

## THE ABSORPTION OF DYES BY CELLULOSE— PART IX.

### MEASUREMENTS OF THE ABSORPTION OF SKY BLUE FF BY COTTON.

BY C. E. F. FISHWICK AND S. M. NEALE.

*Received 28th February, 1946.*

In the preceding papers of this series,<sup>1-8</sup> and in the recent work of Willis, Warwicker, Standing and Urquhart,<sup>9</sup> measurements of the absorption of various purified dyes on regenerated cellulose sheet (Cellophane) have been described. The use of this material as the absorbent is advantageous where the time rate of dyeing is being studied, as the smoothness and small extent of its outer surface (compared with natural cellulose fibres) makes it possible by mechanical agitation to ensure that the rate of take-up of dye is dependent wholly on its diffusion from the surface into the interior of the sheet. Furthermore, the geometrically simple shape confines the diffusion to the direction normal to the surface, so that the mathematical analysis of experimental kinetic data is simplified. As was pointed out by Hanson, Neale and Stringfellow,<sup>6</sup> however, in their thermodynamic treatment of the dyeing of cellulose as a process involving the specific adsorption of the anion, Cellophane is by no means an ideal form of cellulose for the provision of equilibrium absorption data which are to be used to check any quantitative hypothesis which purports to predict the variation of absorption with dye or with salt concentration. It contains ionisable carboxylic acid groups which interfere with the ionic equilibrium and by electrostatic influence depress the absorption of colour anions and alter the shape of the absorption isotherms. The material is not constant in thickness nor in optical anisotropy. The experimenter has, furthermore, no control over the uniformity of other physical and chemical characteristics such as molecular weight and reactivity, which are dependent on conditions of manufacture. Natural cotton cellulose, on the other hand, after the usual technical scour with dilute caustic alkali under pressure followed by a properly controlled hypochlorite bleach, is a reasonably reproducible material much better suited for equilibrium absorption measurements, for its chemical and physical properties do not vary appreciably from one variety of cotton to another, nor are they appreciably dependent on the normal variations of technical bleaching. Any slight variation in the molecular weight can be checked by the sensitive measurement of fluidity in cuprammonium hydroxide. The complications which its irregular cross-section raised in kinetic measurements are of no account when dyeing is continued to equilibrium. It was therefore thought desirable to extend the rather scanty data for the absorption of dye by cotton, which were included in the earlier work of Hanson, Neale and Stringfellow,<sup>6</sup> by more

<sup>1</sup> Neale and Stringfellow, *Trans. Faraday Soc.*, 1933, **29**, 1167.

<sup>2</sup> Garvie, Griffiths and Neale, *ibid.*, 1934, **30**, 271.

<sup>3</sup> Hanson and Neale, *ibid.*, 1934, **30**, 386.

<sup>4</sup> Griffiths and Neale, *ibid.*, 1934, **30**, 395.

<sup>5</sup> Neale and Patel, *ibid.*, 1934, **30**, 905.

<sup>6</sup> Hanson, Neale and Stringfellow, *ibid.*, 1935, **31**, 1718.

<sup>7</sup> Neale, *J. Soc. Dyers Col.*, 1936, **52**, 252.

<sup>8</sup> Garvie and Neale, *Trans. Faraday Soc.*, 1938, **34**, 335.

<sup>9</sup> Willis, Warwicker, Standing and Urquhart, *ibid.*, 1945, **41**, 506.

precise and extensive measurements. The technique and results of some such measurements are described in the present paper.

Sky Blue FF (Colour Index No. 518) \* was used as the dye to provide continuity with previous work, and because its colour is very well suited to visual determination, showing its maximum light absorption at about 6,200 Å. It undergoes slow decomposition losing up to one-fifth of its colour intensity on heating overnight with cotton in a dye bath at 90° C., but is not more unstable under such conditions than the majority of direct cotton colours.

### Experimental.

**Materials.**—The cotton used was a standardised bleached Egyptian cotton cloth made by Messrs. Tootal, Broadhurst, Lee & Co. Ltd. Its characteristics were—warp: 50's Sakel 98 ends per inch; weft: 50's Uppers, 100 picks per inch; copper number 0.94; fluidity (0.5 % soln.) 4.4; the low values of copper number and fluidity indicate freedom from depolymerisation by chemical attack.

The dye was obtained from various sources—highly purified samples were supplied by I.C.I. (Dyestuffs) Ltd. and I.G. Farbenindustrie, and a concentrated sample supplied by Sandoz Chemical Co. Ltd. was purified in the laboratory by the usual process of repeated precipitation with sodium acetate and alcohol, followed by thorough

washing with cold alcohol to remove sodium acetate. Boiling or refluxing with the laboratory alcohol caused the dye to be partly reduced to a reddish substance. The various purified samples were compared in the spectrophotometer.

The optical densities of 20 mg./l. solution of the sample showing the highest colour intensity at 6,200 Å. were as shown in Table I.

**Measurement of Dye Concentration.**—The optical density of solutions in water at 6200 Å. was taken as a measure of the dye content of aqueous solutions in subsequent tests, that at 6300 Å. in 25% aqueous pyridine as a measure of the dye content of "strip solutions" obtained by extraction of dyed cotton. The optical measurements were made visually in a Koenig Martens spectrophotometer, made by Schmidt and Haensch. This instrument has a circular field of view and errors due to inequality of intensity of the two beams of light or to reflection at the cell surface are compensated by an arrangement whereby layers of the solution differing in thickness by 1 cm. are brought alternately into the paths of the two beams. The error of estimation of density is about 0.01, about one-half per cent. of the measured quantity when the concentration is near the optimum of about 20 mg./l.

TABLE I

Wave-length Å.	Log <sub>10</sub> I <sub>0</sub> /I.		
	In water.	In 6.25 % Pyridine.	In 25 % Pyridine.
4600	0.16	0.171	0.174
4800	0.225	0.215	0.206
5000	0.327	0.311	0.300
5200	0.461	0.448	0.420
5400	0.699	0.703	0.650
5600	1.030	0.997	0.938
5800	1.467	1.442	1.374
6000	1.806	1.752	1.685
6200	1.998	1.986	1.918
6300	—	2.058	2.034
6400	1.780	1.922	1.98
6600	1.135	1.187	1.28
6800	0.503	0.40	0.39
7000	0.181	0.11	0.10

\* See Part VIII.

**Conditions of Dyeing.**—The dye solutions were made up by dilution from standard concentrated solutions of dye, A.R. NaCl and distilled water. For the experiments above 25° c. they were contained in Jena G glass tubes of 250 ml. capacity having ground-in water-cooled hollow stoppers to prevent evaporation, immersed in thermostats maintained at the temperature found necessary to give a fixed temperature in the dye solution (e.g. thermostat at 91.3°, dye bath 90° c.). In the hollow stopper was incorporated a long central glass tube through which passed a silver wire connected at its upper end to a solenoid device by means of which the wire was made to rise and fall about 2 cm. about once every second. On the lower end of the wire, immersed in the dye solution, a carefully weighed and "fringed" piece or pieces of cloth were threaded and, in this way, agitated in the dye solution for the time found necessary for the attainment of equilibrium. They were then removed, quickly rinsed in ice-cold water and squeezed between dry filter papers.

TABLE II  
(Showing reproducibility of results.)

<i>(a) Four samples in one bath.</i>					
Temperature of dye bath 90° c.					
NaCl 20 g./l.					
Time (min.) . . . . .		120	180	240	310
Wt. of cotton air-dry (mg.) . . . . .		51.26	50.4	53.2	52.45
ML. pyridine . . . . .		24.94			
Opt. density of strip . . . . .		1.727	1.714	1.830	1.805
Opt. density bath (× 2/5) . . . . .					1.440
End concn. of bath mg./l. . . . .					41.5
% dye on cotton (g./100 g.) . . . . .		0.893	0.888	0.896	0.887
<i>(b) Five separate baths.</i>					
Temperature of baths 70° c.					
NaCl 10 g./l. . . . .					
Time (min.) . . . . .	540				
Air-dry wt. of cotton (mg.) . . . . .	51.1	50.75	51.25	51.5	50.7
ML. pyridine . . . . .	35	35	35	35	35
Opt. density of strip . . . . .	1.540	1.540	1.554	1.572	1.544
Opt. density of bath (× 1/5) . . . . .			1.741		1.741
End concn. of bath mg./l. . . . .			92		92
% dye on cotton . . . . .	1.10	1.11	1.11	1.12	1.11

To allow for decomposition of the dye, the residual dye solutions were, after dilution if necessary, analysed by comparison in the spectrophotometer with the unheated dye bath solution of the same salt content.

It was found that when the dye bath contained 20 g./l. NaCl, as much as 20 % of the blue dye was decomposed on heating at 90° c. for 24 hours, giving rise to a less intensely coloured reddish compound. The decomposition was dependent upon, and increased with the salt content of the bath. The residual dye baths were thereupon all analysed in this way, and their recorded dye contents have been determined by a comparison with a standard solution of the same salt content, at the wave length of maximum absorption. At 25° c., where there was apparently no decomposition, the dye absorptions calculated from the degree of exhaustion of the bath agreed with those determined by stripping the dyed cotton.

**Analysis of the Dyed Cotton.**—The dye was removed by extracting the cotton in a sealed tube at 40° to 60° c. with a volume of 25% aqueous pyridine calculated to give a solution whose optical density would be of the optimum order (1.5 to 2.0). The solution was poured through a sintered glass filter into the spectrophotometer cell, after cracking the sealed tube, and its optical density at 6300 Å. was carefully measured.

Control experiments showed that the shape of the absorption spectrum curve for the stripped dye was the same as that of a pyridine solution of the "pure" solid dye, thus affording some proof of the purity of the latter. From the optical density at 6300 Å. the concentration of dye in the strip solution was calculated by Beer's Law, which was obeyed within less than 1 % over the range 0.01-0.02 g./l. The amount of dye on the cotton was then calculated as weight percentage, grams dye per 100 g. dry cotton. The dye, as originally weighed out, was assumed to retain 2 % of moisture after overnight drying in an air oven at 110° C. and the cotton equilibrium with the atmosphere 6 % of its weight of moisture.

### Results.

In this way the values given in the following tables were obtained; each value is the mean of at least four closely agreeing determinations. A detailed account of two typical experiments is given in Table II.

### Discussion.

The mean values given in Table III are believed to be self-consistent within about one part in a hundred. There is a somewhat larger uncertainty as to their absolute value, on account of the fact that it was impossible to prepare purified samples of the dye showing identical optical properties. The values for absorption and for dye bath concentration have been calculated on the assumption that the optical density of a 20 mg./l. solution in 25 % pyridine is 2.03 at 6300 Å. and in pure water 2.00 at 6200 Å., being somewhat lower in solutions containing salt.

The somewhat lower degree of purity and consequently lower optical density of the dye used by Hanson, Neale and Stringfellow,<sup>6</sup> as well as a temperature error of about 1° due to condensation of vapour on the water-cooled stoppers of the dyeing tubes, not detected in this earlier work, accounts for the fact that the earlier absorption data are consistently higher than those now presented.

The data have been plotted in the forms of graphs (a)  $\log D$  against  $\log c$  at constant salt concentration, and (b) of  $\log D$  against  $\log s$  at constant dye concentration. Good straight lines were thus obtained whose slopes are recorded in Table III.

The theory of Willis, Warwicker, Standing and Urquhart<sup>9</sup> predicts a slope of not more than 0.80 for the  $\log D - \log s$  plot for a tetravalent dye and of not less than 0.2 for the  $\log D - \log c$  plot. The theory of Hanson, Neale and Stringfellow<sup>6</sup> leads to a similar conclusion, i.e. slope  $\log D - \log s \gtrsim 0.80$  approaching 0.80 when  $W$  (the effective water take-up) is assumed small; slope  $\log D - \log c \leq 0.20$  approaching 0.20 when  $W$  (the effective water take-up) is assumed small.

In agreement with this, the value of the  $\log D - \log s$  slope ranges between 0.51 and 0.62 and that of the  $\log D - \log c$  slope ranges between 0.19 and 0.33 at 70° and 90° C. At the lower temperatures, however, the latter slope falls to 0.14. As it does not appear that this can be accounted for by either of the quantitative theories, their precise applicability to the present data will not be further considered in this paper.

It is clear from the recent experiments of Neale,<sup>10, 11</sup> Neale and Peters<sup>12</sup> that cellulose carries in aqueous solutions a negative electric charge, which must influence the absorption of dye anions in some way which is not yet fully determined.

**The Heat of Dyeing.**—Although the present data are not ideally suited to the calculation of this quantity, this has been attempted, by the use of the equation

$$\frac{d \log c}{dT} = \frac{Q}{RT^2}.$$

<sup>10</sup> Neale, *Trans. Faraday Soc.*, 1946, **42**, 473.

<sup>11</sup> Neale, *ibid.* (in course of publication).

<sup>12</sup> Neale and Peters, *ibid.*, 1946, **42**, 478.

TABLE III.—SUMMARY OF ABSORPTION DATA, MOST OF WHICH ARE THE MEANS OF SIX INDEPENDENT MEASUREMENTS IN CLOSE AGREEMENT.

Dye. mg./l. (c).	NaCl. g/l. (s).	Abs. % (D.).	Dye. mg./l. (c).	NaCl. g/l. (s).	Abs. % (D.).
<b>25° C. (Time of dyeing 27 to 37 days.)</b>			<b>70° C. (Time of dyeing 7 to 9 hours.)</b>		
18.0	1	0.470	23.8	2	0.303
16.7	2	0.726	20.9	7.5	0.652
16.9	4	1.12	20.8	10	0.779
12.8	5	1.23	21.4	20	1.15
11.8	6	1.32			
10.2	8	1.52	45.3	1	0.228
			44.5	2	0.363
41	0.5	0.380	43.7	5	0.635
41.5	1	0.567	42.0	7.5	0.810
40.5	2	0.845	42.4	10	0.968
39.6	3	1.10	42.1	15	1.18
38.2	4	1.32	44.3	15	1.18
36.6	6	1.62			
			89.2	2	0.424
86.3	0.5	0.430	87.5	5	0.758
86.5	1	0.623	91.7	5	0.758
90	1.5	0.775	88.1	7.5	0.935
92	2	0.966	92	10	1.11
94	3	1.22	87.5	15	1.40
94	4	1.42			
			176	2	0.505
181	0.5	0.470	174	5	0.867
183	1	0.71	176	7.5	1.11
183	1.5	0.895	177	10	1.315
184	2	1.06	Plot of log <i>D</i> vs. log <i>c</i> gives straight lines of slope 0.19 to 0.25.		
183	3	1.33	Plot of log <i>D</i> vs. log <i>s</i> gives straight lines of slope 0.59 to 0.605.		
			<b>90° C. (Time of dyeing 3 to 20 hours.)</b>		
365	0.125	0.319	41	1	0.141
369	0.25	0.405	41.7	2	0.233
368	0.50	0.567	42	5	0.402
371	1.0	0.822	42	10	0.600
362	2.0	1.15	41.5	20	0.893
			43	20	0.900
Plot of log <i>D</i> vs. log <i>c</i> gives straight lines of slope 0.14 to 0.19.			46	20	0.930
Plot of log <i>D</i> vs. log <i>s</i> gives straight lines of slope 0.51 to 0.60.			50	20	0.970
<b>51.6° C. (Time of dyeing 36 to 48 hours.)</b>			92	1	0.185
20.5	5	0.812	92	2	0.285
20	7.5	1.04	87	5	0.505
20.2	10	1.19	87	10	0.756
			86	20	1.132
44.5	0.5	0.216	183	1	0.234
45	1	0.351	183	2	0.367
44.9	2	0.542	194	5	0.644
42.5	4	0.820	190	10	0.923
44.0	5	0.938	180	20	1.43
43.0	7.5	1.18			
			366	0.5	0.202
64.6	5	0.953	363	1	0.303
			358	2	0.447
			365	5	0.763
			359	10	1.12
Plot of log <i>D</i> vs. log <i>c</i> gives a straight line of slope 0.14.			Plot of log <i>D</i> vs. log <i>c</i> give straight lines of slope 0.27 to 0.33.		
Plot of log <i>D</i> vs. log <i>s</i> gives a straight line of slope 0.62.			Plot of log <i>D</i> vs. log <i>s</i> gives straight lines of slope 0.57 to 0.615.		

The values (Table V) of the dye concentration ( $c$ ) in solutions of fixed salt content ( $s$ ) in equilibrium at the various temperatures with cotton containing a fixed amount of dye ( $D$ ), were obtained by interpolation or extrapolation—(extrapolated values bracketed), from the data of Table III.

TABLE IV

Absorption data at room temperature ( $18^{\circ}\text{C}$ . approx.). Time of dyeing 60 to 90 days. Dye 400 mg./l.

NaCl mg./l. . . .	0	10	20	40	80	160
Absorption % . . .	0.209	0.230	0.254	0.268	0.309	0.402

TABLE V

Temp. $^{\circ}\text{C}$ .			25.	50.6	70.2.	90.
(i) $s = 1.0\text{ g./l.}$	$D = 0.36$	$c\text{ mg./l.}$	(4)	46	180	(520)
(ii) $s = 2.0\text{ g./l.}$	$D = 0.54$	$c\text{ mg./l.}$	(2)	45	230	(676)
(iii) $s = 5\text{ g./l.}$	$D = 0.94$	$c\text{ mg./l.}$	(3.8)	44	266	(76)
(iv) $s = 10\text{ g./l.}$	$D = 1.45$	$c\text{ mg./l.}$	(4.5)	45	250	(930)

The values of  $\log c$  plotted against  $1/T$  should then give a series of straight lines if the activity coefficient of the dye and the heat of absorption are not temperature dependent, and if the device of keeping the dye absorption and salt concentration constant is effective in keeping the fibre potential constant. Actually the series (iv) values give a very good straight line, but the other lines are all slightly curved showing a steeper slope at the lower temperatures. The heats of dyeing calculated from these slopes are as in Table VI.

TABLE VI

(i) $s = 1\text{ g./l.}$	$Q = 16.6\text{ kcal. evolved.}$
(ii) $s = 2\text{ g./l.}$	$Q = 19.2\text{ kcal. evolved.}$
(iii) $s = 5\text{ g./l.}$	$Q = 17.8\text{ kcal. evolved.}$
(iv) $s = 10\text{ g./l.}$	$Q = 18.2\text{ kcal. evolved.}$

As would be anticipated from the hypothesis that the effect of salt upon the absorption is merely due to its effect on the electrostatic forces, the heat of absorption is found to be independent of the salt concentration, within the experimental error, which on account of the necessity for extrapolation in some cases, is magnified in this method of calculating  $Q$  from data not ideally suited for the purpose.

### Résumé.

Des mesures plus précises de l'adsorption de colorants par la cellulose ont été faites sur du coton naturel avec la Diamin FF.

On indique la technique employée et les résultats obtenus ; on compare les pentes des droites :  $\log$  de la concentration du colorant en fonction du  $\log$  de l'adsorption ou du  $\log$  de la concentration en sel neutre, avec celles prévues selon deux théories précédentes.

### Zusammenfassung.

Die existierenden Daten <sup>6</sup> über die Farbstoffabsorption durch Baumwolle sind durch Messungen mit Diaminreinblau FF und natürlicher Baumwollzellulose erweitert worden. Messmethode und Resultate werden angegeben. Die Steigungen der Kurven für die Beziehung zwischen dem Logarithmus der Farbstoffkonzentration einerseits und dem Logarithmus der Absorption und dem Logarithmus der Neutralsalzkonzentration andererseits werden mit den in zwei theoretischen Abhandlungen berechneten verglichen. <sup>6, 9</sup>

College of Technology,  
Manchester, 1.