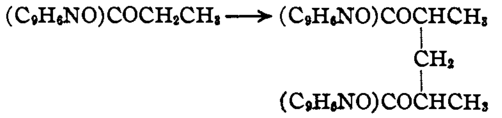
(3) 5-Propionyl-8-hydroxyquinoline gives ω-methylene-bis-5-propionyl-8-hydroxyquinoline.



$$(C_9H_6NO)COCH_2CH_3 \longrightarrow \begin{array}{c}(C_9H_6NO)COCHCH_3\\ |\\ CH_2\\ |\\ (C_9H_6NO)COCHCH_3\end{array}$$

## Experimental

A solution of aminomonoketone (1 g.) in formalin (40% 6–10 cc.) was refluxed on a water-bath for two to three hours, excess formaldehyde removed by evaporation as far as possible and water added. The resulting sirupy mass became solid on standing.

In the case of *p*-dimethylaminodesoxybenzoins, pyridine (10 cc.) was added as a solvent in the reaction.

In conclusion, the author desires to thank Professor Hata for the interest in this work and Professor Goto for the suggestion at which this work was done.

## Summary

1. Condensation of 5-propionyl-8-hydroxyquinoline with formaldehyde gives ω-methylene-bis-5-propionyl-8-hydroxyquinoline.

2. Condensation of formaldehyde either with *p*-aminoacetophenone or with *p*-dimethylaminodesoxybenzoins (α and β) gives the compounds which have an hydroxymethyl group.

TOKYO, JAPAN RECEIVED OCTOBER 1, 1934

---

[CONTRIBUTION FROM THE TECHNICAL LABORATORY, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

# The Dyeing of Cotton: Particle Size and Substantivity. I

BY SAMUEL LENHER AND J. EDWARD SMITH

## Introduction

Recent studies[1–5] of the dyeing of cotton with direct or substantive dyes emphasize the relation between the degree of dispersion of the dye and its characteristic dyeing properties. The particle size of dyes has been frequently calculated from the rate of diffusion by the Einstein[6] equation

$$D = RT/N \times 1/6\pi\eta r \qquad (1)$$

The correct estimation of the degree of dispersion of substantive dyes by this equation is possible only by careful consideration of the factors arising in the diffusion of colloidal electrolytes. Williams and Cady[7] recently surveyed the literature on diffusion measurements and their application to the estimation of particle size. Doubt as to the exact shape of the colloidal masses raises question as to the absolute accuracy of equation (1) in estimating the size of dye particles. Herzog, Illig and Kudar[8] showed that the error caused by assuming the particles to be spheres is relatively small except in cases involving extreme elongation. Hartley and Robinson[9] proved theoretically that diffusion constants of electrolyte free dyes of the type NaR are no criterion of their particle size. This fact has been used as a basis of criticism by Robinson[10] and by Neale[11] of previous work on the degree of dispersion of dyes. However, Hartley and Robinson[9] state that a relatively accurate estimate of the particle size is possible in the presence of large concentrations of inorganic electrolytes containing a common ion. Two methods are generally used for determining diffusion constants of dyes: (1) diffusion into gelatin, and (2) free diffusion into water. The methods are not applicable at the elevated temperatures used in dyeing processes. The known marked difference in the dyeing properties of substantive dyes at varying temperatures makes a study of particle size variation with temperature a matter of extreme importance. The diffusion method of Northrop and Anson,[12] used by McBain and others,[13] depends on the rate of diffusion through a porous diaphragm after a uniform concentration gradient is estab-

---

(1) Kurt and Brass, *Kolloid-Beihefte*, **37**, 56 (1932).

(2) Lenher and Smith, *Ind. Eng. Chem.*, **27**, 20 (1935).

(3) Schäffer, *Z. angew. Chem.*, **46**, 618 (1933).

(4) Schramek and Götte, *Kolloid-Beihefte*, **34**, 318 (1932).

(5) Rose, *Am. Dyestuff Reptr.*, **21**, 52 (1932).

(6) Einstein, *Ann. Physik*, **17**, 549 (1905).

(7) Williams and Cady, *Chem. Rev.*, **14**, 171 (1934).

(8) Herzog, Illig and Kudar, *Z. physik. Chem.*, **167A**, 329 (1934).

(9) Hartley and Robinson, *Proc. Roy. Soc.* (London), **A134**, 20 (1931).

(10) Robinson, *J. Soc. Dyers Colourists*, **50**, 171 (1934).

(11) Neale, *Am. Dyestuff Reptr.*, **22**, 237 (1933).

(12) Northrop and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

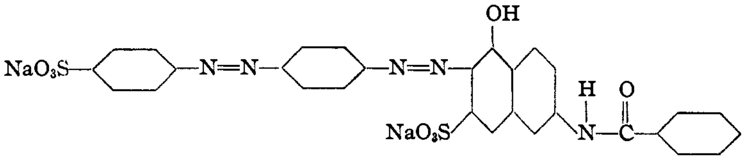
(13) McBain and Liu, THIS JOURNAL, **53**, 59 (1931); McBain and Dawson, *ibid.*, **56**, 52 (1934).

lished. The method gives accurate results at 25° and is capable in principle of use over a wide temperature range.

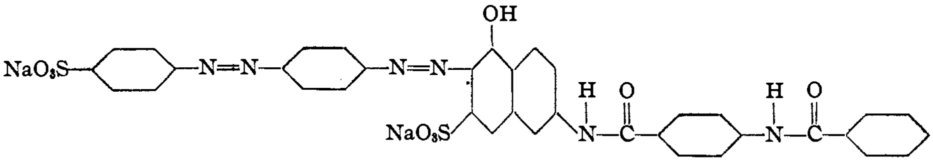
It is the purpose of this paper: (1) to give experimental data confirming the theoretical treatment of diffusion constants by Hartley and Robinson; (2) to describe the variation in the particle size of dyes at varying electrolyte concentrations over a range of temperatures; (3) to show characteristic relationships existing between the particle size and the absorption of dyes by cotton.[14]

## Experimental

Two dyestuffs of closely related chemical structure but which show wide differences in their application characteristics were studied. These are the two azo dyestuffs (1) *p*-sulfobenzene-azo-benzene-azo-6-benzoylamino-1-naphthol-3-sulfonic acid (sodium salt)



and (2) *p*-sulfobenzene-azo-benzene-azo-6-benzoyl-*p*-aminobenzoylamino-1-naphthol-3-sulfonic acid (sodium salt)



Solutions of dye (1) were found by the authors[2] to be less sensitive to electrolytes than those of most colors. This is a property of the dye which is of advantage in a theoretical study of diffusion rates in the presence of inorganic salts. The molecular weight of dye (1) is 675 and of dye (2) is 794. The identifying difference between these two dyestuffs is the presence of a second CONH group in dye (2).

Dye (1) is characterized by its excellent level dyeing properties, poor fastness to washing, and poor exhaust from the dye-bath. Dye (2) in contrast is more difficult to dye level and shows superior wash fastness as well as a high exhaust from the dye-bath. The authors[2] have previously correlated these differences with the degree of salt sensitivity (the sensitivity to aggregation in the presence of low concentrations of inorganic electrolytes) of the dyes.

**Preparation and Purification of Dyes.**—The dyes were prepared[15] by methods in current use for the manufacture of azo colors. The intermediates used were purified by repeated salting with sodium chloride to remove organic impurities. The dyes were also purified by resalting. The absence of electrolytes in the dyes is of the utmost importance in obtaining diffusion measurements for a theoretical study. Methods frequently reported for purification of this type of color are: (1) dialysis of the dye solution[4]; (2) repeated salting with sodium acetate followed by alcohol extraction.[16] The dialysis method gives the dye as a mixture of the free acid and the sodium salt. These methods do not permit the preparation of the pure sodium salt unless great care is taken to eliminate calcium and magnesium salts in the preparation of intermediates. The dyes used in this work were freed of electrolytes by the method of Rose,[17] which possesses obvious advantages. Rose's method consists in the conversion of the dyes to the arylguanidine salts which are insoluble in water. In the present purification, the dyes were converted to the diortho-tolylguanidine salts. The diortho-tolylguanidine salts were washed with water to free them completely from inorganic sulfates and chlorides. The resulting salts gave a negative test for ionic sulfate with barium chloride and a negative test for ionic chlorine with silver nitrate. The electrolyte-free dye salts were dissolved in alcohol and were converted by metathesis to the sodium salt by the addition of sodium hydroxide. The precipitated sodium salts of the dyes were filtered and washed with alcohol until they were free of diortho-tolylguanidine. The dyes were dried at 100° for twenty-four hours.

*Anal.* Dye (1) calcd. for $C_{29}H_{19}O_8N_5S_2Na_2$: C, 51.53; H, 2.84; N, 10.37; S, 9.49; azo N, 8.29. Found: C, 46.77; H, 3.60; N, 9.59; S, 8.65; azo N, 7.61; $H_2O$, 9.1. Dye (2) calcd. for $C_{36}H_{24}O_9N_6S_2Na_2$: C, 54.38; H, 3.05; N, 10.58; S, 8.07; azo N, 7.05. Found: C, 49.15; H, 3.86; N, 9.37; S, 7.33; azo N, 6.32; $H_2O$, 10.1.

The analytical[18] data show that dye (1) contained 91.4% and dye (2) contained 89.8% of anhydrous material. The remainder of each sample was water, probably held as water of crystallization.

---

[14] Since this paper was written several important papers on the mechanism of dyeing with substantive dyes and on the diffusion of colloidal electrolytes have appeared in the preprints of papers presented at the symposium of the Faraday Society on Colloidal Electrolytes in September, 1934.

[15] We are indebted to Dr. E. F. Hitch, Mr. A. R. Murphy and Dr. C. K. Black of the Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., for the preparation and purification of these dyes.

[16] Lubs, *Ind. Eng. Chem.*, **11**, 456 (1919).

[17] Rose, U. S. Patent 1,674,128, June 19, 1928; *Ind. Eng. Chem.*, **25**, 1028 (1933).

[18] These analyses were carried out under the direction of Mr. G. F. Palfrey, Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co.

**Diffusion Experiments.**—Water-soluble substantive dyes are ionized in solution. In the free diffusion of substantive dyes, as the very mobile positive ion diffuses it accelerates the movement of the negative color ion. Hartley and Robinson[9] have shown theoretically that the addition of an electrolyte containing a common positive ion reduces the effect of this ion in accelerating the movement of the color ion. Since measurements of this effect in the diffusion of dyes have not been reported in the literature it appeared advisable to study its magnitude and bearing on the application of diffusion data in the calculation of particle sizes. Measurements were made by two methods: (1) observations were made of the rate of diffusion of the dyes from their solutions into water and into dilute sodium chloride solutions; (2) observations were made of the rate of diffusion of the dyes from solutions containing sodium chloride into water and into sodium chloride solutions. The dye solutions were prepared at the boil with redistilled water and were aged at room temperature for at least eighteen hours. The diffusion constants were determined by the Fürth[19] micro-diffusion method as described by the authors.[2] The data are summarized in Table I. Table I includes values of the particle radius (R) calculated by the Einstein[6] equation. The apparent molecular weight ($m$) of the dye particles may be calculated from the equation

$$m = 4/3\pi r^3 g N \qquad (2)$$

where $g$, the specific gravity of dye (1) is 1.72 and of dye (2) is 1.58.

TABLE I

DIFFUSION OF DYES (1) AND (2) AT 25°

Dye 1 formula wt. 675

| Solution g./l. of Dye (Dry) | + NaCl | Age soln., hours | Diffusing into NaCl soln., g./1 | $D \times 10^{-6}$ sq. cm./sec. | Estimated $R \times 10^{-8}$ cm. |
|---|---|---|---|---|---|
| 1.0 | ... | ... | ... | 8.84 | 2.7 |
| 1.0 | ... | ... | 0.174 | 4.07 | 6.0 |
| 1.0 | ... | ... | .5 | 3.10 | 7.8 |
| 0.5 | ... | ... | ... | 9.01 | 2.7 |
| .5 | ... | ... | .087 | 3.84 | 6.3 |
| 1.0 | 1.0 | 18 | ... | 3.18 | 7.6 |
| 1.0 | 1.0 | 90 | ... | 2.31 | 10.5 |
| 1.0 | 1.0 | 90 | .5 | 2.40 | 10.1 |
| 0.5 | 1.0 | 48 | ... | 2.83 | 8.6 |
| .5 | 1.0 | 48 | .5 | 2.82 | 8.6 |
| .5 | 1.0 | 168 | ... | 2.38 | 10.2 |
| .5 | 1.0 | 168 | .5 | 2.45 | 9.9 |
| Dye 2 formula wt. 794 | | | | | |
| 0.5 | ... | ... | ... | 7.73 | 3.1 |
| .45 | ... | ... | 0.074 | 4.21 | 5.8 |
| .45 | ... | ... | .067 | 2.93 | 8.3 |
| 1.0 | 1.0 | 120 | ... | 0.99 | 24.5 |
| 1.0 | 1.0 | 336 | ... | .96 | 25.3 |
| 1.0 | 1.0 | 312 | .5 | 1.04 | 23.9 |
| 0.5 | 1.0 | 48 | ... | 0.94 | 25.7 |
| 0.5 | 1.0 | 72 | .5 | .93 | 26.1 |

The data in Table I show that the rate of diffusion of the dyes into water is about twice the rate of diffusion into a sodium chloride solution of a concentration sufficient to produce a uniform distribution of sodium ions in the cell (assuming complete ionization of the dye molecule). The results for diffusion into sodium chloride with dye (1) were obtained without difficulty, but those with the highly salt sensitive dye (2) are subject to variation since the accelerated diffusion effect previously described by the authors[20] frequently occurs. The measured values for the diffusion of dye (2) into a salt solution represent three successful determinations in nine trials. The boundary disturbances are probably caused by a non-uniform distribution of sodium ions in the cell, and indicate that dye (2) is considerably aggregated. The extreme sensitivity of dye (2) toward sodium chloride is shown by a variation of 30% in the diffusion constant with a 10% variation in the concentration of the salt solution.

The apparent molecular weights of dyes (1) and (2) calculated from the rate of diffusion into water are approximately 100 and are small fractions of the formula molecular weights. These results are as predicted from the discussions of Hartley and Robinson[9] and show that the Einstein equation is not applicable to solutions of electrolyte free dyes. The potential gradient established between the sodium ions and the color ions of the dyes in the diffusion process can be made negligible by carrying out the diffusion into a solution of sodium chloride of concentration adjusted to provide an equivalence of sodium ions throughout the cell at the beginning of the experiment. With dye (1) this condition was fulfilled (assuming complete ionization) by diffusion from dye solutions of 1.0 g./l. and 0.5 g./l. into sodium chloride solutions of 0.174 g./l. and 0.087 g./l. The molecular weights of the dye in solution as calculated from equation (2) are 900 and 1100, respectively, as compared to a formula weight of 675. Equivalence of sodium ions in the diffusion of dye (2) was obtained in diffusion from a 0.45 g./l. solution of the dye into a 0.067 g./l. solution of sodium chloride. The molecular weight of dye (2) in solution is 2300 by this experiment. The data show that dye (2) in solution is definitely aggregated to form micelles even in the absence of inorganic salts. Dye (1) is much less aggregated in solution under comparable conditions and approaches the molecular state in solution,

(19) Fürth, *Kolloid.-Z.*, **41**, 300 (1927).

(20) Lenher and Smith, THIS JOURNAL, **56**, 999 (1934).

Measurements of the diffusion of dyes (1) and (2) from a dilute sodium chloride solution (1.0 g./l.) into water and into a more dilute sodium chloride solution (0.5 g./l.) show that the diffusion constants obtained by the two methods are almost identical. The quantities of sodium chloride in the dye solutions give sodium ion concentrations of 10–30 times that present from the ionization of the dye. It is apparent that the diffusion of sodium ions from these solutions is accompanied by movement of the highly mobile chloride ions in quantities that prevent the establishment of a potential gradient between the sodium and dye ions. The data show that the condition of electroneutrality of the dye particles is not important for the calculation of particle sizes in the application of the diffusion data obtained in the presence of low concentrations of inorganic salts.

**Effect of Electrolytes on the Particle Size of Dyes.**—The effect of various electrolytes, used in dyeing processes, on the agglomeration of dyes (1) and (2) was measured at 25°. The range of electrolyte concentrations covered those used in commercial dyeing practice. Measurements with dye (1) in the presence of sodium chloride and sodium sulfate were made in duplicate to establish the reproducibility of the data. The method was as follows: the dye solutions were prepared at the boil and aged at 25° in a water thermostat. The diffusion constants were determined by the Fürth method using a cell housed in an air thermostat controlled to ±0.5°. The particle radii of the dyes were calculated by equation (1) and the molecular weights of the micelles by equation (2). The data are summarized in Table II.

The diffusion measurements for individual solutions are reproducible within 6%. The data show that sodium chloride, sodium sulfate and sodium sulfate + acetic acid exert an agglomerating effect at 25° on both dyes (1) and (2). Sodium chloride is much stronger in its action than sodium sulfate. The addition of a small amount of acetic acid has little added effect in the presence of sodium sulfate. Dye (2) is the more highly aggregated of the two colors and the average radius of its micelles is larger than the limiting dyeing size of 17 × $10^{-8}$ cm. previously described by the authors (2). Dye (1) remains in relatively small aggregates which can be readily absorbed by cotton at 25°. These results confirm those obtained by the authors[2] with commercial materials.

TABLE II

AGGLOMERATION OF DYES (1) AND (2) BY ELECTROLYTES AT 25°

| Solution (g./l.) of Dye (1) + NaCl | | | Age of dye soln., hrs. | $D \times 10^{-6}$, sq. cm./sec. | Estimated $R \times 10^{-8}$ cm. |
|---|---|---|---|---|---|
| 0.5 | 6.25 | | 20 | 1.52 | 16.0 |
| .5 | 6.25 | | 116 | 1.57 | 15.5 |
| .5 | 6.25 | | 117 | 1.41 | 17.2 |
| .5 | 2.5 | | 22 | 2.08 | 11.7 |
| .5 | 2.5 | | 118 | 1.63 | 14.9 |
| .5 | 2.5 | | 137 | 1.72 | 14.1 |
| Dye (1) + $Na_2SO_4$ | | | | | |
| 0.5 | 6.25 | | 19 | 2.50 | 9.7 |
| .5 | 6.25 | | 115 | 2.39 | 10.2 |
| .5 | 6.25 | | 113 | 2.49 | 9.7 |
| .5 | 2.5 | | 21 | 3.19 | 7.6 |
| .5 | 2.5 | | 117 | 3.01 | 8.1 |
| .5 | 2.5 | | 117 | 3.13 | 7.8 |
| Dye (1) + $Na_2SO_4$ + $CH_3COOH$ | | | | | |
| 0.5 | 2.5 | 0.1 | 18 | 3.14 | 7.7 |
| .5 | 2.5 | .25 | 18 | 2.76 | 8.8 |
| Dye (2) + NaCl | | | | | |
| 0.5 | 6.25 | | 21 | 0.71 | 34.2 |
| .5 | 6.25 | | 141 | .67 | 36.2 |
| .5 | 2.5 | | 23 | .72 | 33.7 |
| .5 | 2.5 | | 143 | .79 | 30.7 |
| Dye (2) + $Na_2SO_4$ | | | | | |
| 0.5 | 6.25 | | 18 | 1.60 | 15.2 |
| .5 | 6.25 | | 114 | 1.42 | 17.1 |
| .5 | 2.5 | | 21 | 1.32 | 18.4 |
| .5 | 2.5 | | 141 | 1.42 | 17.1 |
| Dye (2) + $Na_2SO_4$ + $CH_3COOH$ | | | | | |
| 0.5 | 2.5 | 0.25 | 42 | 1.18 | 20.6 |

**Dye Particle Size Variation with Temperature.**—Measurements were made of the diffusion constants and related particle sizes of dyes (1) and (2) in the presence of sodium chloride at temperatures ranging from 50–95°. The McBain[13] type of diffusion cell[21] was used for this work. The calculations of the diffusion constants were made by the Fick equation

$$ds = DA\,\frac{dc}{dx}\,dt \qquad (3)$$

The value of ($ds/dt$) was taken as the quantity of dye diffusing through the membrane per twenty-four hours. It was assumed that the diffusion occurred into water; consequently ($dc/dx$) was taken as the initial concentration of the solution in the cell. Since the cell concentration varied less than 2% during a run the error introduced by the assumption is negligible for the pur-

---

[21] These cells were obtained from Schott and Gen., Jena, Germany; American agents, Fish-Schurman Corporation, 230 East 45th Street, New York, N. Y,

poses of this work. Three cells were used; two were of an average pore size, 8–10 microns and the third of an average pore size, 1.5 microns. Each cell was calibrated to obtain the value of (A) with a solution of dye (2) in the following manner. The cell was cleaned with a potassium dichromate–sulfuric acid mixture and rinsed with water until the wash water was neutral. A solution of 1.0 g./l. of dye (2) in 6.25 g./l. of sodium chloride was prepared at the boil and aged at 25° in a thermostat for four days. The cell was rinsed with the dye solution, filled to the level of the stopcock, and then clamped in a vertical position on a ringstand. The porous glass diaphragm was leveled with a large surface of water, and the cell then immersed to the stem in 250 cc. of a 6.25 g./l. sodium chloride solution in a glazed porcelain pot. The temperature was controlled at 25.1 ± 0.05° by a water thermostat. Calibration of each cell was made by obtaining from six to nine measurements of the rate of diffusion of the dye through the membrane. The analytical data were obtained spectrophotometrically on the basis of Beer's law. The error in this method of analysis is about 2%. Simultaneous measurements of the diffusion constant were made by Fürth's method. The value of $A$ in equation (3) was calculated by substitution of the values obtained for $(\mathrm{d}s/\mathrm{d}t)$, $D$ and $(\mathrm{d}c/\mathrm{d}x)$.

Measurements over a temperature range were made for diffusion from a solution containing 1.0 g./l. of dye and 6.25 g./l. of sodium chloride into a sodium chloride solution of equal concentration. The temperature was maintained by a water thermostat to ±0.05 at 50° and ±0.1 at 95°. Wool felt insulation at the top of the pots retarded evaporation from the salt solution. The volume was maintained by additions of water. The data are summarized in Table III.

TABLE III

DYE PARTICLE SIZE VARIATION WITH TEMPERATURE

| Dye | $T$, °C. | $D \times 10^{-6}$ cm.$^2$/sec. | Estimated $R \times 10^{-8}$ |
|---|---|---|---|
| (1) | 50.1 | 3.10 ± 0.07 | 13.7 |
| (1) | 65.8 | 5.61 ± .11 | 10.2 |
| (1) | 80.0 | 7.70 ± .18 | 9.3 |
| (1) | 95.5 | 10.05 ± .3 | 9.0 |
| (2)[a] | 25.1 | 0.96 ± .06 | 25.3 |
| (2) | 50.2 | 1.75 ± .05 | 24.6 |
| (2) | 65.5 | 2.26 ± .08 | 25.2 |
| (2) | 80.6 | 3.86 ± .10 | 18.8 |
| (2) | 95.4 | 7.80 ± .18 | 11.3 |

[a] Value obtained by Fürth method during calibration of cells.

Each result in Table III is the average of at least seven individual determinations during two runs in individual cells. An error of less than 3% enters in each average. This accuracy is comparable with the spectrophotometric analyses.

The data of Table III show that increase of temperature causes a marked lowering of the micelle radius in solutions of substantive dyes containing electrolytes. The effect is continuous with dye (1) but with dye (2) the breaking up of the micelle does not begin until a temperature greater than 65° is reached. The most marked decrease with dye (2) occurs at temperatures above 80°. At temperatures near the boil both dyes (1) and (2) are present in the bath as aggregates of 4–8 molecules.

**Dyeing Experiments.**—A study was made of the absorption of dyes (1) and (2) by cotton of ash contents 0.08 and 0.3%. The cotton of 0.3% ash content was a high grade absorbent surgical cotton. The cotton of low ash content was prepared from this cotton by treatment with 0.0005 $N$ hydrochloric acid at 60° at a ratio of 1:100 for four hours. The cotton was freed of acid by washing in distilled water, hydroextracted and air dried at 80°. The dried cotton was left in the air at room temperature for a week to rehumidify.

The absorption tests were made at temperatures varying from 25–100° with various electrolyte concentrations. Fifty milligrams of dye, 2.5 g. of cotton and a 100 cc, volume was used in each test. This quantity of dye is sufficient to produce at exhaustion a 2% dyeing of the electrolyte free dye and corresponds to a dyeing stronger than those usual in practical dyeing operations. The dye solutions used at 25° were prepared as above for particle size determinations. The cotton was submerged in the dye solution in a wide-mouthed glass bottle and was turned frequently with a glass rod during the first hour. No agitation was provided after the first hour in experiments of longer duration. Tests at 50–85° were run in pint Mason jars rotated in a Launder-Ometer,[22] the standard washing machine of the American Association of Textile Chemists and Colorists.[23] Tests at the boil were run under reflux. The amount of dye absorbed was determined by difference from the quantity of dye

---

[22] Manufactured by the Atlas Electric Devices Co., 360 W. Superior St., Chicago, Illinois.

[23] Appel, Smith and Christison, *Am. Dyestuff Reptr.*, **17**, 679 (1928).

TABLE IV

ABSORPTION EXPERIMENTS AT 25 AND 100°

Tests with suffix (A) were with cotton of 0.08% ash; the other tests were with cotton of 0.3% ash. The maximum possible strength is 2.0 g. per 100 g. of cotton.

| Dye | Electrolyte Series | T, °C. | Time, hrs. | NaCl 6.25 g./l. g. dye 100 g. cotton | NaCl 2.5 g./l. g. dye 100 g. cotton | $Na_2SO_4$ 6.25 g./l. g. dye 100 g. cotton | $Na_2SO_4$ 2.5 g./l. g. dye 100 g. cotton | $Na_2SO_4$ + $CH_3COOH$ 2.5 g./l. + 0.25 g./l. g. dye 100 g. cotton | $CH_3COOH$ 0.25 g./l. g. dye 100 g. cotton | No assistant |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 25 | 1 | 0.600 | 0.468 | 0.570 | 0.420 | 0.388 | 0.098 | 0.058 |
| 1 | 1A | 25 | 1 | .640 | .460 | .580 | .380 | .400 | .070 | .010 |
| 1 | 2 | 25 | 24 | 1.416 | .928 | 1.268 | .816 | .856 | .220 | .120 |
| 1 | 2A | 25 | 24 | 1.336 | .800 | 1.100 | .650 | .680 | .156 | .110 |
| 1 | 3 | 100 | 1 | 0.700 | .460 | 0.610 | .388 | .420 | .088 | .028 |
| 1 | 3A | 100 | 1 | .616 | .340 | .500 | .330 | .330 | .040 | .014 |
| 2 | 4 | 25 | 1 | .140 | .064 | .140 | .064 | .040 | .024 | .004 |
| 2 | 4A | 25 | 1 | .100 | .064 | .080 | .020 | .160 | .080 | .024 |
| 2 | 5 | 25 | 24 | .240 | .160 | .200 | .160 | .140 | .100 | .040 |
| 2 | 5A | 25 | 24 | .240 | .160 | .180 | .160 | .300 | .160 | .080 |
| 2 | 6 | 100 | 1 | 1.060 | .840 | 1.020 | .800 | .800 | .180 | .010 |
| 2 | 6A | 100 | 1 | 0.980 | .810 | 1.040 | .750 | .790 | .180 | .080 |

retained in the solution at the end of the test. The analysis of the solution was carried out spectrophotometrically. The data for the absorption tests are summarized in Tables IV and V.

TABLE V

ABSORPTION TESTS AT VARYING TEMPERATURES

Time, 1 hr. NaCl concn., 6.25 g./l. Dye concn., 0.500 g./l. Volume, 100 cc. Cotton, 2.5 g.

| T, °C. | Dye (1) Dye absorbed per 100 g. cotton, g. | Dye (2) Dye absorbed per 100 g. cotton, g. |
|---|---|---|
| 50 | 0.872 | 0.175 |
| 65 | .860 | .414 |
| 80 | 1.008 | 1.050 |
| 100 | 0.570 | 1.126 |

Tests were run at 25 and 100° with both dyes to determine the time required to reach an equilibrium distribution of dye between the bath and the cotton. The data are summarized in Table VI.

TABLE VI

STUDY OF EQUILIBRIUM ABSORPTION OF DYES (1) AND (2)

Volume, 100 cc. Dye concn., 0.500 g./l. Cotton, 2.5 g.

| Time, hrs. | T, °C. | No asst. | NaCl 6.25 g./l. |
|---|---|---|---|
| Dye (1) absorbed per 100 g. cotton, g. | | | |
| 120 | 25 | 0.180 | ... |
| 335 | 25 | .170 | ... |
| 50 | 25 | ... | 1.412 |
| 553 | 25 | ... | 1.432 |
| 0.5 | 100 | ... | 0.540 |
| 1.0 | 100 | ... | .570 |
| 3.0 | 100 | ... | .570 |
| 6.0 | 100 | ... | .570 |
| Dye (2) absorbed per 100 g. cotton, g. | | | |
| 54 | 25 | 0.240 | ... |
| 557 | 25 | .240 | ... |
| 211 | 25 | ... | 0.380 |
| 576 | 25 | ... | .380 |
| 0.5 | 100 | ... | .844 |
| 1.0 | 100 | ... | 1.126 |
| 3.0 | 100 | ... | 1.240 |
| 6.0 | 100 | ... | 1.330 |
| 24.0 | 100 | ... | 1.480 |

## Discussion

The authors have shown in an examination of twelve commercial dyestuffs[2] that in considering the chemical constitution of substantive dyestuffs the presence of groups known to be effective in producing substantivity in a molecule also acts to increase the sensitivity to electrolytes. The present study of pure dyestuffs in this paper and in the following paper[24] gives further evidence that even with two structurally similar dyestuffs the criterion of salt sensitivity is a more reliable measure of substantivity than consideration of the presence of so-called substantive groups.

Both dyes are only slightly absorbed by cotton in solutions containing no added electrolyte even over a period of weeks. This low absorption is not due to failure of the dye particles to penetrate the cotton fiber since the dye particles are known to be quite small under these conditions. The addition of salts causes an increase, frequently greater than ten-fold, in the absorption of the dyes. The concentration of inorganic matter in cellulose fibers is known[25] to have a decided influence on the degree of absorption of dyes. Our results show that cotton containing 0.08% ash has, in general, slightly less affinity for dyes than does cotton of 0.3% ash content.

Dyes (1) and (2) are strikingly different in their behavior at various temperatures. Dye (1) is absorbed best at 25°; elevation of the temperatures to the boil lowers the degree of ab-

---

(24) Lenher and Smith, THIS JOURNAL, **57**, 504 (1935).

(25) Weltzien and Schultze, *Kolloid-Z.*, **62**, 46 (1933).

sorption by 60%. Dye (2) is scarcely absorbed at 25° but is highly substantive at the boil. These differences are directly related to the observed particle size of the dye micelles. The quantities of electrolyte required to induce marked absorption of the dyes cause aggregation of dye (1) and highly marked aggregation of dye (2) at 25°. The average particle radius of dye (1) is less than $17 \times 10^{-8}$ cm., the limit previously set by the authors as the limiting maximum size for dyeing, while the average particle radius with dye (2) is greater than $17 \times 10^{-8}$ cm. Although an increase in temperature reduces the size of the micelles of both dyes, particles of dye (2) do not reach the optimum dyeing range until the bath is at 80°. Neale[26] and his co-workers have shown that for many substantive dyes the amount of dye absorbed at equilibrium decreases with increase in temperature. Dye (2), which is highly salt sensitive, does not fit in this generalization. The absorption of dye (2), under non-equilibrium conditions, begins to be marked at about 80°. At this temperature the micelles are of radius $18.8 \times 10^{-8}$ cm. This value corresponds closely to the limiting maximum particle size for dyeing at 25°. Since the capillaries of cotton expand in water with increase in temperature it is to be anticipated that absorption of dyes at higher temperatures may be accomplished with particles of radius greater than those which give dyeing at 25°.

Equilibrium in dyeing is established more rapidly with dye (1) than with dye (2). This phenomenon is explained by the higher rate of diffusion of the smaller micelles of dye (1) under comparable conditions.

The data show that sodium sulfate and sodium chloride are equally effective as assistants at equal weight concentrations although the two assistants are markedly different in their aggregating effect. The absorption of dye from solutions containing acetic acid is markedly lower. The addition of acetic acid to solutions of each color containing sodium sulfate has little effect on the particle size or dyeing characteristics on cotton. These dyes are absorbed by wool and in a bath containing both wool and cotton the addition of the acid causes preferential absorption by the wool. The data show from particle size characteristics that this preferential absorption is not caused by interference with the penetration of the micelles of the dyes into cotton, but must be ascribed to an increased affinity for the wool.

The data from the absorption tests show that the more highly salt sensitive dye (2) is more strongly substantive than dye (1) whenever penetration into the cellulose fiber can occur. The important part played by the electrolyte in the dyeing process indicates that the same forces which produce agglomeration of dye molecules are intimately related to the forces which produce absorption.

## Summary

Two representative substantive dyes for cotton which vary widely in their application characteristics are shown to be markedly different in the ease with which they are agglomerated in the presence of inorganic salts. The degree of aggregation depends upon the temperature as well as the nature of the electrolyte and its concentration in the solution. The diffusion constants of the dyes have been measured under several conditions.

Electrolyte free dyes in water solution are absorbed only slightly by cotton of low ash content. The addition of an electrolyte to the bath induces absorption of the color. A maximum particle size is shown to exist above which dyes are not readily absorbed by cotton. The salt sensitivity (sensitivity to aggregation at low concentrations of inorganic electrolytes) of a substantive dye is a qualitative measure of its absorption characteristics.

WILMINGTON, DEL.

RECEIVED OCTOBER 11, 1934

---

[26] Neale and Stringfellow, *J. Text. Inst.*, **24**, 145 (1933); Garvie, Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 271 (1934).