THE PHYSICAL CHEMISTRY OF DYEING. ACID AND BASIC DYES.

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Introduction

The various theories which have been proposed from time to time to account for the phenomena of dyeing may be classified, in general, as either physical or chemical. In the latter class are grouped all explanations based on the assumption that a chemical reaction occurs between the dye and the fiber. In the physical interpretation the presence of chemical reactions is denied except in a few special cases, it being believed that in the majority of cases dyeing is due to physical forces or, more specifically, to adsorption of the dye by the fiber.

The adsorption or colloidal theory of dyeing has been summarized and elaborated by Bancroft.² Its application to acid dyes³ may be stated briefly as follows. When any fiber is placed in a dyebath, it may adsorb any or all of the constituents of the bath. (In the case of acid dyes in acidified baths these constituents are hydrogen ions, sodium ions, (assuming the dye to have been a sodium salt), anions of the dye, anions of the acid, and undissociated compounds.) Hydrogen ions being, in general, more strongly adsorbed than other univalent cations will be taken up largely and the fiber will become charged positively relative to the solution. This positive charge, in turn, will lead to an increased adsorption of anions,⁴ and by this secondary process of adsorption the charge on the fiber will be more or less neutralized. The

¹ A thesis submitted by Arthur W. Bull to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Jour. Phys. Chem., **18**, 1, 118, 385 (1914); **19**, 50, 145 (1915).

³ An acid dye is one which contains the color in the acid radical and which dissociates in water solution to give colored anions.

⁴ Bancroft: Jour. Phys. Chem., **18**, 10 (1914); "Applied Colloid Chemistry," 115 (1921).

anions of dye and of acid will both be taken up in amounts which are determined for a given fiber by the nature of the ions and by their concentrations. Since, in being adsorbed, the anions of an acid dye have to compete with the other anions of the bath, it follows that the addition of other strongly adsorbed anions will decrease the amount of dye taken up. In a similar way, the addition of a strongly adsorbed cation will cause an increase in the amount of an acid dye taken up, other factors remaining constant. In all cases there may be some concurrent adsorption of undissociated dyes. On the basis of this theory it is possible to explain the facts met with in dyeing with acid dyes.

The final effect produced by the addition of any given reagent to a dyebath may be the resultant of several different factors. In general, the added reagent may affect either the fiber or the dyebath. It may act on the fiber chemically as in the case of sodium hydroxide on wool, or it may be adsorbed by the fiber thereby modifying the extent of adsorption of other substances.

The effect on the dyebath may be more complex. The dye may be decomposed chemically by the formation of a salt or by the production of the free color acid or base. If the dye is in true solution, the reagent may change its solubility, thereby affecting the amount of dye adsorbed. If the dye is in suspension, the added reagent will produce some change in its degree of dispersion and will therefore influence the amount of dye adsorbed. This latter action is of prime importance in the case of substantive dyes. Finally, the added reagent may change the hydrogen ion concentration of the dyebath. It will be shown subsequently in this paper that the hydrogen ion concentration of the dyebath is the most important single factor affecting the process of dyeing.

In the experiments described in this paper no evidence of any chemical action of the reagents on the fiber was obtained, except with relatively high concentrations of sodium hydroxide. Experiments on the diffusion of the acid dyes employed in this work showed these dyes to be presumably

in true solution, at least in neutral, weakly acid, or weakly alkaline baths. Electrometric titration of Orange II indicated that the free acid of the latter is strongly ionized and the other acid dyes used are presumably similar in this respect since they are all sodium salts of sulfonic acid derivatives. It was therefore concluded that in all baths containing acid dyes, with the exception of certain special cases to be noted later, the color was present in solution almost entirely in the form of dye anions. With the basic dyes investigated, however, the evidence obtained from experiments on diffusion showed that these dyes, while in true solution in a neutral dyebath, became increasingly colloidal on the addition of sodium hydroxide, even in relatively small amounts.

The hydrogen ion concentration of the dyebath is probably the most important variable as emphasized previously; but, so far as we are aware, no former investigator has controlled this factor quantitatively, although Pelet-Jolivet¹ pointed out its importance. Many of the assistants or restrainers, used in dyeing, produce an appreciable and often a great change in the hydrogen ion concentration of the dyebath and their action in many cases is due more to this change than to any other specific action.

The colloidal or adsorption theory agrees well with the facts of dyeing but much of the earlier work on which the theory was based was not quantitative and uncontrolled variables were often present. It therefore seemed advisable to carry out a more rigid investigation, controlling, so far as possible, all the variables involved, but particularly the hydrogen ion concentration of the dyebath. This paper deals with the results obtained with acid and basic dyes.

Experimental

Materials used.—Two separate lots of wool (Fleisher's Knitting Worsted) purchased at different times, were used and found to give closely agreeing results. The yarn was first treated with a warm, dilute solution of Ivory soap and was then

¹ Rev. gén. mat. color., 12, 97 (1908); Abstracts, 2, 2159 (1908).

rinsed thoroughly in tap water followed by many changes of hot distilled water. The air-dried yarn was kept in a large bell jar above a saturated solution of calcium chloride to keep the humidity constant, since Wright¹ has shown that changes in humidity cause an appreciable variation in the moisture content of wool. A small piece of yarn was also kept under the bell jar to serve as a control and was weighed from time to time to detect any such change. No appreciable variation was observed over a period of several months.

In making preliminary experiments to determine the time required for equilibrium to be established between wool and dyebath, it was discovered that the amount of Crystal Ponceau taken up from a neutral bath passed through a maximum as the length of the boiling period was increased, as shown in Table I.

TABLE I

Boiling period in minutes	45	60	75	90
Milligrams of dye adsorbed	9.6	17.5	15.6	12.7

This unexpected result was finally traced to the presence in the wool of small amounts of soap apparently retained from the previous washing. It is probable that long-continued boiling brought about hydrolysis of this soap and that the fatty acid thus formed was carried by steam to the lower portions of the return condenser where it solidified, leaving the solution slightly more alkaline. Since Crystal Ponceau is adsorbed by wool less readily from an alkaline solution than it is from a neutral or acid one, a portion of the dye already adsorbed was removed as the bath became alkaline.

All reagents except sodium hydroxide were of the standard grade marked "Chemically Pure." Carbonate-free alkali was prepared by an electrolytic method.² The dyes employed in the preliminary experiments were supplied through the courtesy of the National Aniline and Chemical Company. For the later experiments specially purified dyes were made

¹ Jour. Soc. Chem. Ind., **28**, 1020 (1909).

² Jorissen and Filippo: Zeit. angew. Chem., **23**, 726 (1910).

available through the co-operation of E. I. du Pont de Nemours and Company.

Experimental Procedure.—The following procedure was followed throughout this investigation. A dyebath of known composition and of a total volume of 250 cc was brought to boiling while attached to a return condenser to prevent evaporation. A one-gram sample of the fiber to be tested was placed in this bath and slow but steady boiling was continued for forty-five minutes. In many previous investigations the fiber was allowed to remain in the bath after boiling until the solution had cooled. The latter course is open to serious criticism. Lake¹ has shown that the amount of dye taken up may vary greatly with the temperature of the bath while it is also certain that equilibrium between the fiber and the solution is reached comparatively slowly at low temperatures. If the fiber is allowed to remain in the bath until the solution is cold, the amount of dye adsorbed is probably neither the amount taken up at the boil nor at room temperature, but will be some intermediate value depending on the degree of approach to the room temperature equilibrium. In this work, therefore, the dyed sample was removed directly from the boiling solution at the end of forty-five minutes.

The dyebath was then analyzed for the amount of dye left unadsorbed, the free acid present, or for any other substances as desired. Aliquot volumes were taken for analysis and it was thus unnecessary to correct for the amount of solution retained by the wool.

Determination of the Amount of Dye Adsorbed.—The amount of dye removed by the fiber under given conditions may be determined in two ways. The dyed fiber may be compared with a series of color standards in which the amount of dye is known, or the quantity of dye removed may be secured by difference after the amount of dye left behind in the bath is determined. The first method is difficult to apply to the deeper shades and the standards are hard to prepare. The dye left in the bath, however, can be estimated

¹ Jour. Phys. Chem., 20, 761 (1916).

rather easily in the case of certain dyes. In the earlier experiments the Kober colorimeter was used for this purpose. As the investigation progressed, however, certain difficulties and possible sources of error in the colorimetric method became evident. The colorimetric analysis of a dye solution is based on the assumption that the intensity of color is proportional to the concentration of dye. On testing this assumption experimentally it was found not to be in strict accord with the facts.¹ For accurate results it is therefore necessary to compare an unknown solution with a color standard of nearly equal concentration. On varying the hydrogen ion concentration of a dyebath, it was observed that acids and bases not only affected the color intensity of the latter, but in many instances also produced a distinct change in the color itself. The following experiment serves to illustrate this effect. 50 cc of a standard solution of Crystal Ponceau were placed in each of three Erlenmeyer flasks. To one flask 10 cc of water were added, to the second, 10 cc of N/10 sulfuric acid, and to the third, 10 cc of N/10 sodium hydroxide. The solutions were then compared colorimetrically. The acid solution was found to be apparently eight percent and the alkaline solution no less than three hundred percent more concentrated than the neutral solution, although the difference of color between the neutral and alkaline solutions rendered exact matching difficult. It is thus evident that color comparisons, at least with this particular dye, must be made between neutral solutions or between those containing the same concentration of acid or base. Salts have but little effect at low concentrations on the color intensity and shade, but in stronger solutions they must also be taken into account. The boiling of wool in the dyebath also renders the bath slightly cloudy and makes exact matching with a clear standard very difficult. Furthermore, the colorimetric method is tedious and the eyes become tired quickly. It was therefore deemed advisable to abandon the

¹ Compare Gordon: *Color Trade Jour.*, 6, 61 (1920); *Chem. Abstracts*, 14, 2420 (1920).

colorimetric method and to employ some other means of analysis.

Titration with titanium trichloride, as suggested by Knecht¹ was thereupon tried and was found to give satisfactory results with many dyes. It was found advisable to make a few preliminary experiments with each new dye to determine whether the addition of Rochelle salt was necessary. The titanium chloride reagent was standardized directly in terms of the dye under investigation by titrating a standard solution of the dye to a colorless end-point. All titrations were carried out in boiling solutions from which air was excluded, in accordance with Knecht's directions.

Determination of Hydrogen Ion Concentration.—Throughout this investigation the hydrogen electrode was used to determine the hydrogen ion concentration of the exhausted dyebaths and in some cases also, in the titration of free residual acid. Various types of electrodes and electrode vessels were employed. Free acid was titrated with the Hildebrand² electrode. Clark's³ rocking cell, the Bunker⁴ electrode and a simplified form of the device of Lewis, Brighton, and Sebastian⁵ were all used in this work at various times for the determination of pH.

The application of the hydrogen electrode proved difficult under the conditions met with in much of this work. Adsorption of dye by the electrode tended to lower the adsorption of hydrogen and to render the electrode inaccurate. Traces of grease on the wool were apparently transferred to the dyebaths on boiling and subsequently decreased the activity of the platinum black. Following a suggestion of Dr. E. T. Oakes⁶ the activity of the electrodes was restored by immersion in chromic acid cleaning mixture after each de-

¹ Ber. deutsch. chem. Ges., **36**, 1552 (1903); **40**, 3819 (1907).

² Jour. Am. Chem. Soc., **35**, 847 (1913).

³ Jour. Biol. Chem., **23**, 475 (1915).

⁴ Ibid., **41**, 11 (1920).

⁵ Jour. Am. Chem. Soc., **39**, 2250 (1917).

⁶ Personal communication to the author.

termination of pH. Some dyes are reduced by hydrogen in contact with platinum black and this depolarizing action also introduces an error.

It may be mentioned here that an electrode which was known to be giving low readings in a dye solution was found to indicate correct values of pH when used in buffer solutions. It proved to be an easy matter to check buffer solutions; but dyebaths presented greater difficulties. The Lewis¹ type of vessel with a partially submerged electrode was found to be most satisfactory. The Bunker² electrode gave good results in solutions of inorganic electrolytes, but owing to its smaller surface it was more quickly contaminated than were the larger electrodes of the other types when placed in the dye solutions.

The hydrogen electrodes were supplied with electrolytic hydrogen from a tank. Immediately before use the gas was passed through a quartz tube containing a heated nichrome spiral, to make certain of the complete removal of oxygen.

Normal and saturated calomel electrodes were used as standards and were frequently checked for accuracy. Potentials were measured at room temperature to the nearest millivolt by means of a Leeds and Northrup "Student Type" potentiometer. In view of the sources of error met with in determining the pH of dyebaths, as discussed in the previous paragraphs, the use of a potentiometer of extreme precision was not deemed worth while.

Adsorption of Hydrochloric Acid by Wool.—The adsorption of acids by wool has been studied previously by several investigators.³ Since the amount of acid taken up varies with the specimen of wool, and as the experimental conditions used by previous workers did not correspond entirely with those under which the present experiments on dyeing were to be

¹ Jour. Am. Chem. Soc., **39**, 2250 (1917).

² Jour. Biol. Chem., **41**, 11 (1920).

³ Georgievics and Pollak: Monatsheft., **32**, 655 (1911); Mills and Takamine: Jour. Chem. Soc., **43**, 142 (1883).

carried out, it seemed advisable to redetermine the adsorption isotherm for hydrochloric acid and wool.

One gram portions of the yarn were placed in boiling solutions of hydrochloric acid of known concentrations, all the solutions having a volume of 250 cc. After boiling for forty-five minutes (tests had shown this time to be sufficient for the establishment of equilibrium), the yarn was removed and 100 cc portions of the cooled solutions were titrated to determine the amount of unadsorbed acid. The data are given in Table II.

TABLE II
Adsorption of Hydrochloric Acid by Wool

cc N/10 HCl at start	cc N/10 HCl at end	cc N/10 HCl adsorbed
1.00	0.87	0.13
2.00	1.77	0.23
3.00	2.60	0.40
5.00	4.28	0.72
7.00	6.05	0.95
10.00	8.47	1.53
15.00	13.05	1.95
25.00	22.30	2.70

The isotherm (Figure 1) drawn from the data in Table II is more suggestive of solid solution following Henry's law than of adsorption, but when it is considered that the highest concentration of acid remaining behind in the bath amounted only to about one-hundredth normal, it is seen that the curve, as drawn, really constitutes the first portion of the complete adsorption isotherm and is, therefore, practically a straight line over the small range shown. Georgievics and Pollak¹ have shown conclusively that the taking up of acids by wool is strictly an adsorption phenomenon.

Experiments were next performed to determine the adsorption of acid from a bath containing both acid and dye to see whether the adsorption of acid by wool is affected by the simultaneous adsorption of dye. Fort and Swares and Fort and Andersen² have taken up this question and they present

¹ Monatsheft., **32**, 655 (1911).

² Jour. Soc. Dyers and Colorists, **31**, 80, 96 (1915).

data to show that when both dye and acid are present in a bath, less acid is taken up by the wool than when acid alone is present. There is apparently, therefore, a displacement of acid by the dye.

One gram portions of wool were treated as previously

Fig. 1

Adsorption of Hydrochloric Acid by Wool

described in boiling dyebaths containing hydrochloric acid and Crystal Ponceau. The amounts of dye and free acid left in the bath were determined respectively with the colorimeter and the hydrogen electrode. In all cases the weight of dye at the start was seventy-five milligrams; the acid content was varied as stated in Table III; and the total volume of the bath was maintained at 250 cc. Larger quantities of

acid were not used because at the highest concentration given, practically all of the dye was taken up by the wool. The values given are the averages of duplicate determinations.

TABLE III

Adsorption of Hydrochloric Acid in the Presence of Crystal Ponceau

cc N/10 HCl at start	Final pH of bath	cc N/10 Acid left	cc N/10 Acid removed	Mgs dye adsorbed
0.00	5.3	—	—	4.5
1.00	5.1	0.15	0.85	34.9
2.00	4.2	0.47	1.53	56.3
3.00	3.6	1.20	1.80	67.9
5.00	3.0	2.93	2.07	73.4
7.00	2.75	4.65	2.25	74.2

If one compares these data or the corresponding isotherm (Figure 2) with the previous data and isotherm (Figure 1), it is at once apparent that much more hydrochloric acid has

disappeared from the bath containing acid and dye than was the case with the bath containing acid alone. It does not necessarily follow, however, that this increase represents a greater adsorption of hydrochloric acid. Crystal Ponceau has the formula $C_{10}H_7N : NC_{10}H_4OH(SO_3Na)_2$ and contains 9.16 per-

cent sodium. It is probable that the dye, being a sodium salt, is largely dissociated in aqueous solution. In these acidified dyebaths we probably have hydrogen ions strongly adsorbed by the wool. In order that the fiber shall remain electrically neutral there must be an adsorption of some anion, in this case, the dye anion. As a result, sodium ions remain in the bath, together with the anions from the mineral acid, the adsorption process resulting in a replacement of the free mineral acid with its sodium salt. The disappearance of hydrochloric acid in the

above experiment may therefore be due, not to increased adsorption of the acid, but to its neutralization. If hydrochloric acid has been neutralized, all the chloride ions will be left in the bath while adsorption of the acid will remove chloride ions. The following experiments were performed to answer this question.

Two dyebaths were prepared containing 108.5 milligrams of Crystal Ponceau and 7.00 cc of N/10 hydrochloric acid in a total volume of 267 cc. One gram samples of wool were boiled in each bath for forty-five minutes and then removed. The

Fig. 2

Adsorption of Hydrochloric Acid and Crystal Ponceau by Wool.

($\frac{1}{4}$ the ordinates gives milligrams Crystal Ponceau adsorbed)

resulting solutions were analyzed for unadsorbed dye, for free acid, and for chlorides. Chlorides were determined by decolorizing the solutions with electrolytic hydrogen and then titrating with N/10 silver nitrate using potassium chromate as an indicator. The results are given in Table IV.

Fig. 3

Typical Curve obtained in the Electrometric Titration of 20 cc N/10 NaCl

(A saturated calomel electrode was used for the other half of the cell)

The data from these two trials indicate that the actual adsorption of hydrochloric acid has been practically unaffected by the presence of the dye (Compare (c) and (h)) while most of the disappearance of the free acid was due to its neutralization. The amount of hydrochloric acid actually neutralized was almost exactly one-half of the calculated maximum, pointing to an adsorption of the dye as an acid or primary sodium salt. This explanation becomes more probable if it is remembered that the sulfonic acid groups in the dye are in such a position that one of them acts as a much stronger acid group than the other.

To determine whether other dyes behaved in a similar manner, experiments were performed in which Croceine Orange replaced Crystal Ponceau. In dyeing, the same procedure was followed, the dyebath containing seventy-five

TABLE IV
Adsorption of dye and acid from the same bath

	I	II
(a) cc N/10 HCl at start.....	7.00	7.00
(b) Total N/10 chlorides left in bath.....	6.31	6.47
(c) HCl adsorbed (a — b).....	0.69	0.53
(d) cc free acid left in bath.....	4.26	4.39
(e) HCl neutralized by sodium in dye (b — d).....	2.05	2.08
(f) Milligrams of dye adsorbed.....	104.8	104.6
(g) Calculated possible HCl neutralized by dye.....	4.17	4.17
(h) Adsorption of HCl from solution without dye Figure 1.....	0.65	0.67

milligrams of the dye and a known amount of hydrochloric acid in a total volume of 250 cc. One gram portions of wool were placed in the boiling dyebaths for forty-five minutes. Unadsorbed dye was determined colorimetrically. Free acid was estimated by titration with the hydrogen electrode and

Fig. 4

Adsorption of Hydrochloric Acid and Croceine Orange by Wool

total chlorides were determined electrometrically. Croceine Orange cannot be readily decolorized with hydrogen so it became necessary to employ a volumetric method for the determination of chlorides in colored solutions. This problem was solved by the use of a silver electrode.¹ The average of

¹ Behrend: Zeit. phys. Chem., 11, 462 (1893). The potential of a silver electrode against any solution in which it is placed is a function of the silver ion concentration of the solution. If one measures the potential of a silver electrode immersed in a chloride solution to which silver nitrate is being added, the curve

duplicate experiments with Croceine Orange are given in Table V. They have been plotted in Figure 4.

TABLE V
Adsorption of Croceine Orange and Hydrochloric Acid from the Same Bath

cc N/10 HCl at start	cc N/10 HCl at end	cc N/10 Cl' at end	Mg dye adsorbed	pH
0.00	—	—	5.1	6.8
1.00	0.13	0.87	33.8	5.0
2.00	0.68	1.96	48.5	3.8
3.00	1.36	2.99	55.4	3.3
5.00	2.89	4.88	65.5	2.9
7.00	4.88	6.73	68.2	2.6
10.00	7.57	9.44	68.5	2.4
15.00	12.18	14.11	70.7	2.2
25.00	21.44	23.43	71.8	2.0
cc N/10 HCl at start	cc N/10 HCl adsorbed	cc N/10 HCl found	neutralized calc.	pH
1.00	0.13	0.74	0.96	5.0
2.00	0.04	1.28	1.38	3.8
3.00	0.01	1.63	1.58	3.3
5.00	0.16	1.95	1.87	2.9
7.00	0.27	1.85	1.94	2.6
10.00	0.56	1.87	1.96	2.4
15.00	0.89	1.93	2.02	2.2
25.00	1.57	1.99	2.05	2.0

These curves and data show that Croceine Orange unquestionably diminishes the adsorption of hydrochloric acid by wool. Croceine Orange is a monobasic salt with the formula: $C_6H_5N:NC_{10}H_5OH(SO_3Na)$ with 6.567 percent sodium. In this case the calculated values for the total possible amount of hydrochloric acid neutralized by the sodium in the dye agree

shown in Figure 3 is obtained. So long as silver chloride is precipitated, the silver ion concentration of the solution is extremely small and roughly constant. As soon as an excess of silver nitrate is added, however, the concentration of the silver ions in the solution rises rapidly and a sudden change in the potential of the electrode occurs. It is thus possible to determine chlorides in colored solutions, provided that no other substance is present which forms a precipitate or a complex ion with the silver nitrate. In measuring the potential of the silver electrode, it is, of course, necessary that the calomel electrode be connected with the solution through an ammonium nitrate or similar salt bridge to prevent contamination of the solution with potassium chloride from the electrode.

quite well with the experimental values. It is thus apparent that Croceine Orange is adsorbed by wool largely as the free dye acid. It should be observed that these calculations are based on the assumption that any decrease in chlorine ion concentration is due only to adsorption of hydrochloric acid. It is possible of course that the decrease may be caused by adsorption of sodium chloride. Experiments were performed to determine whether this was actually the case and no adsorption of sodium chloride by wool could be detected.

Adsorption of Acid Dyes and pH of Dyebath. Addition Agents.—The next step in the development of the general problem was to determine quantitatively the relation between the

Fig. 5

Adsorption of Croceine Orange by Wool

hydrogen ion concentration of the dyebath and the adsorption of various acid dyes by wool and from this to proceed to the quantitative determination of the effect of various addition agents.

Using nitric and hydrochloric acids, two series of experiments were made on Croceine Orange to determine the relation between pH and the amount of dye adsorbed. One gram of wool was boiled for forty-five minutes in a bath containing seventy-five milligrams of dye in a total volume of 250 cc. The results are given in Table VI and in Figure 5.

TABLE VI
pH and Adsorption of Croceine Orange

cc N/10 HCl added	Final pH	Mgs. dye adsorbed	cc N/10 HNO ₃ added	Final pH	Mgs dye adsorbed
0.0	5.91	4.0	—	—	—
0.5	5.35	7.0	0.5	5.25	7.0
1.0	5.07	21.4	1.0	5.15	17.2
1.5	4.85	35.7	1.5	4.72	39.1
2.0	4.53	47.8	2.0	4.55	47.9
3.0	3.60	58.9	3.0	3.53	53.6
4.0	3.12	63.5	4.0	3.13	62.5
8.0	2.61	68.8	8.0	2.70	67.7
15.0	2.30	70.4	15.0	2.32	70.1

This curve shows that the amount of Croceine Orange adsorbed by wool increases as the hydrogen ion concentration is made greater. The fact that the chloride and nitrate ions have no specific effect may be accounted for by the assumption that they are either not adsorbed or that they are adsorbed equally.

To show that a change in hydrogen ion concentration produces a similar effect on the adsorption of other acid dyes, experiments were performed using Lake Scarlet R. The experimental conditions were kept the same as those used with Croceine Orange, except that the colorimetric method was abandoned and the amount of dye remaining in the baths was determined by titration with titanium chloride. Curve (a) of Figure 6 represents the data obtained (Table VII).

It is apparent that over a considerable range, the amount of Lake Scarlet R adsorbed by wool is directly proportional to the hydrogen ion concentration of the bath. As the total amount of dye in solution was only seventy-five milligrams, it is obvious that this is a limiting value which accounts for

the sudden upward bend in the curve, since this upward bend represents practically complete removal of the dye. If more dye had been used, it is probable that the proportionality between adsorption and pH would have continued over a still greater range.

TABLE VII
pH and Adsorption of Lake Scarlet R

cc N/10 HCl added	Final pH	Mgs dye adsorbed
0.0	6.43	0.6
0.5	5.58	10.2
1.0	4.90	25.6
1.5	4.31	39.9
2.0	3.88	51.3
3.0	3.37	68.0
5.0	2.85	73.9
8.0	2.57	74.4
15.0	2.13	74.8

In accordance with the theory of dyeing previously outlined in the introduction to this paper, the addition to the dye-bath of substances forming strongly adsorbed anions will cause a decrease in the adsorption of an acid dye, and in general the greater the valence of the added anion, the greater will be its restraining action. The substitution of sulfuric or phosphoric acid for hydrochloric acid should therefore cut down the adsorption of acid dyes. A similar effect should be obtained if salts such as sodium sulfate, sodium phosphate or even sodium chloride are added to dyebaths containing hydrochloric acid.

Pelet-Jolivet,¹ Lake,² and others have investigated this point and have shown that the addition of sulfate and phosphate does actually decrease the amount of dye adsorbed by wool. But none of these investigators were careful to allow for the change in pH of the dyebath which the added salt might produce. The results already presented in this paper make it evident that a quantitative determination of the relative and absolute effect of restrainers such as chloride, sulfate, and

¹ "Die Theorie des Färbeprozesses" (1910).

² Jour. Phys. Chem., 20, 76 (1916).

phosphate, can only be made in dyebaths of equal hydrogen ion concentrations.

Data were therefore obtained to determine the action of restrainers on Lake Scarlet R. The experimental conditions were those described in the previous work, the dyebaths (250 cc) each containing seventy-five milligrams of dye plus different amounts of other reagents as denoted in the table of data (Table VIII). The final pH of each dyebath was ascertained as before and the amount of dye taken up by wool was determined. Curves were then drawn between pH and milligrams of dye adsorbed in the presence of the different addition agents. (Curves b, c, d, and e of Figure 6).

Fig. 6

Effect of Anions on the Adsorption of Lake Scarlet R.

An inspection of these curves brings out several interesting points. The amount of dye adsorbed always increases with the hydrogen ion concentration of the bath. In order to determine the relative effect of the different addition agents, it is essential that comparisons be made at equal values of pH. This is done readily by finding where the curves cross a line parallel to the X axis representing the desired pH. Thus at a pH of 4.0, the amount of dye adsorbed in the presence of hydrochloric acid was 48 mg, in the presence of phosphoric acid, 46.5 mg, and in the presence of sulfuric acid, 30 mg, the order of dye adsorption being $\text{HCl} > \text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4$.

TABLE VIII

The Effect of Addition Agents on the Adsorption of Lake Scarlet R

cc N/10 H ₂ SO ₄	Final pH	Mgs dye adsorbed	
0.5	4.81	1.3	
1.0	4.40	10.6	
1.5	4.13	28.1	
2.0	3.84	40.9	
2.8	3.50	57.5	
4.5	3.14	65.8	
cc N/10 H ₃ PO ₄	Final pH	Mgs dye adsorbed	
1.2	4.98	10.8	
2.5	4.55	22.6	
4.2	4.25	39.0	
5.5	3.93	48.6	
7.0	3.62	57.8	
8.8	3.45	64.6	
12.5	3.11	68.7	
20.0	2.75	73.9	
cc N/10 HCl	cc N/10 NaCl	Final pH	Mgs dye adsorbed
0.5	25.00	4.90	10.0
1.0	25.00	4.55	20.9
1.5	25.00	4.15	35.7
2.2	25.00	3.77	49.1
3.3	25.00	3.28	65.9
5.0	25.00	3.00	69.1
8.0	25.00	2.68	71.6
cc N/10 HCl	cc N/10 NaSO ₄	Final pH	Mgs dye adsorbed
0.5	25.00	4.55	8.6
1.0	25.00	4.05	18.9
1.5	25.00	3.80	27.9
2.0	25.00	3.80	31.0
3.0	25.00	3.36	44.0
5.0	25.00	2.88	54.5
8.0	25.00	2.70	62.0
15.0	25.00	2.37	68.5
25.0	25.00	2.07	73.1

These results are in agreement with the theory. The strongly adsorbed divalent sulfate anion would be expected to cut down the amount of dye anion adsorbed. It is also evident that less dye was adsorbed from hydrochloric acid baths when sodium chloride was added and this is likewise in agreement with the theory. In a similar way, less dye

was adsorbed when sulfuric acid was substituted for hydrochloric acid in the dyebath, although the effect was not as marked for sulfuric acid alone as for hydrochloric acid plus sodium sulfate, because in the latter case the concentration of sulfate ions was greater and the two experiments are not comparable. It is often the custom among colloid chemists to regard phosphate solutions as a source of tri-valent phosphate ions.^{1,2} Were this true we might therefore expect phosphate to be a more effective restraining agent than di-valent sulfate, assuming the valence rule. The data, however, show that phosphate is much less effective. The reason for this perhaps unexpected result probably lies in the fact that in phosphate solutions we do not really have tri-valent ions to any appreciable extent. Phosphoric acid dissociates very largely as a monobasic acid, slightly as a dibasic acid, and only very weakly as a tribasic acid. The effective valence of the anions in phosphate solutions should therefore be between one and two, and we should expect the curve for phosphoric acid to lie between the curves for hydrochloric and sulfuric acids. Inspection of Figure 6 shows that this is indeed the case. Lake³ has reported that the addition of sodium phosphate to dyebaths containing hydrochloric acid almost completely prevented the taking up of acid dyes by wool. He ascribed the effect to the tri-valent phosphate ion. As Lake used an excess of di-sodium hydrogen phosphate, solutions of which have a pH value of about 9.2, it seems probable that the very considerable change in hydrogen ion concentration resulting from the addition of this salt was, to a large extent, the cause of the restraining action that he reported.

An attempt was made to use potassium ferri- and ferrocyanides as sources of tri-valent and tetravalent anions, but in each case these substances reacted with the dye, and the experiments could not be completed.

To show that the phenomena observed in the case of Lake

¹ Lake: *Jour. Phys. Chem.*, **20**, 786 (1916).

² Compare Loeb: *Jour. Gen. Physiology*, **3**, 248 (1920).

³ *Jour. Phys. Chem.*, **20**, 786 (1916).

Scarlet R were general for the acid dyes, another series of experiments was performed with du Pont Orange II. This dye can be titrated readily with titanium chloride in the presence of Rochelle Salt and is therefore easily determined in solution. In each of the experiments in this series one gram of wool was boiled for forty-five minutes in a dyebath (250 cc) containing seventy-five milligrams of dye plus the various addition agents specified in Table IX. In each of the sets of experiments comprising Table IX, however, the total amount of sulfate or phosphate was kept approximately the

Fig. 7

Effect of Anions on the Adsorption of Lake Scarlet R

same and only the pH of the dyebaths was varied; in this regard the series differs from the one with Lake Scarlet R. Thus in the two sets of experiments with sulfuric acid and sodium sulfate, the quantity of acid and the quantity of salt were each varied, but their total was kept constant at 25 cc of either N/10 or M/10 sulfate solution in a dyebath of 250 cc. The results are plotted in Figure 7.

Attempts were made to determine the effect of di-valent and tri-valent cations, but the three (barium, magnesium, and aluminum) whose chlorides were added to the dyebath caused the dye to precipitate. It is well known, however,

TABLE IX

The Effect of Addition Agents on the Adsorption of Orange II

Hydrochloric Acid Alone		
cc N/10 HCl	Final pH	Mgs dye adsorbed
0.5	4.34	28.8
0.7	4.23	33.6
0.8	4.16	34.8
1.0	4.03	35.4
1.3	3.70	47.0
1.5	3.60	51.7
2.0	3.38	54.5
3.0	3.18	59.2
6.0	2.76	63.0
10.0	2.49	69.7

Hydrochloric Acid plus Sodium Chloride			
cc N/10 HCl	cc N/10 NaCl	Final pH	Mgs dye adsorbed
0.3	24.7	4.88	16.4
0.6	24.4	4.68	20.2
0.8	24.2	4.30	29.0
1.0	24.0	3.84	35.0
2.0	23.0	3.56	48.0
3.0	22.0	3.29	57.0
4.5	20.5	2.97	61.7
7.0	18.0	2.68	63.5
10.0	15.0	2.45	66.7

Sulfuric Acid plus Sodium Sulfate			
cc N/10 H ₂ SO ₄	cc N/10 Na ₂ SO ₄	Final pH	Mgs dye adsorbed
0.3	24.7	4.12	13.5
1.0	24.0	3.83	25.0
2.0	23.0	3.50	29.9
3.0	22.0	3.27	36.1
4.5	20.5	2.96	42.5
7.0	18.0	2.71	48.6
11.0	14.0	2.32	53.2
cc N/10 H ₂ SO ₄	cc N/10 Na ₂ SO ₄	Final pH	Mgs dye adsorbed
0.15	24.85	4.08	13.5
1.50	23.50	3.24	28.8
5.50	19.50	2.33	45.9

Phosphoric acid plus di-sodium hydrogen phosphate

N/10 H_3PO_4	N/10 Na_2HPO_4	Final pH	Mgs dye adsorbed
12.4	12.6	4.80	9.6
12.5	12.5	4.75	13.0
12.6	12.4	4.57	14.0
12.9	12.1	4.47	15.3
13.5	11.5	4.00	24.5
14.0	11.0	3.82	31.0
15.5	9.5	3.44	44.0
17.0	8.0	3.30	55.0
18.0	7.0	3.22	57.2
19.2	5.8	3.05	60.8
20.7	4.3	2.89	61.0
23.7	1.3	2.65	65.6
25.0	0.0	2.52	67.5
M/10 H_3PO_4	M/10 Na_2HPO_4	Final pH	Mgs dye adsorbed
12.83	12.17	4.30	18.4
15.34	9.66	3.08	55.1
23.67	1.33	2.28	66.0

that when the calcium or magnesium salt of an acid dye is soluble, it will be taken up more readily than the sodium salt of the same dye.

At low concentrations the effect of such anions as sulfate on the adsorption of an acid dye by wool is due, as stated before, to adsorption of the inorganic anion in place of some of the dye. It is easily possible, however, that at higher concentrations of sulfate the solubility of the dye may be diminished so that its tendency to be adsorbed may actually be increased. In other words, the restraining effect of sodium sulfate on acid dyes may pass through a maximum as the sulfate concentration is increased.

To test this point a series of experiments¹ was carried out with dyebaths which contained more sulfate than was the case previously. General conditions otherwise were kept as before. Each dyebath contained seventy-five milligrams of du Pont Orange II and five cc of N/10 sulfuric acid in 250 cc. One gram of wool was boiled in each bath for forty-five minutes.

¹ We are indebted to Mr. W. W. Paddon for aid in this series of experiments.

The partially exhausted baths were then analyzed for unadsorbed dye. Although equal amounts of acid had been added to all the baths, the hydrogen ion concentrations after dyeing were not the same throughout, probably because of the influence of the salt on the dissociation of the acid. Final hydrogen ion concentrations in this particular series of baths could not be determined by means of the hydrogen electrode because of some peculiar influence of the dye under these conditions. It was therefore necessary to resort to an indirect method for securing pH values. Mixtures of sodium sulfate and sulfuric acid were prepared corresponding to the concentrations existing in the dyebaths and the pH values of these solutions were secured. The values thus obtained were applied to the dyebaths.

In order that the effect of changing the sodium sulfate concentration may be determined, it is necessary that all other variables shall be controlled. The final pH values must therefore be the same throughout the series or the results must be corrected to a constant pH value. The latter method was employed and all adsorption values were corrected to a pH of 3.50, as follows. It was assumed that, over the short range of pH involved, the curves between milligrams of dye adsorbed and pH values were straight lines like those shown in Figure 7 for N/10 and M/10 sodium sulfate and that they were approximately parallel to these lines. For each of the baths a point was placed on Figure 7 at the position representing the milligrams of dye adsorbed and the pH as found. Lines were then drawn through these points parallel to the curve for M/10 sodium sulfate. The intersection of these new lines with the pH line equal to 3.50 gave, by direct reference to the X axis, the corrected milligrams of dye adsorbed.

Another method of comparing the effects of various concentrations of sodium sulfate is to compute the restraining action of the sulfate in each case by comparison with the adsorption curve in Figure 7 for hydrochloric acid alone at the same pH value. The results by both methods are given in Table XI. It is plainly evident that the restraining action

of the sodium sulfate passed through a maximum as its concentration was increased.

TABLE XI
 The Effect of Sodium Sulfate on the Adsorption of Orange II

No.	Bath conc. Na_2SO_4	pH	Mgs dye absorbed	Mgs dye adsorbed corrected	Method 2 restraining effect of sulfate
1	N/100	3.5	29.9	29.9	21.1
2	N/50	3.2	28.8	24.1	33.4
3	N/10	3.1	17.0	10.1	42.5
4	N/5	3.2	14.0	9.9	43.5
5	N	3.5	12.2	12.4	38.8
6	2N	3.6	27.3	28.4	21.7
7	3N	3.6	41.5	43.4	7.5
8	4N	3.7	47.1	50.8	-0.6

In order to show that the effect of the sulfate in the higher concentrations was actually due to a decrease in solubility, portions of baths 5, 6, 7, and 8 were placed in collodion thimbles after dyeing and immersed in solutions of sodium sulfate of the same concentrations as those inside the thimbles. At the end of forty-eight hours Number 5 showed strong diffusion, 6 slightly less, and 7 and 8 only very slight diffusion with 8 less than 7, showing that the sodium sulfate had lowered the solubility of the dye.

Basic Dyes

Experiments were next undertaken with basic dyes of which Methylene Blue was chosen first as a typical example. This dye proved to be a convenient one because it may be determined readily and accurately by titration with titanium chloride. Diffusion experiments¹ (Fig. 8) indicated that the

Fig. 8
 Diffusion Tube

¹ A glass tube (AB) of about 2 mm inside diameter and sealed at the top is filled with distilled water and then placed with its open end just below the surface of the dye solution to be tested. If the dye is in true solution, diffusion will be evident in a few hours and after several days the color will have extended nearly to the top of (AB). Colloidal suspensions show little or no diffusion. In case electrolytes have been added to the dye-bath, the tube (AB) should be filled with an equivalent solution of

dye forms true solutions in either neutral, weakly acid or weakly basic solutions. In more strongly basic solutions however, the dye forms a suspension and may be almost completely precipitated as the alkalinity is increased further.

Fig. 9

Adsorption of Methylene Blue by Wool

By following the general procedure that was employed with the acid dyes, the amount of methylene blue taken up by wool in the presence of addition agents was determined. As in the previous work, one gram of wool was boiled for forty-five

these electrolytes instead of with pure water, to prevent any change in the condition of the dye as it diffuses up the tube. It should be recognized that between true solutions and colloidal suspensions we may and do have all degrees of combination of the two states. Part of the dye may be in true solution while the rest is colloidal.

minutes in a dyebath of 250 cc containing seventy-five milligrams of dye.

The first step was to ascertain the relation between hydrogen ion concentration and the amount of dye adsorbed. The data given in Table XII and in Figure 9 represent the results

Fig. 10
Adsorption of Methylene Blue by Wool

obtained. It will be noted that the effect of a change in pH is not so marked with this dye as it was in the case of acid dyes. It is also apparent that the total amount of base used is as important as the final pH of the solution. To bring out this point the curves in Figure 10 have been prepared by plotting total base added as ordinates instead of pH. Since the amount

TABLE XII
The Adsorption of Methylene Blue by Wool

In the Presence of Sodium Hydroxide			
cc N/10 NaOH	Final pH	Mgs dye adsorbed	
0.0	4.50	4.0	
1.0	4.72	9.0	
1.7	4.73	16.3	
2.3	5.03	27.0	
2.9	5.69	38.7	
3.4	6.02	42.0	
4.0	8.05	41.5	
7.0	8.40	23.7	
10.0	9.81	11.9	
In the Presence of Sodium Chloride			
cc N/10 NaOH	cc N/10 NaCl	Final pH	Mgs dye adsorbed
1.0	25.0	4.80	6.4
1.7	25.0	4.80	11.6
2.3	25.0	5.12	17.1
2.9	25.0	5.29	21.4
3.4	25.0	5.66	28.9
4.0	25.0	6.18	46.9
In the Presence of Sodium Sulfate			
cc N/10 NaOH	cc N/10 Na ₂ SO ₄	Final pH	Mgs dye adsorbed
1.0	25.0	5.00	14.2
1.7	25.0	5.13	21.4
2.3	25.0	5.35	29.4
2.9	25.0	5.48	37.6
3.4	25.0	5.78	39.6
4.0	25.0	6.17	37.1
In the Presence of Barium Chloride			
cc N/10 NaOH	cc M/10 BaCl ₂	Final pH	Mgs dye adsorbed
1.0	25.0	4.80	4.3
1.7	25.0	4.96	8.4
2.3	25.0	5.08	9.9
2.8	25.0	5.05	10.8
3.4	25.0	5.17	13.2
4.0	25.0	5.35	15.6
6.0	25.0	5.50	17.0
8.0	25.0	6.06	17.6
10.0	25.0	6.70	28.5
12.0	25.0	7.61	32.3
15.0	25.0	8.72	14.2

of dye adsorbed at first is practically proportional to the total base added, it seems probable that the dye base is taken up more strongly than its hydrochloride and that the adsorption of dye is roughly proportional to the amount of free dye base present.

A striking feature of each of these curves is the presence of a point of maximum adsorption. There are apparently two reasons for such a point. It will be recalled from the experiments on diffusion previously described that methylene blue passes from true to colloidal solution as sodium hydroxide is added and that when the latter is present in fairly large quantities, flocculation occurs. It is probable that sodium hydroxide removes hydrochloric acid from the methylene blue and sets free the dye base which is insoluble in water and which remains in suspension.

The dye now being distinctly in colloidal solution, a modification of the dyeing process results. All dyes behave like the substantive or direct dyes if their solutions become colloidal. For this reason, Methylene Blue, as soon as it has been rendered colloidal by the addition of sodium hydroxide, acts as a substantive dye and no longer behaves as a true basic dye. Briggs and Kakiuchi and Briggs and Woodward¹ have shown that the adsorption curves for substantive dyes pass through a maximum as the concentration of electrolytes is increased. Since Methylene Blue is colloidal in alkaline solution, it is to be expected that it would behave in a similar way. This supposition is confirmed by the data given in Table XII.

The other factor tending to produce a maximum point in the curves, is the action of the sodium hydroxide on the wool. The samples dyed at the higher concentrations of alkali showed very appreciable decomposition.

In those experiments the Methylene Blue was adsorbed strongly by the hydrogen electrode and after a few minutes the readings of the electrode showed a gradual falling off. Table XIII contains a series of readings made under such conditions.

¹ Results will be published in a subsequent paper.

TABLE XIII

Voltage reading....	.460	.562	.560	.558	.558	.556	.553	.548
Time in minutes....	1	2	3	5	7	10	20	27

"Time in minutes" means minutes elapsed from the time hydrogen was first started bubbling through the solution under test. The voltage rises quickly, remaining at a nearly constant value for several minutes and then gradually falls off again. This secondary decline is probably due to an adsorption of the dye by the electrode. By treating the hydrogen electrode with chromic acid cleaning mixture after each determination, the film of dye is stripped off and the surface renewed.

If the theoretical hydrogen ion concentrations of the dye-baths given in Table XII are calculated, it will be found that in all cases the observed pH values are lower than one would

Fig. 11

expect, even though one allows for the hydrochloric acid liberated from the Methylene Blue. In order to make sure that the dye had not affected the hydrogen electrode and caused it to give consistently low readings, the apparatus shown in Figure 11 was prepared. In this device the hydrogen electrodes were partially immersed in distilled water contained in a collodion sac (S). The latter was then immersed in a dye bath of Methylene Blue whose pH value had been previously determined in the usual way. The bath chosen was a strongly alkaline one

which had gone almost completely colloidal on boiling. Alkali began at once to pass into the sac and the rate of diffusion was followed by observing the change in the potential of the electrode. The dye did not diffuse through the col-

lodian membrane so its possible effect on the electrodes was eliminated. The final pH value obtained in this way corresponded closely (8.72 and 8.79) with the value obtained in the usual manner where the electrodes were immersed directly in the dyebath.

One gram of wool was boiled forty-five minutes in 250 cc of sodium hydroxide solution containing 15.0 cc of N/10 sodium hydroxide. The free base left after this treatment was titrated with hydrochloric acid using phenolphthalein as indicator. It was found that only 5.0 cc of free base remained. The action of the alkali on the wool and its removal by the latter will therefore account for the high concentrations of hydrogen ion found in the experiments on Methylene Blue.

Summary

1. The process of dyeing wool with acid and basic dyes has been investigated from the standpoint of the adsorption theory of dyeing as formulated by Pelet-Jolivet and Bancroft.

2. The effect of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes has been determined quantitatively for typical acid dyes.

3. It has been shown that the taking up of dyes is a case of adsorption and that the amount of dye adsorbed varies continuously with a change in the hydrogen ion concentration of the dyebath. No evidence of chemical action between dyes and wool has been found.

4. The use of the hydrogen electrode has made it possible to control a hitherto neglected variable.

5. The action of assistants has been studied and has been found to be strictly in accord with the theory.

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