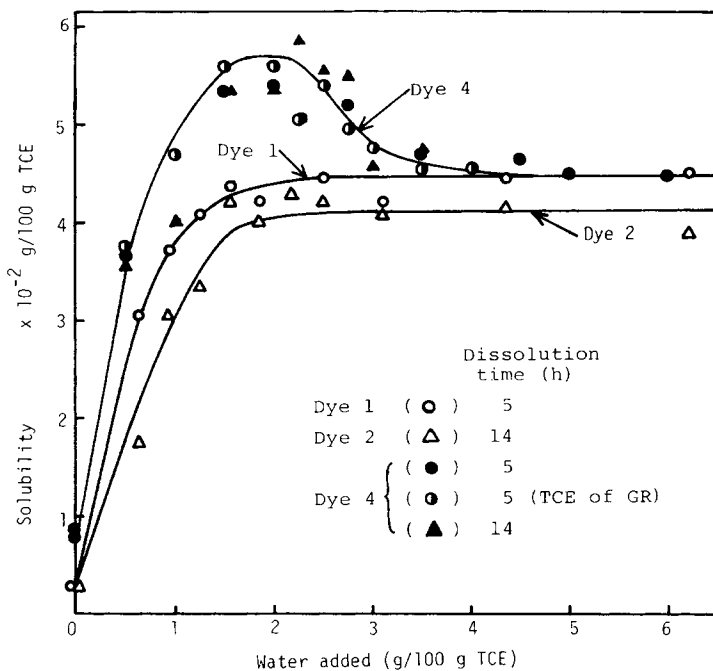


Fig. 7. Solubilities of water in the TCE dyebaths contained C.I. Disperse Yellow 42 (dye 1), Red 15 (dye 2), and Violet 8 (dye 4) at 90°C.

was observed at a few percent of water addition, which was much higher than the solubility, might be attributed to the dissolution behavior of water. The effect of water on color yield of commercial dyes from the TCE dyebath under practical dyeing conditions has been observed in such an amount of water addition.<sup>1,2</sup>

The solubility of water in the TCE dyebath in the presence of disperse dyes shown in Figure 7 shows some differences from that in pure TCE. Those in the presence of Violet 8 have a distinct peak, and the solubility curves in the presence of dye 1 and 2 are shifted to the larger addition of water than in the case of pure TCE. The solubility of water in TCE in the presence of Violet 8 was gradually increased and reached a maximum (0.05 g H<sub>2</sub>O/100 g TCE) at a water addition of 1.3 g H<sub>2</sub>O/100 g TCE, and then decreased to the final solubility (0.045 g H<sub>2</sub>O/100 g TCE) with increasing addition of water. No effect on the solubility was observed by the amount of dye added to the TCE dyebath above the dye solubility (0.02 g dye/100 g TCE), by the dissolution time (5 and 14 hr), by occasional shaking, and by using TCE of reagent grade. A peak in the diffusion coefficient of Violet 8 appeared at a water addition of 1.4 g H<sub>2</sub>O/100 g TCE, as shown in Figure 4. Although there seems to be a little difference in the shape between the curves of the dissolution of water and the diffusion coefficients of Violet 8 (Figs. 4 and 7), it may be concluded that both behaviors had a close correlation with each other and that the unique effect of water addition on the diffusion of Violet 8 may be attributed to the dissolution of water in the TCE dyebath in which Violet 8 was contained, because the unusual phenomenon was only observed in the case of Violet 8. The essential cause, however, is not yet clear.

From the solubility curves of water in TCE in the presence of dyes 1 and 2, the point where the saturated dissolution of water was attained was found at a water addition of 1.6 g H<sub>2</sub>O for dye 1 and of 1.7 g H<sub>2</sub>O/100 g TCE for dye 2, and was higher than that in the case of pure TCE. These points were nearly equal to the similar ones of the diffusion coefficients mentioned earlier. The solubilities of water in the TCE dyebath were measured to be 0.045 (the same value as dye 4) in the presence of dye 1 and 0.041 g H<sub>2</sub>O/100 g TCE in the presence of dye 2, respectively, and thus were dependent upon the dye structure dissolved in the TCE dyebath.

As mentioned earlier, the acceleration effect of water on the diffusion of dye is attributed to the water dissolved in the TCE dyebath. The role of water is the additional swelling of PET swollen previously by TCE.

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