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

The Dyeing of Cotton: Particle Size and Substantivity. II

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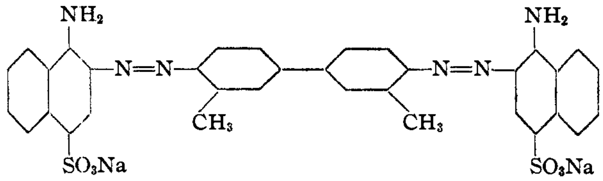
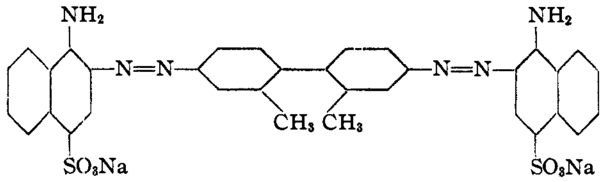
Introduction

Benzopurpurine 4B and its isomer prepared from *m*-tolidine are of especial interest in a theoretical study of substantive dyeing. The structural formulas of these two dyes are


Benzopurpurine 4B


Benzopurpurine 4BI

The spacial change in the position of the methyl groups in tolidine is associated with a great difference in the substantivity of the dyestuffs. Robinson and Mills[1] and Robinson and Moillet[2] made extensive studies of the properties of solutions of the pure dyes and have found that of the two, benzopurpurine 4B is more highly aggregated in solution and is much more readily flocculated by inorganic electrolytes. Griffiths and Neale[3] showed that benzopurpurine 4B is much more highly absorbed by cotton than the isomer and that the rates of absorption of the two dyes are quite different. The authors[4] have recently correlated the particle size of a number of dyes in the dye-bath and their degree of salt sensitivity (sensitivity to aggregation at low concentrations of inorganic electrolytes) with their dyeing characteristics. In the present paper the dyeing characteristics of pure benzopurpurine 4B and its pure isomer from *m*-tolidine are correlated with the particle size and salt sensitivity.

Experimental

Preparation of Dyes.—The dyes were prepared[5] from purified intermediates by current methods used for the manufacture of these colors. The dyes were freed of inorganic salts by the method of Rose.[6,7] In this purification both dyes were converted into their diortho-tolylguanidine salts and washed with water until free of inorganic salts. The sodium salt of benzopurpurine 4B was obtained by metathesis with sodium hydroxide in ethyl alcohol; the sodium salt of the isomer was obtained by metathesis in methyl alcohol. The precipitated sodium salts of the dyes were washed repeatedly with alcohol to remove the diortho-tolylguanidine and were air dried at 100°.

Anal. Calcd. for $C_{34}H_{26}O_6N_6S_2Na_2$: C, 56.32; N, 11.6; S, 8.85. Benzopurpurine 4B, Found: C, 52.16; N, 10.41; S, 7.98. Benzopurpurine 4BI, Found: C, 52.45; N, 10.8; S, 8.15.

The analyses[8] show that the benzopurpurine 4B contained 90.8% and the isomer contained 92.8% of anhydrous dye. The remainder of the samples was water.

Diffusion Measurements.—Measurements of the diffusion constants of the two dyes were made over a range of concentrations of sodium chloride and sodium sulfate from 0.01 to 0.1 *N* and over a range of temperatures from 25 to 94.2°. The measurements at 25° were made by the Fürth[9] microdiffusion method as previously described by the authors.[4] The measurements were carried out in an air thermostat which was controlled to ±0.5°. The measurements at higher temperatures were made with a McBain[10] type cell by the technique previously described by the authors.[7] In applying this method, diffusion of the dye was carried out from a solution of given electrolyte concentration into a solution of the electrolyte at the same concentration. The data obtained are summarized in Table I. The measurements at 25 and 50° were with solutions prepared at the boil and aged for eighteen hours at the temperature of measurement. Solutions studied at higher temperatures were aged for the time necessary to reach a steady state through the diaphragm of the diffusion cell, which was about four hours.

Table I includes the particle radius (r) of the micelles, calculated by the Einstein[11] equation

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[1] Robinson and Mills, *Proc. Roy. Soc.* (London), **131A**, 576, 596 (1931).

[2] Robinson and Moillet, *ibid.*, **143A**, 630 (1934).

[3] Griffiths and Neale, *Trans. Faraday Soc.*, **30**, 395 (1934).

[4] Lenher and Smith, *Ind. Eng. Chem.*, **27**, 20 (1935).

[5] We are indebted to Dr. E. F. Hitch, Mr. A. R. Murphy, Dr. S. S. Rossander and Dr. H. E. Woodward of the Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., for the preparation and purification of these dyestuffs.

[6] Rose, *Ind. Eng. Chem.*, **25**, 1028 (1933).

[7] Lenher and Smith, THIS JOURNAL, **57**, 497 (1935).

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

[9] Fürth, *Kolloid Z.*, **41**, 300 (1927).

[10] McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

[11] Einstein, *Ann. Physik*, **17**, 549 (1905).

$$D = \frac{RT}{N} \times \frac{1}{6\pi\eta r} \qquad (1)$$

In applying this equation it is considered that the dye micelles are spherical. The following observations appear to justify this point of view. Solutions of both dyes, identical to those used for the diffusion experiments at 25°, were prepared and aged in the manner described above, and were examined in the ultramicroscope. Ultramicrons appearing as disks were observed in solutions of both dyes; the particles were much more numerous in solutions of benzopurpurine 4B. Upon aging solutions of benzopurpurine 4B for two weeks, many needle-like ultramicrons mixed with the disk-like appearing particles were formed. Solutions of benzopurpurine 4B in 0.0025 N calcium chloride or magnesium sulfate showed needle-like ultramicrons within twenty-four hours after preparing the solutions. The addition of sodium chloride or sodium sulfate to solutions of the dye containing calcium or magnesium ions markedly increased the extent of the needle-like formation. Solutions of the isomer, in contrast to those of benzopurpurine 4B, did not show elongated ultramicrons in calcium chloride or magnesium sulfate solutions until after aging for two weeks. The ultramicrons appeared in the field as threads or rods rather than as needles. Beger[12] stated that the addition of sodium chloride to solutions of pure benzopurpurine 4B produced immediate formation of needle-like particles. Seidentopf[13] reported the presence of needle-shaped ultramicrons in fresh solutions of benzopurpurine 4B, while Beger obtained similar results with the technical dye.

TABLE I

DIFFUSION CONSTANTS OF BENZOPURPURINE 4B AND ISOMER (1.0 G./L. SOLUTIONS)

Temperature, °C.		25.0		50.5		65.2		94.2	
Electrolyte	Concn., N	$D \times 10^{-6}$ sq. cm./sec.	Estd. $R \times 10^{-8}$ cm.	$D \times 10^{-6}$ sq. cm./sec.	Estd. $R \times 10^{-8}$ cm.	$D \times 10^{-6}$ sq. cm./sec.	Estd. $R \times 10^{-8}$ cm.	$D \times 10^{-6}$ sq. cm./sec.	Estd. $R \times 10^{-8}$ cm.
				Benzopurpurine 4B					
NaCl	0.01	2.69	9.0	5.25	8.2				
	.025	0.92	26.4	4.3	10.0				
	.05	.39	62.2	3.35	12.9	5.32	10.6		
	.075			1.19[a]	36.3				
	.1	Flocculated				3.5	16.2	10.92	8.1
Na_2SO_4	.01	4.52	5.4						
	.025	1.91	12.7						
	.05	0.75	32.3	4.09	10.6	5.76	9.8		
	.075			1.28[a]	33.8				
	.1	Flocculated				4.83	11.7	11.62	7.6
				Benzopurpurine 4BI					
NaCl	.01	2.99	8.1						
	.025	2.02	12.0						
	.05	2.06	11.8						
	.1	1.64	14.8					11.8	7.5
Na_2SO_4	.01	4.45	5.5						
	.05	4.20	5.8						
	.1	3.49	7.0					12.88	6.9

[a] Dye in cell partially flocculated.

It appears possible from the results summarized that the appearance of needle-like ultramicrons or particles of irregular shape in fresh solutions of pure benzopurpurine 4B and sodium chloride as reported by others[1,12] may be explained by the presence in the dye of small quantities of calcium or magnesium salts which accelerate the aging phenomenon. Other factors in the application of the Einstein equation have been discussed previously by the authors.[4,7]

The molecular weights of the dye micelles, included in Table I, may be calculated by the equation

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

The value of (g) for benzopurpurine 4B is 1.52 and for the isomer is 1.60.

The data in Table I show that benzopurpurine 4B and its isomer are characteristically different in the extent to which they agglomerate in the presence of electrolytes. Benzopurpurine 4B is highly sensitive to electrolytes; solutions of a relatively low inorganic salt concentration contain micelles of several hundred molecules at 25°.

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[12] Beger in Zsigmondy, *Z. physik. Chem.*, **111**, 211 (1924).

[13] Seidentopf, *Kolloid-Z.*, **6**, 3 (1910).

TABLE II

ABSORPTION OF BENZOPURPURINE 4B AND BENZOPURPURINE 4BI BY COTTON

Concn., *N*		0.0	0.01	0.025	0.05	0.075	0.10	0.20
Electrolyte	*T*, °C.	Dye absorbed, g. per 100 g. cotton						
				Benzopurpurine 4B				
Na_2SO_4	25	0.208	0.338	0.368	0.194	...	0.178	0.177
NaCl	25	.200	.313	.351	.194	...	.180	...
Na_2SO_4	50	.432	.600	.714	.739	0.726	.725	.597
NaCl	50	.305	.570	.697	.734	.731	.718	.573
Na_2SO_4	100	.288	.503	...	.719	...	.738	...
NaCl	100	.283	.525	...	.712	...	.730	...
				Benzopurpurine 4BI				
Na_2SO_4	25	0.125	0.374	0.519	0.635	...	0.696	0.679
NaCl	25	.180	.415	.546	.653	...	.704	.736
Na_2SO_4	50	...	.544	...	.610	...	.672	.693
NaCl	50	.157	.382	...	.618	...	.687	.722
Na_2SO_4	100	.136	.211	...	.320	...	.370	...
NaCl	100	.140	.217	...	.307	...	.358	...

At complete exhaustion of the bath the absorption of dye is 0.75 g. per 100 g. cotton.

The degree of aggregation is strongly influenced by the electrolyte concentration and by the temperature. The properties of the isomer in solution are in marked contrast to those of benzopurpurine 4B. Even in 0.1 *N* sodium chloride the dye is agglomerated to less than 20 molecules per micelle at 25° while at lower concentrations of the electrolytes and at higher temperatures the degree of aggregation is much lower.

Benzopurpurine 4B and its isomer are only slightly aggregated near the boil at the concentration of inorganic salts customarily present in dye-baths. The differences between these dyes at lower temperatures are similar to those which exist between other dyes of widely divergent application characteristics, which are reported in Part I of this paper.[7]

Dyeing Experiments.—Absorption tests on cotton pongee were made with the two dyes at varying concentrations of sodium chloride and sodium sulfate over a range of temperatures. The cotton pongee, of 0.2% ash content, used was as described in a previous paper.[4] Each test was carried out on 10 g. of the pongee in 250 cc. of a dye solution containing 0.075 g. of dye. The dye solutions were prepared and aged similarly to those used for the diffusion experiments. Dyeings at 25, 50° and the boil were made as previously described.[4] The data for the amounts of dye absorbed under the various conditions are summarized in Table II.

Tests on the reversibility of the dyeing process were made over a range of temperatures and a range of concentrations of sodium chloride. Tests at 25 and 50° were carried out by rinsing 2.5-g. pieces of the dyed goods in 250 cc. of the wash solution in pint Mason jars containing 10 monel metal balls. The jars were rotated in a Launder-Ometer,[14] the standard washing machine of the American Association of Textile Chemists and Colorists.[15] Tests at the boil were made under reflux. All tests were run for three hours and the rinse solution was changed at the end of each hour. The determination of the amount of dye removed was made by a spectrophotometric analysis for the amount of dye in the rinse solution. Check evaluations for the amount of dye left on the goods were also made by the method of reflectivities, as described by the authors.[4] The variation between the two methods was about 15%. The results of the wash tests are summarized in Tables III and IV. The evaluations for the amount of dye removed are reported by analysis for the dye in the solution except for tests in which distilled water at the boil was used. In all the tests except the latter the determinations by examination of the solutions showed the greater removal of dye.

Discussion

Various workers[4,16–19] have shown that the equilibrium distribution of the dye between the solution and the fiber; the rate of diffusion of the dye into the cellulose; the size of the dye

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(14) Manufactured by Atlas Electric Device Co., 360 W. Superior St., Chicago, Illinois.

(15) Appel, Smith and Christison, *Am. Dyestuff Reptr.*, **17**, 679 (1928).

(16) Georgevics in Alexander, "Colloid Chemistry," Chemical Catalog Co., 1932, Vol. IV, p. 197.

(17) Neale and Stringfellow, *Trans. Faraday Soc.*, **29**, 1167 (1933).

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

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

TABLE III

RINSE TESTS WITH BENZOPURPURINE 4B AND BENZOPURPURINE 4BI

Each result given is a composite of six tests with dyeings made at different salt concentrations.

Initial dyeings made at............. T, °C.	Bath	25° % Dye removed	50°	100°
		Benzopurpurine 4B		
25	Water	43.9	25.7	15.4
100	Water	91.0	95.6	93.5
25	0.1 *N* NaCl	0.8	0.4	0.45
100	0.1 *N* NaCl	9.9	14.4	16.4
		Benzopurpurine 4BI		
25	Water	79.8	76.6	74.7
100	Water	99.9	99.9	99.9
25	0.1 *N* NaCl	8.9	8.7	5.6
100	0.1 *N* NaCl	77.7	80.5	70.7

TABLE IV

RINSE TESTS WITH BENZOPURPURINE 4B AND BENZOPURPURINE 4BI AT VARYING CONCENTRATIONS OF SODIUM CHLORIDE

The original dyeings were prepared at the boil. Each result is an average of two tests.

NaCl concn., *N*........... T, °C.	0.0 % Dye removed	0.01	0.05	0.1	0.25
	Benzopurpurine 4B				
25	15.4	..	0.5	0.4	..
50	40.2	3.4	1.1	0.7	..
	Benzopurpurine 4BI				
25	74.7	38.5	8.7	3.7	0.7
50	79.6	..	32.8	20.9	11.4

micelles; and the electrolyte content of the cellulose are all important factors in describing the mechanism of dyeing. The dyeing experiments in this paper were run by a uniform procedure to study the influence of dye micelle size in the dyeing process.

The data show that marked differences in the behavior of the benzopurpurine 4B and its isomer toward inorganic salts are reflected in the dyeing process. Absorption of the isomer increases with increasing electrolyte concentrations and decreasing temperatures. With benzopurpurine 4B an optimum concentration of electrolyte exists above which the degree of absorption is decreased at 25 and 50°. This decrease corresponds with the attainment of an average particle radius in the dye-bath greater than the limiting radius of 17 × 10^{-8} cm. previously described.[4] The concept of the existence of a maximum particle size for dyeing must not be applied rigidly in interpreting data obtained from diffusion experiments. For example a 95% exhaust is obtained in one hour with benzopurpurine 4B at 50° from a 0.075 *N* electrolyte solution even though the dye is partially flocculated in the bath. The average radius of the micelles in these solutions is about 35 × 10^{-8} cm., which leads to the conclusion that many particles in the dyeing range are present. It appears logical that as the smaller particles are absorbed, the larger micelles dissociate to maintain an equilibrium distribution of particle sizes in the bath. As a consequence it is possible for dyeing to proceed continuously to 95% exhaust. Since the particle size of benzopurpurine 4B is markedly influenced by the temperature, it is not surprising that the rate at which absorption occurs, accompanied by a redistribution in the size of the micelles in the bath, is much faster at 50° than at 25°.

When dyeings of benzopurpurine 4B prepared at temperatures varying from 25 to 100° are rinsed in water at 25° the color is removed most readily from the dyeings made at the lower temperatures. In dyeings made at the lower temperatures where a large particle size predominates, the dyeing process must be characterized by absorption on the surface of the fibers rather than by an extensive penetration into the pores which predominates at the boil. Dyeings made with the isomer, whose particle size is much lower than that of benzopurpurine 4B under dyeing conditions, do not show this contrast.

Sodium chloride and sodium sulfate are equally effective at equivalent concentrations as dyeing assistants although they do not promote particle growth to the same extent. This indicates that the major effect of the particle size in the dyeing process arises from the extent to which it retards or prevents diffusion of the dye micelles into the fiber. There is no indication that a limited particle size range exists which promotes mechanical retention by the fibers.

The wash tests with the two dyes show that dyeing with the isomer is completely reversed by treatment of the dyeings with distilled water at the boil. Comparatively large concentrations of salt in the bath are required to prevent bleeding of the dye from the fiber. In contrast, from 5 to 10% of the highly electrolyte sensitive benzopurpurine 4B is retained by cotton after treatment in boiling water and dyeings of this color are relatively fast in sodium chloride solutions of low concentration. The reversibility of the dyeing process (wash fastness) is closely related to the ease with which the dyes are agglomerated in small concentrations of electrolytes.

It is shown in this paper that the dyeing characteristics of benzopurpurine 4B and its isomer are explained by the particle size of the colors in the dye-bath and by the sensitivity of the dyes to the building up of agglomerates in the presence of electrolytes. Other factors in the dyeing process are related to these two. Thus the distribution of the dye between the bath and the fiber obviously depends on the salt sensitivity of the dye while the particle size of the micelles is the controlling factor in establishing the rate at which dyeing proceeds.

Summary

Benzopurpurine 4B is shown to be much more highly aggregated in solution than its isomer by additions of sodium chloride or sodium sulfate. The degree of aggregation of benzopurpurine 4B is readily influenced by the electrolyte concentration and the temperature. The particle size of the micelles and the salt sensitivity (sensitivity to agglomeration at low concentrations of electrolytes) of the dyes are shown to be controlling factors in their dyeing characteristics.

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Contractions Accompanying the Swelling of Gelatin[1]

BY LEO FRIEDMAN AND BETTY BROWN

Two distinct methods are used to study the volume changes which take place when a solid protein is placed in a solution. The first measures the volume change of the solid alone, which is commonly known as swelling, whereas the second measures the total volume change. The results of the first method indicate the degree of water absorption, while those of the second supposedly indicate the degree of hydration. A knowledge of the latter should lead to a better understanding of the phenomenon of swelling.

Relatively few measurements of the total volume changes occurring during the swelling of proteins have been made, and the results which have been published are not in good agreement. Marie and Marinesco[2] have reported that the total volume contractions observed when gelatin is placed in solutions of varying *p*H is a minimum at the isoelectric point and increases in acid and basic solutions. The range covered by their experiments was *p*H 3.5 to 8.5, at both of which points they reported maxima. Neville, Thies and K'Burg[3] and Svedberg[4] have reported the opposite effect, namely, that when contraction is plotted against *p*H a maximum contraction is observed at the isoelectric point while increasing or decreasing *p*H is accompanied by a decrease in the contraction.

Experimental Procedure.—The total volume changes were measured by use of a simple dilatometer similar to that described by Hampton.[5] An air-dry gelatin disk (containing 15% water) was placed in a small copper gauze container and suspended in carbon tetrachloride by means of No. 35 copper wire threaded through the capillary. After the system had come to an equilibrium in the thermostat at 10°, the gelatin was raised into the aqueous solution by means of the wire. Eastman Kodak electrodialyzed gelatin was used in all of the experiments. Solutions of acid and base were made up from standard solutions of hydrochloric acid and sodium hydroxide, and the *p*H was determined electrometrically before and after swelling.

Experimental Results.—The contraction per gram of the original gelatin occurring when the disks were permitted to swell in water at 10° for varying intervals of time is shown in Fig. 1. Since the curve becomes nearly horizontal after about eight hours, the determinations in acid and basic solutions were made after this time interval. The contraction per gram of water imbibed, also shown in Fig. 1, was found to be a constant quantity.

The effect of *p*H upon the total volume contraction during the swelling of gelatin at 10° is shown

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[1] Presented at the 88th meeting of the American Chemical Society, Cleveland, Ohio, September, 1934.

[2] C. Marie and N. Marinesco, *Compt. rend.*, **193**, 736 (1931).

[3] H. A. Neville, E. R. Thies and R. B. K'Burg, *Ind. Eng. Chem.*, **22**, 57 (1930).

[4] The Svedberg, THIS JOURNAL, **46**, 2673 (1924).

[5] H. C. Hampton, *Science*, **63**, 49 (1926).