EFFECT OF INORGANIC IONS

ON

COTTON DYEING

A THESIS

Presented to

the Faculty of the Graduate Division

by

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ON

COTTON DYEING

Approved:

Date Approved by Chairman: *March 14, 1953*

DEDICATION

To my father,

Yong Soon Chun

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To my father,

Yong Soon Chun

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Continued)

SUMMARY

The purpose of this investigation was (1) to determine the effect of various inorganic monovalent ions (and one divalent anion) on cotton dyeing, such as their effect on rate of dyeing, the shade produced, and (2) to devise a theory to explain the results obtained.

Cotton samples were dyed at the boil from one to five hours, in the presence of various inorganic ions, and the effect of these ions on rate of dyeing and equilibrium adsorption was determined with the aid of a colorimeter. A stable direct dye, Calcodur Resin Fast Grey 2G, was chosen for this experiment in order to eliminate the effect due to the decomposition or the buildup of direct dyes in aqueous solution. The various inorganic ions were added to the dyebath on the equiweight basis as well as on the equimolar basis, and the results were compared.

From the results obtained after five hours of dyeing on the equiweight basis using ammonium salts, it was found that the order of anions producing increasing adsorption of Calcodur Resin Fast Grey 2G is:

$$I^- < Br^- < NO_3^- < F^- < SCN^- < SO_4^= < Cl^-$$
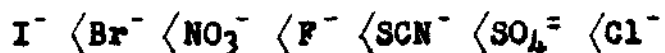
From the results obtained after five hours of dyeing on the equimolar basis using potassium salts, it was found that the order of anions producing increasing adsorption

of the dye under consideration is:

$$SCN^+ < I^+ < F^+ < Cl^+ < NO_3^+ < Br^+$$
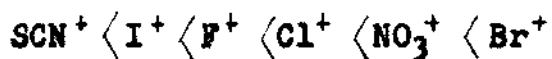
However, the difference in per cent exhaustion obtained using bromide or thiocyanate ion was only 2.8, which is within the scope of the experimental errors. This result indicated that the nature of the anions appears to be of secondary importance.

From the results obtained after five hours of dyeing on the equimolar basis using chlorides, it has been found that the order of cations producing increasing adsorption of the dye under consideration was:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$
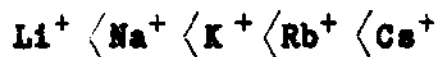
From the above series, it has been concluded that the size of the hydrated inorganic monovalent positive ion will certainly affect the adsorption of dye on the cotton fiber.

During the course of this investigation, it has also been found that lowering the pH of the dyebath will increase the adsorption of direct dye on the cotton fiber.

When the effect of pH of the dyebath was kept to a minimum, two similar ions, such as potassium and ammonium ions, gave similar results in increasing the per cent exhaustion of the dyebath.

CHAPTER I

INTRODUCTION

Stages of Dyeing Process.--The phenomenon of the combination
of dyes with fibers is known as the dyeing process. The
stages of the dyeing process may be classified as follows (1):

1. Diffusion of dye through the aqueous dyebath to
    the surface of the fiber.

2. Adsorption of dye on the outer surface of the
    fiber.

3. Diffusion of dye inside the fiber from the surface
    towards the center.

Of the three stages, adsorption of dye on the surface of the
fiber is most rapid. Diffusion within the fiber is much
slower than in the aqueous solution due to mechanical
obstruction to movement presented by the network of fibers
and also because of the restraining chemical attractions
between dye and fiber.

Direct dyestuffs ionize in solution to DSO_3^- and Na^-,
i.e. into a dye ion which carries a negative charge, and a
colorless sodium ion. Since cotton acquires a negative
surface charge when it is placed in an aqueous dyebath, the
first stage of the dyeing process is hindered by the natural
force of repulsion of like-charged bodies.

To minimize the above-mentioned repulsion force, salt
has been used for many years in the application of direct

dyestuffs to cotton fibers. When salt is added to a dyebath, the salt molecules dissolve and ionize into positively charged sodium ions and negatively charged chloride ions. The positively charged sodium ions are attracted by the negatively charged cotton surface, and by the negatively charged dye ions. In effect, the sodium ions neutralize some of the negative charges and thereby lower the overall potential difference between the fiber and dyebath interface. Due to this lowering of potential difference, the negatively charged dye ions may approach the negatively charged cotton surface and become adsorbed by polar or nonpolar van der Waals's forces.

Because of the important role of salt in cotton dyeing, much work has been done to determine the effect of electrolytes on cotton dyeing. Most of this work was concerned with the effect of common salt, NaCl, or the effect of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$. The effect of electrolytes other than the above salts on dyeing has been studied to some extent, although for economic reasons there is little likelihood of sodium chloride and sodium sulfate being displaced from practical usage.

Historical Background.--The subject seems to have been first studied by Wictoroff (2), who measured the amount of dye adsorbed by cellulose in an arbitrarily fixed time from solutions containing various electrolytes. The results have little quantitative significance, as no attempt was made to

establish equilibrium, but when using sulfates it was found that the order of cations producing increasing adsorption of Benzo Pure Blue was:

$$NH_4^+ < Na^+ < K^+ < Mg^{++} < Ni^{++} < Mn^{++} < Zn^{++} < Cd^{++} < Al^{+++}$$
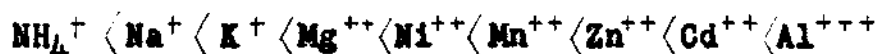
Similar experiments for three hours at 20°C. were made by Schramek and Gotte (3), who, using Dianil Blue R (CI 23690), arrived at the series:

$$NaOH < Na_2CO_3 < Na_2SO_4 < NaCl < MgSO_4$$

This series contains simultaneous variations of anions, cations, and pH, and the experiment was quite inadequate for equilibrium.

Boulton, Delph, Fothergill, and Morton (4) found that adsorption of direct dyes is approximately the same from dyebaths containing equivalent quantities of different inorganic electrolytes containing a univalent cation, but is increased if the cation is divalent.

Neale and Patel (5) examined the effect of several cations on the rate and equilibrium adsorption of Benzo-purpurine 4B (CI 23500) and Chlorazol Sky Blue FF (CI 24410). The order of effectiveness varies somewhat with concentration, but in N/10 solutions using Chlorazol Sky Blue FF the order was:

$$Na_2HPO_4 < KH_2PO_4 < NaCl < NH_4Cl < MgCl_2 < ZnSO_4 < CaCl_2 < BaCl_2$$
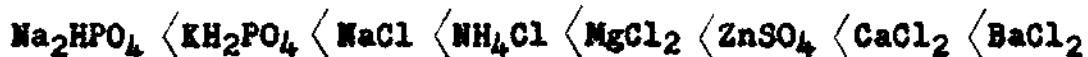
In these experiments aluminum was also used but produced only low adsorption, which Neale and Patel attribute to the

formation of the insoluble aluminum salt of the dye. Insoluble salts were also formed with cerium, copper, and thorium ions.

All of the above results, being expressed mainly in graphical form, are not available for quantitative treatment. The observations indicate that the nature of the cation of a salt, and particularly its valency, is of great importance in promoting adsorption of direct dyes on cellulose. The nature of the anion appears to be of secondary importance.

The instability of certain direct dyes was observed and reported by Vickerstaff and Lemin (6); by Thomson (7) for Direct Red 75 (CI 25390); by Neale and Stringfellow (8) for Direct Red 2 (CI 23500) and Direct Yellow 12 (CI 24895); by Speakman and Clegg (9); and by Holmes and Standing (10) for Direct Orange 26 (CI 29150).

Millson (11) studied many direct dyestuffs, and concluded that the direct dyes can be divided into three groups as follows:

1. Dyes which decompose.

2. Dyes which are stable.

3. Dyes which build up.

Millson also found, through the experiments, that in many instances the addition of ammonium thiocyanate retards or inhibits decomposition, and also causes dyes which are normally slow in reaching their potential color-value development

to attain, within one hour, a depth of shade approaching that obtained by boiling four to six hours without ammonium thiocyanate. However, no explanation was given for the above phenomena, and no work concerning other salts was reported.

Purpose of Investigation.--The purpose of this research was to determine the effects of various inorganic ions on cotton dyeing, such as their effect on rate of dyeing, and the shade produced, and to devise a theory to explain the results obtained.

Cotton samples were dyed in the presence of various inorganic ions, for one to five hours, and the effect of these ions on rate of dyeing and equilibrium adsorption was determined with the aid of a colorimeter. A stable direct dye was chosen for this experiment in order to eliminate the effect due to decomposition or buildup.

CHAPTER II

THEORIES OF DIRECT DYEING

Introduction.--The annual production of coal-tar dyes in the
United States amounts to approximately 150,000,000 lbs, of
which about 60 per cent is used for cellulosic fibers. The
two dye types making up most of this 60 per cent are the
direct dyes and the vat dyes. The majority of direct dyes
are organic azosulfonic acid salts which are water-soluble
and which have marked affinity for cellulose. If a 10 g.
sample of cotton is immersed in 500 ml. of a dilute aqueous
solution of a direct dye containing added electrolyte at 50
degrees C. to 100 degrees C., the dye, as a colored anion,
will be exhausted more or less rapidly onto the cotton,
causing the solution to lose much of its color. This prop-
erty of a dye to be preferentially absorbed is called "substan-
tivity." Since many colored compounds have no substantivity,
the substantivity is a unique property of dyes.

The mechanism by which dyes transfer from solution to
fiber, the factors which control the rate and equilibrium
value in dyeing, and the reasons for substantivity have
been investigated for several years. The book written by
Vickerstaff (12) covers the subject excellently. It is the
purpose of the present chapter to cover the important
principles in the dyeing of cellulosic materials.

The nature of the substrate, cellulose, and the properties of dyes and dye solutions will be considered briefly before discussing the dyeing process itself.

The Substrate.--Cellulose is a long chain molecule made up of unit molecules of glucose condensed together, and linked by glucosidic linkages. The repeating unit of two glucose units is called cellobiose, and the length of the cellobiose unit is 10.3 Å.

The molecular weight of cellulose varies with its origin and covers a wide range of values, but it is agreed that the number of glucose residues in the cellulose chain is of the order of 10,000 in natural form.

The arrangement of cellulose chains in cellulosic fibers is agreed to be roughly parallel to the fiber axis. There are regions in the fiber where a large number of chains may run parallel to each other for a portion of their length and these regions, in which the chains are tightly packed together and held by hydrogen bonds, are crystalline and are often referred to as crystallites or micelles. The ratio of crystalline to amorphous regions in the fibers largely determines the differences in many properties between one fiber and another.

By virtue of the three hydroxyl groups per glucose unit, cellulose is a hydrophylic substance and is readily wet by water. It swells on immersing in water, the increase in

size of a fiber being due largely to sorption of water by the amorphous regions. The water, in a sense, surrounds the cellobiose chains. In dyeing, this makes possible the approach of dye molecules to the surface of the chains where they may become attached. If this picture is correct, the total available surface area of the amorphous regions is therefore important in considering the dyeing phenomenon. Hunt, Blaine, and Rowen (13) reported a surface area of 71 m.^{2}/g. from nitrogen sorption measurements on caustic-swollen and solvent-dried cotton linters. These authors calculated from these data a "pore size" of 20 Å. for caustic-swollen cotton and 16 Å. for water-swollen cotton. Much work has been done to measure the pore size of cellulose. On the whole, however, all the evidence is in fairly good agreement with the view that pores of mean radius 15-30 Å. exist in water-swollen cellulose which are large enough to permit the passage of dye molecules.

Dyes and Dye Solutions.--Dyes may have high or low substantivity and may vary considerably in their fastness properties when dyed samples are rinsed repeatedly in distilled water.

Vickerstaff (14) reviewed the work of many investigators who studied the relationship between chemical structure and substantivity, and summarized the following requirements which should be fulfilled in order for a dye to be substantive to cellulose:

1. The molecule should be capable of assuming a
linear configuration.

2. The aromatic nuclei should be capable of as-
suming a coplanar arrangement.

3. The molecule should contain groups capable of
forming hydrogen bonds.

4. The presence of a conjugated system of double
bonds, which by resonance promotes coplanarity
of the molecule and probably favours hydrogen
bond formation by the groups at the ends of the
conjugated chain.

5. Widely spaced hydrogen bond-forming groups.

6. The presence of the minimum number of solubili-
sing groups necessary for solubility.

7. The disposition of the solubilising groups along
one side of the dye molecules and of hydrogen
bonding groups along the other side.

The hydrogen bonding which is believed to hold dye
molecules onto cellulose undoubtedly occurs with the hy-
droxyl groups of cellulose. Such bonding may occur with
either electron-donating or electron-accepting groups on
the dye molecule. For example, an amino group on the dye
would provide the bonding electrons

$$dye - \overset{H}{\underset{H}{N}} \rightarrow H - O \text{ -cellulose}$$
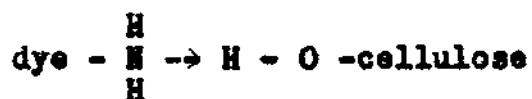
while in the case of an amide group the bonding electrons
might be furnished by the cellulosic oxygen as follows:

$$H - N - H \longleftarrow O - cellulose$$

$$\begin{array}{c} H \\ | \\ dye --- \quad C = O \end{array}$$
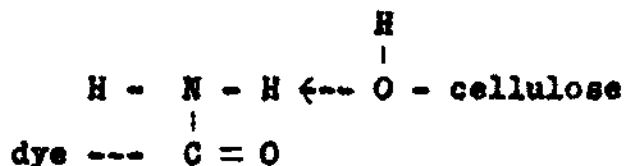
The properties of dyes in aqueous solutions are im-
portant in a consideration of dyeing, since, in general,
dyes are applied from aqueous solutions. Although there
are some exceptions, the aggregation of most direct dyes in
water solution is, perhaps, a characteristic feature of this
class. The degree of aggregation varies widely depending
on the dye, the temperature, electrolyte concentration, and
certain other factors. The presence of hydrogen-bonding
groups on direct dyes is probably responsible for inter-
molecular aggregation. Valko (15) pointed out that the
residual valence forces which are responsible for substan-
tivity of a dye for cellulose are probably the same as those
which cause aggregation. The addition of salt to a dyebath
increases both the exhaustion of dye onto cellulose and the
degree of aggregation of the dye in solution. This is due to
the effect of the electrolyte in lowering the electrostatic
force of repulsion between a dye anion and negatively charged
cellulose in the case of dyeing, and between two or more dye
anions in the case of aggregation. Because of the parallelism
between dye aggregation and dye exhaustion on the addition of
salt to a dyebath, an older theory of dyeing regarded dye

exhaustion as a "salting out" of dye onto cellulose, purely
as a result of decreased solubility. It is now believed that
the presence of salt in direct dye solutions causes dye ex-
haustion to take place in spite of aggregation and not because
of it.

The Dyeing Process.--Royer, McCleary, and deBruyne (16) studied
the rate and equilibrium of the direct dyeing process, using a
commercial direct dye, Sky Blue FF (CI 24410). It has been
found that an increase in temperature causes a decrease in
the equilibrium amount of dye transferred to the fiber.
This means that the reaction

Dye (solution) -----> dye (cellulose)

is exothermic, and ΔH for the reaction is therefore negative.

It has also been found that both the rate of dyeing
and the equilibrium dye adsorption are increased by increase
of salt concentration.

The mechanism by which a direct dye is exhausted from
solution and transferred onto and through a fiber of cellulose
is best understood by the following simplified picture of
dyeing. Let a fiber be immersed into a large dye bath so
that during dyeing there will be essentially no change in the
bath concentration. Almost immediately after immersion of
the fiber, dyeing of an infinitesimally thin surface portion
of the fiber takes place, with establishment of an equilibrium
between the concentration of dye in this layer and the concen-

tration in solution. Dyeing then proceeds by diffusion of
dye from this surface region towards the center of the fiber
until the fiber is uniformly dyed throughout. Dyeings in
which the bath is of finite size are more complex because
the concentration of dye in the fiber surface is continually
decreasing during dyeing in order to maintain equilibrium
with the exhausting dye bath. This situation complicates the
systematic interpretation of data, but does not change the
picture of the process.

Crank (17) made a thorough study of the diffusion of
direct dyes into cellulose from a theoretical point of view.
Experimental methods for the determination of diffusion coef-
ficients of dyes in cellulose have included (a) dyeing of
cellophane in an infinitely large-volume dye bath and (b)
dyeing of cylindrical fibers in an infinite bath. The mathe-
matics of the second method are more complex than the first.
Crank has worked out the mathematics for a third experimental
method, the dyeing of cylindrical fibers in a finite-volume
bath. This involves correction for the exhausting dye bath
and makes the method for determining diffusion coefficients
comparable to practical dyeing methods.

There have been two principal pictures of the mechanism
of cellulosic dyeing expressed by various investigators. The
first picture regards the intercrystalline regions of water-
swollen cellulose as being made up of semipermanent capillaries
or pores filled with water, through which dye molecules may

diffuse and become attached to cellulose chains along the walls.

The second picture regards swollen cellulose as a matrix of chains knotted together at random points to form "crystallites," the intercrystalline regions being filled with a viscous solution of flexing cellulose chains in water. Dye ions diffuse through this solution and become attached to the chains.

A simplified view of the diffusion of dye within cellulose is to regard it as free diffusion in water modified by the following factors: (a) the hindrance of the network of cellulose chains which get in the way of diffusing dye molecules; (b) the affinity of cellulose for dye; this causes dye molecules, which otherwise might have diffused farther, to attach themselves to cellulose chains; (c) the hindrance of diffusion because of electrical repulsive forces between diffusing dye anions and cellulose chains, which are negatively charged due to carboxyl groups and/or adsorbed dye anions.

Neale and Stringfellow (18) studied the effect of salt on dyeing and observed the striking effect of salt concentration on the apparent diffusion coefficient D, of dye in cellulose. D increases very rapidly at low concentration, and then passes through a maximum with further increases in salt.

Two effects may be noted here: (a) with no salt there

is virtually no diffusion. This is due to the electrical repulsion of negatively charged cellulose and dye anions. Addition of small amounts of salt rapidly lowers this potential barrier, permitting a sharp increase in diffusion. (b) The diffusion coefficient passes through a maximum. This is due to the increasing adsorption of dye anions by cellulose chains with increasing salt concentration and possibly to other factors such as aggregation.

It is important to mention that there is a large range of diffusion rates among direct dyes. Boulton (19) measured the "times-of-half-dyeing" for a long list of direct dyes, and found them to vary over a range of 1 to 3,700. Boulton emphasized the desirability of choosing dyes which have similar diffusion rates in order to obtain uniformity of shade and strength on the dyed material.

A committee of the Society of Dyers and Colourists in England made a survey of a large number of direct dyes (20), and divided them into three classes--namely, (a) self-levelling," (b) "salt-controllable," and (c) "temperature-controllable." These classifications refer to dyeing behavior of the dyes, and the descriptive terms indicate the variable which must be controlled in order to obtain uniform dyeings on cellulosic materials.

The theoretical aspects of the effect of salt and of temperature on direct-dyeing equilibrium have been considered by a number of investigators, prominent among whom are Neale

and his coworkers, Standing and his coworkers (21), Crank
(22), and Peters and Vickerstaff (23). One of the most
successful approaches is the thermodynamic treatment of
Peters and Vickerstaff, which was applied to a number of
dyes by Marshall and Peters (24). The standard free energy
change in dyeing was expressed as RT times the logarithm of
the ratio of activities of dye in fiber and in solution.
The activity of dye in the fiber was taken as the product
of its ion concentrations, each divided by an "effective
volume," V, of the cellulose. The Donnan membrane equilibrium
was assumed to hold. It was then possible to calculate the
concentration of sodium ions in the fiber from the analysed
concentration of dye anions in the fiber and the known concen-
trations of both dye and salt in solution. Knowing all these
concentrations, it was possible to calculate directly the
standard free energy change from any set of equilibrium
dyeing data. Two important features of these calculations
are: (a) The sodium ion concentration in the fiber is not
assumed to be simply that associated with dye anions; thus
the concentration of salt within the fiber is not neglected.
(b) There is some controversy as to the physical significance
of V, the "effective volume" of cellulose. It must be de-
termined by dye adsorption experiments. It appears to be
related to the effective volume of solvent water within the
swollen cellulose phase.

The most significant finding in this work of Marshall
and Peters is that ΔH and ΔF values are essentially the same
for four types of cellulose studied; hence, the mode of
attachment of direct dyes to different cellulosic fibers is
the same. According to these authors, this supports the view
that dyeing with such dyes consists in a molecular attraction
between the dye molecule and the cellulose chain molecule,
the energy changes on adsorption thus being independent of
the physical structure of the fiber, but highly dependent
upon the molecular structure of the dye. Assuming the linking
of dye and fiber to arise from hydrogen bonds, then at least
two such bonds are present in the dyes tested. The differ-
ences in dyeing behavior of the various cellulosic fibers
must arise solely from differences in their physical structure,
particularly as it affects the effective volume of the cellulose
phase for adsorbed ions. The fact that cuprammonium rayon
will absorb more dye than viscose rayon is due to a greater
number of cellulose-chain sites in the former fiber upon
which dye molecules may become attached.

CHAPTER III

MATERIALS AND EQUIPMENT

The following materials and equipment were used in this work.

A. **Fabric.**--

 Cotton, 71 x 61, plain weave, scoured and bleached.

B. **Dye.**--

 Calcodur Resin Fast Grey 2G.

C. **Chemicals.**--

 1. Ammonium Bromide, solid reagent.

 2. Ammonium Chloride, solid reagent.

 3. Ammonium Fluoride, solid reagent.

 4. Ammonium Iodide, solid reagent.

 5. Ammonium Nitrate, solid reagent.

 6. Ammonium Sulfate, solid reagent.

 7. Ammonium Thiocyanate, solid reagent.

 8. Cesium Chloride, solid C.P.

 9. Lithium Chloride, solid reagent.

 10. Potassium Bromide, solid reagent.

 11. Potassium Chloride, solid reagent.

 12. Potassium Fluoride, solid reagent.

 13. Potassium Iodide, solid reagent.

 14. Potassium Nitrate, solid reagent.

15. Potassium Thiocyanate, solid reagent.

16. Rubidium Chloride, solid C.P.

17. Sodium Chloride, solid reagent.

D. Equipment.--

1. Beckman pH Meter, Model H-2.

2. Christian-Becker Chainomatic Analytical Balance.

3. Constant Temperature Oven.

4. Lumetron Photoelectric Colorimeter, Model 402-E.

5. Precision Torsion Balance.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Preparation.--A 5 gram sample of cotton was weighed for each experimental dyeing. Since the fabric had been scoured and bleached by the manufacturer, it was not necessary to wet the sample before dyeing.

Calcodur Resin Fast Grey 2G, a stable direct dye, was used for the experimental dyeing throughout this work. The concentrated dye solution was made by dissolving 5 grams of dyestuff, which was weighed accurately using the analytical balance, in deionized water, and adjusting the final volume to 1 liter using a 1000 ml. volumetric flask. Consequently, 10 ml. of the prepared concentrated dye solution contained 0.05 grams of dyestuff.

The desired amount (12.5 grams) of the following salts was weighed accurately on the analytical balance, and in each case the weighed salt was dissolved in deionized water, and the final volume was adjusted to 1 liter using a 1000 ml. volumetric flask.

1. Ammonium Bromide
2. Ammonium Chloride
3. Ammonium Fluoride
4. Ammonium Iodide

5. Ammonium Nitrate

6. Ammonium Sulfate

7. Ammonium Thiocyanate

8. Sodium Chloride

Twenty ml. of each of the above concentrated salt solutions contained 0.25 grams of salt.

The desired amount (0.5 gram-moles) of each of the following salts was weighed accurately on the analytical balance, and in each case the weighed salt was dissolved in deionized water; the final volume was adjusted to 1 liter using a 1000 ml. volumetric flask.

1. Ammonium Chloride

2. Cesium Chloride

3. Lithium Chloride

4. Potassium Bromide

5. Potassium Chloride

6. Potassium Fluoride

7. Potassium Iodide

8. Potassium Nitrate

9. Potassium Thiocyanate

10. Rubidium Chloride

11. Sodium Chloride

Twenty ml. of each of the above concentrated salt solutions contained 0.01 mole of salt.

The Experimental Dyeing.--The experimental dyebath was pre-
pared by adding the required amount of dye and salt to the
bath, followed by the addition of sufficient deionized water
to bring the volume to 200 ml. The required amount of dye
and salt were pipetted separately into each beaker from the
appropriate concentrated solution.

A 5.0 gram cotton sample was then placed in each
dyebath and the beakers were placed on a gas burner. The
valve of the gas burner was controlled to heat the dyebath
slowly. In each experimental dyeing, the dyebath reached
the boil in about fifteen minutes and a rolling boil was
maintained throughout the dyeing. Deionized water was added
from time to time in order to keep the total volume constant
throughout the dyeing; also the dyebath was agitated constant-
ly by hand with a glass stirrer in order to obtain level
dyeing.

The desired amount of dye in this work was 1 per cent
on the weight of fabric, and therefore 0.05 grams of dye
were added to each dyebath by pipetting 10 ml. of the
concentrated dye solution. The required amount of salt, the
kind of salt, and the time of dyeing are listed in Tables
1 and 2.

After the dyebath had been boiled for the desired time,
the dyed sample was taken from the bath, rinsed in tap water,
and dried in the constant temperature oven. The exhausted

Table 1. Record of Dyeing Conditions I
Weight Basis

Dyebath Sample Number	Amount of NaCl Used (% o.w.f.)[1]	Kind of Second Salt Used	Amount of Second Salt Used (% o.w.f.)[1]	Time of Dyeing (Hours)
1	10	None	0	1
2	10	None	0	3
3	10	None	0	5
4	10	NH_4SCN	5	1
5	10	NH_4SCN	5	3
6	10	NH_4SCN	5	5
7	10	NH_4I	5	1
8	10	NH_4I	5	3
9	10	NH_4I	5	5
10	10	NH_4Br	5	1
11	10	NH_4Br	5	3
12	10	NH_4Br	5	5
13	10	NH_4NO_3	5	1
14	10	NH_4NO_3	5	3
15	10	NH_4NO_3	5	5
16	10	NH_4Cl	5	1
17	10	NH_4Cl	5	3
18	10	NH_4Cl	5	5

[1] The per cent is based on the weight of fiber being dyed.

Table 1. (Continued) Record of Dyeing Conditions I
Weight Basis

Dyebath Sample Number	Amount of NaCl Used (% o.w.f.)	Kind of Second Salt Used	Amount of Second Salt Used (% o.w.f.)	Time of Dyeing (Hours)
19	10	$(NH_4)_2SO_4$	5	1
20	10	$(NH_4)_2SO_4$	5	3
21	10	$(NH_4)_2SO_4$	5	5
22	10	NH_4F	5	1
23	10	NH_4F	5	3
24	10	NH_4F	5	5
25	15	None	0	1
26	15	None	0	3
27	15	None	0	5

Table 2.   Record of Dyeing Conditions II
Mole Basis

Dyebath Sample Number	Kind of Salt Used	Amount of Salt Used (Gram Moles)	Dyebath pH before entering the Cotton	Time of Dyeing (Hours)
28	LiCl	0.01	6.10	1
29	LiCl	0.01	6.10	3
30	LiCl	0.01	6.10	5
31	NaCl	0.01	5.90	1
32	NaCl	0.01	5.90	3
33	NaCl	0.01	5.90	5
34	KCl	0.01	6.30	1
35	KCl	0.01	6.30	3
36	KCl	0.01	6.30	5
37	RbCl	0.01	6.60	5
38	CsCl	0.01	6.50	5
39	KSCN	0.01	6.80	1
40	KSCN	0.01	6.80	3
41	KSCN	0.01	6.80	5
42	KF	0.01	5.80	1
43	KF	0.01	5.80	3
44	KF	0.01	5.80	5
45	KBr	0.01	6.45	1
46	KBr	0.01	6.45	3
47	KBr	0.01	6.45	5

Table 2. (Continued) Record of Dyeing Conditions II
Mole Basis

Dyebath Sample Number	Kind of Salt Used	Amount of Salt Used (Gram Moles)	Dyebath pH before entering the cotton	Time of Dyeing (Hours)
48	KI	0.01	6.60	1
49	KI	0.01	6.60	3
50	KI	0.01	6.60	5
51	KNO_3	0.01	6.55	1
52	KNO_3	0.01	6.55	3
53	KNO_3	0.01	6.55	5
54	LiCl	0.01	3.00	1
55	LiCl	0.01	3.00	3
56	LiCl	0.01	3.00	5
57	NaCl	0.01	3.00	1
58	NaCl	0.01	3.00	3
59	NaCl	0.01	3.00	5
60	KCl	0.01	3.00	1
61	KCl	0.01	3.00	3
62	KCl	0.01	3.00	5
63	RbCl	0.01	3.00	3
64	RbCl	0.01	3.00	5
65	CsCl	0.01	3.00	3
66	CsCl	0.01	3.00	5

Table 2. (Continued) Record of Dyeing Conditions II
Mole Basis

Dyebath Sample Number	Kind of Salt Used	Amount of Salt Used (Gram Moles)	Dyebath pH before entering the cotton	Time of Dyeing (Hours)
67	NH_4Cl	0.01	6.30	1
68	NH_4Cl	0.01	6.30	3
69	NH_4Cl	0.01	6.30	5

dyebath was cooled and poured into a 200 ml. volumetric flask, and the final volume adjusted to 200 ml. by adding deionized water. The diluted dyebath was then used to determine the amount of dye left in the dyebath after the dyeing.

The pH of the dyebath was measured for each experimental dyeing by the use of the Beckman pH Meter, before and after the dyeing period.

The Measurement of the Dyebath Concentration.--Colorimetric measurements were used to determine the exhaustion of the dyebath after the dyeing. Colorimetric instruments are comparative; they only compare the optical properties of a given colored solution with those of another standard solution. The Lumetron Colorimeter which was used in these experiments measures the transmission of light through a solution. The colorimeter was first used to measure the per cent light transmission of the dye solution of known concentration in the presence of various salts. From these data, a plot of per cent transmission versus concentration was made for each dyeing condition. The concentration of a dyebath of unknown concentration after the dyeing, was then obtained from its per cent transmission by referring to this plot of transmission versus concentration.

The per cent transmission of dye solutions of known concentration, containing a particular salt, was measured with the colorimeter. Four parts of the initial dyebath were

diluted with one part of deionized water. The per cent transmission of this diluted dyebath was measured and recorded. This diluting and measuring procedure was continued until one part of the initial dyebath had been diluted with nineteen parts of deionized water. The concentration of this final diluted dye solution was 0.0125 grams of dye per liter of solution.

The above procedure was followed for each dyeing condition which involved a different salt. The dye concentration of the initial dyebath in each case was 0.25 grams of dye per liter of solution. In the dyeings on the weight basis, the initial dyebath contained the required amount of sodium chloride or the required amounts of sodium chloride and second salt. In the dyeings on the mole basis, the initial dyebath contained the required amount of a salt.

For the above measurements of per cent transmission, the proper filter had to be selected for the dye under consideration. In order to determine the proper filter for the dye, colorimeter readings were taken for each of the twelve available filters covering the entire range of visible light, using the solution containing 0.25 grams of dye per liter. Thus the filter giving the greatest per cent transmission, was determined for the dye under consideration. These absorption values are shown in Table 6 in the Appendix.

With this filter, readings of light transmission for each of the initial and diluted dye solutions were taken with the colorimeter. These values are shown for each dyeing condition in Tables 7 through 32 in the Appendix.

In operating the colorimeter, deionized water was used as a standard reference solution in all cases. One centimeter cuvettes were used as dye sample holders; and a sensitivity ratio of twenty-five galvanometer graduations to ten transmission dial graduations was used.

CHAPTER V

RESULTS AND DISCUSSION

The results obtained with salts added on an equiweight basis have little quantitative significance, as different numbers of ions were present in every dyeing. However, using ammonium salts it has been found that the order of anions producing increasing adsorption of Calcodur Resin Fast Grey 2G was:

$$I^- \langle Br^- \langle NO_3^- \langle F^- \langle SCN^- \langle SO_4^= \langle Cl^-$$
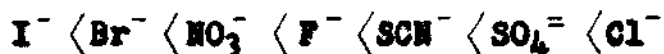
The above series was made from the results obtained after five hours of dyeing. Since the series was obtained using the same weight of salt in each case, it will be interesting to the practical dyer. Millson (11) mentioned in his article that ammonium thiocyanate is very effective in increasing the per cent exhaustion of many direct dyes, but it seems that ammonium chloride or ammonium sulfate is more effective than ammonium thiocyanate for Calcodur Resin Fast Grey 2G. In each of these dyeings, a drop in pH of the dyebath was observed. This was due to the hydrolysis of the ammonium salts in aqueous solution. Referring to Table 3, the difference of pH of the dyebath before and after the dyeing was about two in each dyeing.

Since the above series does not show the effectiveness of different ions on direct dyeing, the experiments were con-

Table 3. Results of Dyeing I
Weight Basis

Dyebath Sample Number	pH of the Initial Dyebath	pH of the Exhausted Dyebath	Per Cent Transmission of the Exhausted Dyebath	Dye Concentration of the Exhausted Dyebath (g/l)	Per Cent Exhaustion
1	9.40	8.25	14.7	0.141	43.6
2	9.40	8.50	16.6	0.131	47.6
3	9.40	8.25	15.5	0.137	45.2
4	6.60	4.55	30.0	0.082	67.2
5	6.60	4.15	33.1	0.075	70.0
6	6.60	4.15	35.9	0.069	72.4
7	6.80	4.90	24.9	0.097	61.2
8	6.80	4.30	30.5	0.082	67.2
9	6.80	4.20	33.3	0.076	72.4
10	6.60	4.65	25.7	0.097	61.2
11	6.60	4.20	32.0	0.080	66.0
12	6.60	4.10	34.6	0.074	70.4
13	6.50	4.69	28.8	0.087	65.2
14	6.50	4.15	34.2	0.073	70.8
15	6.50	4.00	34.3	0.073	70.8
16	6.35	4.40	32.1	0.077	69.3
17	6.35	4.15	38.0	0.066	73.6
18	6.35	3.95	38.0	0.066	73.6

Table 3. (Continued) Results of Dyeing I
Weight Basis

Dyebath Sample Number	pH of the Initial Dyebath	pH of the Exhausted Dyebath	Per Cent Transmission of the Exhausted Dyebath	Dye Concentration of the Exhausted Dyebath (g/l)	Per Cent Exhaustion
19	6.35	4.15	31.3	0.081	67.6
20	6.35	3.75	36.9	0.069	72.4
21	6.35	3.58	37.3	0.068	72.8
22	6.40	5.05	29.0	0.086	65.6
23	6.40	5.00	32.2	0.078	68.8
24	6.40	4.90	35.4	0.071	71.6
25	8.20	7.75	16.5	0.129	48.4
26	8.20	8.25	17.3	0.125	50.0
27	8.20	8.30	18.9	0.118	52.8

ducted on an equimolar basis. Using chlorides it has been found that the order of cations producing increasing adsorption of Calcodur Resin Fast Grey 2G was:

$$Li^+ \langle Na^+ \langle K^+ \langle Rb^+ \langle Cs^+$$
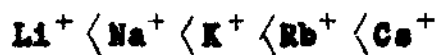
The above series was made from the results obtained after five hours of dyeing. Since the series was obtained using the same number of moles of salt in each case, the difference in the effectiveness of ions was solely due to the characteristics of the ions themselves, excluding the effect of pH of the dyebath. Theoretically, the pH of the dyebath should not increase during the dyeing, but the pH of the dyebath did increase by about one in each case. The data on the change in pH of the dyebath are shown in Table 4. This increase in pH was due to a finishing agent left on the sample fabric. By boiling the fabric alone in deionized water under the same condition as in the experimental dyeing, it was observed that the pH of the deionized water increased by 2.2 units after five hours.

Similar experiments were conducted in which the initial pH of the dyebath was adjusted to 3.0 with concentrated hydrochloric acid. Although the per cent exhaustion was increased in every case, the same order was obtained for the above cations. The above series is significant, because there was a difference in the per cent exhaustion of about fifteen per cent both with and without added hydrochloric acid, which is more than the experimental

Table 4. Results of Dyeing II
Mole Basis

| Dyebath Sample Number	pH of the Initial Dyebath	pH of the Exhausted Dyebath	Per Cent Transmission of the Exhausted Dyebath	Dye Concentration of the Exhausted Dyebath (g/l)	Per Cent Exhaustion
28	6.10	6.80	16.0	0.128	48.8
29	6.10	6.80	17.5	0.122	51.2
30	6.10	6.80	17.8	0.121	51.6
31	5.90	6.50	18.5	0.117	53.2
32	5.90	6.90	20.0	0.111	55.6
33	5.90	7.10	20.0	0.111	55.6
34	6.30	6.58	20.2	0.113	54.8
35	6.30	6.65	21.5	0.108	56.8
36	6.30	6.78	22.2	0.106	57.6
37	6.60	7.70	23.6	0.100	60.0
38	6.50	7.00	27.3	0.087	65.2
39	6.80	7.30	18.8	0.118	52.8
40	6.80	7.40	19.5	0.115	54.0
41	6.80	7.91	21.0	0.108	56.8
42	5.80	6.90	19.7	0.115	54.0
43	5.80	7.15	20.2	0.113	54.8
44	5.80	7.15	21.8	0.107	57.2
45	6.45	7.20	18.7	0.112	55.2

Table 4. (Continued) Results of Dyeing II
Mole Basis

Dyebath Sample Number	pH of the Initial Dyebath	pH of the Exhausted Dyebath	Per Cent Transmission of the Exhausted Dyebath	Dye Concentration of the Exhausted Dyebath (g/l)	Per Cent Exhaustion
48	6.60	7.65	18.6	0.117	53.2
49	6.60	7.71	20.5	0.109	56.4
50	6.60	7.90	21.4	0.107	57.2
51	6.55	7.40	19.0	0.115	54.0
52	6.55	7.55	21.0	0.108	56.8
53	6.55	7.99	22.1	0.104	58.4
54	3.00	3.05	27.9	0.087	65.2
55	3.00	3.30	28.3	0.086	65.6
56	3.00	4.50	23.5	0.099	60.4
57	3.00	3.39	30.8	0.082	67.2
58	3.00	3.60	35.1	0.072	71.2
59	3.00	3.90	31.6	0.079	68.4
60	3.00	3.40	36.6	0.069	72.4
61	3.00	3.50	39.0	0.064	74.4
62	3.00	3.50	39.0	0.064	74.4
63	3.00	3.25	33.1	0.078	68.8
64	3.00	3.25	40.7	0.062	75.2
65	3.00	3.31	36.5	0.071	71.6
66	3.00	3.31	40.4	0.054	76.4

Table 4. (Continued) Results of Dyeing II
Mole Basis

Dyebath Sample Number	pH of the Initial Dyebath	pH of the Exhausted Dyebath	Per Cent Transmission of the Exhausted Dyebath	Dye Concentration of the Exhausted Dyebath (g/l)	Per Cent Exhaustion
67	6.30	4.50	32.3	0.078	68.8
68	6.30	4.10	38.5	0.066	73.6
69	6.30	3.80	42.5	0.058	76.8

errors.

Neale and Peters (25) investigated the surface potential of cotton in mono-monovalent electrolytes, and found that the surface potential of the cotton fiber is much smaller in dilute solutions of hydrochloric acid than in equimolar solutions of the neutral salts. Among the neutral salts, potassium chloride gave a smaller potential than sodium chloride, and sodium chloride gave a smaller potential than lithium chloride. From the trend, it may be expected that rubidium or cesium would give lower potentials than the examined salts. The observed increase in dye adsorption in the presence of cesium ions as compared to lithium ions therefore can be explained as a result of the lowering of the potential barrier.

Neale and Peters also indicated that the chemically neutral fibers cotton and vinyon show potentials which are not markedly pH sensitive over the range pH 10-5, but which fall rapidly when the solution is more acid than pH 4. The lowering of the barrier at pH's below 4 would account for the observed increase in per cent exhaustion when dyeings were carried out in a dyebath where the initial pH of the dyebath was adjusted to 3.0.

Due to the difference in this lowering of the potential barrier, the dye anion was adsorbed more in the presence of cesium ion than in the presence of lithium ion

was more acidic.

Evidently the size of the cation is of importance, as the adsorption increases with increasing ionic size. Therefore, van der Waals forces seem to contribute more to the lowering of the surface potential of cotton than Coulomb forces.

Robinson and Mills (26) have shown that dyes exist in the form of colloidal electrolytes having negatively charged ionic micelles. The stability of the micelles is due to their hydration and the electric charge, so that any factor that will bring about destabilization of the micelles will tend to increase adsorption of the dye by any absorbent. It may be assumed that changing the nature of the salt from lithium chloride to cesium chloride does not cause the cellulose to undergo any appreciable change which would affect the adsorption in a marked manner. Therefore, it is quite plausible to assume that the increased adsorption is due to some change in the condition of the dye solution. Many dyes undergo simultaneous hydrolysis, ionization and association in aqueous solution. The extent to which these factors will be affected by salt addition will depend upon the nature and the concentration of the particular salt. The addition of neutral salts will generally decrease ionization and thus increase the molecular aggregation. In the case of certain dyes, however, the conductivity of the

be that of destabilizing the dye micelles. It is, therefore,
to be expected that the salt concentration, the valency of
the cation, or the size of the cation will affect the dye
solution and bring about an increased adsorption.

No adequate theoretical model based on the atomic
characteristics of the ions has yet been developed which is
capable of accounting for the thermodynamic properties of
aqueous solutions over wide ranges of concentration. For
dilute solutions of completely ionized electrolytes, however,
expressions have been derived by Debye and Hückel which
predict exactly the limiting behavior of activity coef-
ficients in an infinitely dilute solution, and which provide
very useful equations for describing these quantities at small
finite concentrations.

At ionic strengths near 0.01 it is convenient
frequently to use the following form of the Debye-Hückel
expression: (31)

$$\log \gamma = \frac{-Az^2 \sqrt{\mu}}{1-Ba_i \sqrt{\mu}}$$

where A and B are constants for a given solvent at a specified
temperature, z is the number of charges on the ion, μ is the
ionic strength for a given solvent, and a_i may be thought
of as the "effective diameter" of the ion in the solution.
Since no truly independent method is available for evaluating
a_i, this quantity is essentially an empirical parameter, but

it is a fact that the a_i's are of a magnitude expected for ion sizes.

In connection with the use of the above equation, Kielland (27) has assembled a series of "effective diameters" for a large number of ions, grouped according to charge. Some of these values of a_i are listed in Table 5. It is very interesting to note that the effective diameters of hydrated cesium and rubidium ions are much less than the effective diameters of hydrated sodium and lithium ions. This is just the reverse of the order of the radii of the bare ions.

Because the effective diameter of a hydrated cesium ion is less than the effective diameters of other ions under consideration, more cesium ions can be adsorbed by a unit area of cotton surface due to the steric effect. Therefore, more positive charges will be distributed per unit area of cotton surface, and this in turn will lower the surface potential more.

Due to the shorter effective diameter of a hydrated cesium ion, a cesium ion can attach itself closer to the negatively charged cotton surface than other ions; and this too will make cesium ions more effective in lowering the surface potential barrier than other ions. The positive charge density at the cotton surface will be higher due to the shorter distance between the surface of cotton and the

Table 5. Effective Diameters of Hydrated
Ions in Aqueous Solution

$10^8 a_i$	Inorganic Ions: Monovalent
9	H^+
6	Li^+
4-4.5	Na^+
3.5	OH^-, F^-, SCN^-,
3	K^+, Cl^-, Br^-, I^-, NO_3^-
2.5	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+

	Inorganic Ions: Divalent
8	Mg^{++}
6	Ca^{++}
5	Sr^{++}, Ba^{++}, Hg^{++}
4.5	Pb^{++}
4	Hg_2^{++}

Table 5. (Continued) Effective Diameters of Hydrated
Ions in Aqueous Solution

Inorganic Ions: Trivalent

9	Al^{+++}, Fe^{+++}, Cr^{+++}, Sc^{+++}, Y^{+++}, La^{+++}, In^{+++}, Ce^{+++}, Pr^{+++}, Nd^{+++}, Sm^{+++}
4	$Cr(NH_3)_6^{+++}$, $Co(NH_3)_6^{+++}$

Inorganic Ions: Tetravalent

11	Th^{++++}, Zr^{++++}, Ce^{++++}, Sn^{++++}

Organic Ions: Monovalent

8	$(C_3H_7)_4N^+$
7	$(C_3H_7)_3NH^+$
6	$(C_2H_5)_4N^+$, $(C_3H_7)_2NH_2^+$
5	$(C_2H_5)_3NH^+$, $(C_3H_7)NH_3^+$
4.5	$(CH_3)_4N^+$, $(C_2H_5)_2NH_2^+$
4	$(CH_3)_3NH^+$, $C_2H_5NH_3^+$
3.5	$CH_3NH_3^+$, $(CH_3)_2NH_2^+$

charge density decreases with increase in distance from the center of the ion; that is, since the forces of attraction fall off as the square of the distance, the atmosphere becomes more diffuse and loses its identity at some distance from the center of the ion.

With the values of a_i, it is possible to calculate individual ion activity coefficients from the Debye-Hückel expression for solutions of ionic strength below 0.01. However, under the dyeing conditions considered, the activity coefficients of various ions varied to a very slight extent, and it is reasonable to assume that there were no variations among the activity coefficients of the ions under consideration. If one attempts to investigate the effects of these ions on cotton dyeing at a higher concentration, a consideration should be given to the activity coefficients.

In order to eliminate the effect of pH of the dyebath, potassium salts have been used to determine the effectiveness of the various anions on cotton dyeing. It has been found that the order of anions producing increasing adsorption of Calcodur Resin Fast Grey 2G on the equimolar basis was:

$$SCN^- \langle I^- \langle F^- \langle Cl^- \langle NO_3^- \langle Br^-$$

The above series was made from the results obtained after five hours of dyeing. The difference in per cent exhaustion

is within the scope of the experimental errors.

These results indicate that the nature of the anion
is of secondary importance. Therefore, it appears that the
result obtained by Millson (11) is primarily due to the
effect of pH of the dyebath as well as the effect of ammonium
and sodium ions present. Thiocyanate ions probably did not
contribute anything toward the acceleration or the increase
of adsorption of dye on the fiber or toward the prevention
or the retardation of decomposition of dye.

Since the experimental dyeings were carried out for
five hours at the boil, it is reasonable to assume that the
dyeing process had almost reached the equilibrium steady
state in every experimental dyeing. This has been confirmed
by plotting the per cent exhaustion versus the hours of
dyeing; the slope of each curve reached zero after about three
hours in most cases.

Practically no investigations of the effect of salts
other than sodium chloride on the aggregation of direct
dyes or on the diffusion coefficients of direct dyes, is
recorded. In general, the addition of salt to the dyebath
will increase the aggregation of direct dyes and decrease
the diffusion coefficient of these dyes. However, it is
probable that different ions will affect the aggregation and
the diffusion coefficients of direct dyes in different degrees
due to their size, hydration number, dielectric

shape, and other characteristics.

Since the cotton sample used in this experiment had been scoured and bleached, it no doubt contained some oxycellulose. It is known that carboxyl groups in oxycellulose reduce dye uptake. During the experimental dyeing, it was observed that lowering the pH led to increased adsorption. The explanation of this effect is probably that the ionization of the carboxyl groups in the fiber is repressed in acidic dyebaths, so that the surface potential of the fiber is reduced to the value shown by the unoxidized surface and dyeing is more easily facilitated.

Since unoxidized cellulose will be dyed heavier the lower the pH, the above explanation is not enough to explain the effect of pH on cotton dyeing. According to Kielland (27), the effective diameter of hydrated hydrogen ions is the largest of the monovalent positive inorganic ions. From the above fact, it may be expected that the hydrogen ion would be least effective in lowering the surface potential of cotton fiber. However, Neale and Peters (25) showed through experiment that the surface potential of cotton is much smaller in dilute solutions of hydrochloric acid than in equimolar solutions of the neutral salts. Therefore, there must be another factor in hydrogen ion which affects the surface potential of the cotton fiber.

It is interesting to note that hydrogen ions have much higher mobilities in water than any other ions, and this is believed to be a result of the fact that a positive charge may be transferred along a chain of adjacent water molecules without the actual transport of a hydrogen ion (28). This is illustrated in the following figure, which represents (a) the approach of a hydrogen ion to a group of oriented water molecules and (b) the departure of a different hydrogen ion from the water molecule on the right.

$$H^+ \quad O-H \quad O-H \quad O-H \quad H-O \quad H-O \quad H-O \quad H^+$$
$$\qquad\quad | \qquad\quad | \qquad\quad | \qquad\qquad | \qquad\quad | \qquad\quad |$$
$$\qquad\quad H \qquad\quad H \qquad\quad H \qquad\qquad H \qquad\quad H \qquad\quad H$$

$$\qquad\qquad\qquad (a) \qquad\qquad\qquad\qquad\qquad\qquad (b)$$
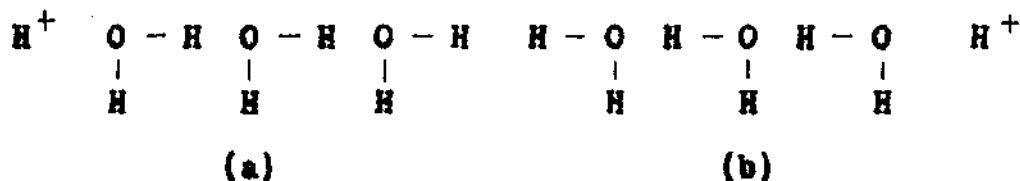
Therefore, under the lower pH condition, hydrogen ion can be easily transferred onto the surface of the cotton fiber and neutralize the charges on the surface. Even though other ions have smaller hydrated volumes, they can not transfer a positive charge along a chain of adjacent water molecules. This means that the movement of these ions in the dyebath will be hindered partially by the surrounding anions in the dye solution. Also these ions must "drag" along a shell of water when they move, because they are hydrated. This will also hinder, partially, the movement of the ions.

After eliminating the effect of pH of the dyebath,

approximately the same per cent exhaustion. This explains
the importance of the size and shape of ions on cotton
dyeing. Since potassium and ammonium ions are similar in
size, shape, and charge, they were expected to give similar
results.

The pH of the deionized water varied from day to day,
to a slight extent, because it was not possible accurately
to control the rate of flow through the ion-exchange column
every time. This introduced a slight error in the measurement
of pH in this work.

A finishing agent left on the sample was the main
cause of the increase in pH of the dyebath during the dyeings
on the mole basis. It may be assumed that every sample had
the same amount of the agent, and its effect was the same
in every dyeing, but it certainly introduced an error in
the experiment.

Because it was necessary to dilute the solutions
containing known amounts of dye and salt in order to obtain
the per cent transmission of these solutions, the amounts of
the various salts in these standard solutions were less than
in the dyebaths. This certainly introduced some errors, but
the presence of salt in the dyebath did not affect the
reading of per cent transmission to a great extent.

The fabric samples were not conditioned before dyeing, and therefore each sample may have had a different amount of moisture when it was weighed. This may have introduced a small error in the experiments.

The cesium and rubidium chlorides used in this work were not reagent quality, and some other ions present may have introduced errors.

CHAPTER VI

CONCLUSIONS

From the data obtained in this investigation the following conclusions may be drawn:

1. The size of the hydrated inorganic monovalent positive ion added as an electrolyte affects the adsorption of dye by cotton fibers.

2. Lowering the pH of the dyebath increases the adsorption of dye by cotton fibers.

3. When the effect of pH of the dyebath is kept to a minimum, two similar ions give similar results in increasing the per cent exhaustion of the dyebath.

4. The nature of the anion appears to be of secondary importance in increasing the per cent exhaustion of direct dyes.

CHAPTER VII

RECOMMENDATIONS

1. It is recommended that an investigation be under-taken to determine the effect of the inorganic monovalent ions on cotton dyeing when the direct dyestuffs, which decompose or build up, are used.

2. Since it is believed that the charge of the inorganic cation is of importance in direct dyeing, investi-gations of the effect of the inorganic divalent, trivalent, and tetravalent ions on cotton dyeing, is recommended. Some of these ions are listed in Table 5.

3. Jirgensons and Straumanis (29) showed that the adsorption affinities of cations on Amberlite IR-1 are mainly determined by their charge and by the radii of the hydrated ions; the series obtained agrees well with the results of this investigation with the exception of hydrogen ion. The series is as follows:

$$La^{+++} \rangle Y^{++} \rangle\rangle Ba^{++} \rangle\rangle Cs^{+} \rangle Rb^{+} \rangle K^{+} \rangle Na^{+} \rangle H^{+} \rangle Li^{+}$$

Therefore, it is strongly recommended that an investigation be undertaken to study especially the effect of lanthanum, yttrium, and barium ions on cotton dyeing, using Calcodur Resin Fast Grey 2G.

4. Since it is believed that the size of the
cations is of importance in cotton dyeing, the effect of

large organic cations on cotton dyeing should also be investigated.

5. Cohen (30) determined the smallest concentration of hydrochloric and sulfuric acid which would show a measurable effect when cotton is boiled in the acids for one hour and then dried at 100 degrees C. The following concentrations are the smallest that will show a change in copper number and a reduction in tensile strength:

HCl: 0.0007 N H_2SO_4: 0.0016 N

Since the pH of 0.0007 N hydrochloric acid solution is approximately 3, it is believed that cotton fabrics may be dyed under acidic conditions as long as the pH of the dyebath does not become lower than 3. Since the lowering of the pH of the dyebath improves the per cent exhaustion in cotton dyeing, the effect of pH should be investigated thoroughly.

6. Since there are a few direct dyestuffs which are expensive and exhaust poorly, an investigation of the effect of a mixture of cesium and potassium chlorides on the above direct dyestuffs, is also recommended.

7. It would be very interesting to investigate the effect of various inorganic and organic ions on the aggregation of direct dyes. From this information, the factors which will bring about destabilization of the dye micelles,

may be found. If these factors are used properly, it will increase the per cent exhaustion of the direct dyeing.

8. The use of a spectrophometer in place of the colorimeter for the above investigations is recommended.

9. It is also recommended that purified dyestuffs be used for the above investigations.

APPENDIX

Table 6. Light Absorption Percentages
for Calcodur Resin Fast Grey 2G

Value of Transmission of Monochromatic Filter (millimicrons)	Color	Percentage Transmission of Light
390	Violet	1.7
420	Blue	2.0
440	Blue	2.0
460	Blue	6.5
490	Green	3.4
515	Green	2.5
550	Green	0.8
575	Amber	0.5
595	Orange	0.2
620	Red	0
640	Red	0
660	Red	0

Concentration of Dye Solution Used: 0.25 g/l

Table 7. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Per Cent Transmission
0	100.0
0.0125	82.2
0.0250	68.3
0.0500	47.2
0.1000	23.4
0.1500	12.5
0.2000	7.5
0.2500	5.2

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 8. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (gram/liter)	Concentration of Sodium Chloride (grams/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.125	82.8
0.0250	0.250	68.8
0.0500	0.500	47.6
0.1000	1.000	23.9
0.1500	1.500	13.4
0.2000	2.000	7.9
0.2500	2.500	5.5

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 9.   Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Thiocyanate (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.5
0.0250	0.250	0.1250	69.0
0.0500	0.500	0.2500	47.5
0.1000	1.000	0.5000	23.5
0.1500	1.500	0.7500	12.5
0.2000	2.000	1.0000	7.3
0.2500	2.500	1.2500	4.5

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 10. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Iodide (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.5
0.0250	0.250	0.1250	68.7
0.0500	0.500	0.2500	47.5
0.1000	1.000	0.5000	24.0
0.0500	1.500	0.7500	12.9
0.2000	2.000	1.0000	7.5
0.2500	2.500	1.2500	4.8

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 11. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Bromide (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.6
0.0250	0.250	0.1250	69.1
0.0500	0.500	0.2500	48.0
0.1000	1.000	0.5000	24.4
0.1500	1.500	0.7500	13.0
0.2000	2.000	1.0000	7.7
0.2500	2.500	1.2500	4.8

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 12. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Nitrate (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.9
0.0250	0.250	0.1250	68.8
0.0500	0.500	0.2500	47.7
0.1000	1.000	0.5000	24.0
0.1500	0.500	0.7500	13.0
0.2000	2.000	1.0000	7.4
0.2500	2.500	1.2500	4.6

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 13. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Chloride (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.6
0.0250	0.250	0.1250	68.8
0.0500	0.500	0.2500	47.5
0.1000	1.000	0.5000	23.8
0.1500	0.500	0.7500	12.9
0.2000	2.000	1.0000	7.5
0.2500	2.500	1.2500	4.5

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 14. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Sulfate (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.4
0.0250	0.250	0.1250	68.8
0.0500	0.500	0.2500	47.5
0.1000	1.000	0.5000	23.8
0.1500	0.500	0.7500	12.7
0.2000	2.000	1.0000	7.2
0.2500	2.500	1.2500	4.4

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 15. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Concentration of Ammonium Fluoride (grams/liter)	Per Cent Transmission
0	0	0	100.0
0.0125	0.125	0.0625	82.5
0.0250	0.250	0.1250	68.7
0.0500	0.500	0.2500	47.9
0.1000	1.000	0.5000	23.9
0.1500	1.500	0.7500	12.8
0.2000	2.000	1.0000	7.5
0.2500	2.500	1.2500	4.5

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 16. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (grams/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.1875	82.3
0.0250	0.3750	68.6
0.0500	0.7500	47.6
0.1000	1.5000	24.0
0.1500	2.2500	13.0
0.2000	3.0000	7.5
0.2500	3.7500	5.3

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 17. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Lithium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.8
0.0250	0.0050	68.3
0.0500	0.0100	47.2
0.1000	0.0200	23.3
0.1500	0.0300	12.3
0.2000	0.0400	6.9
0.2500	0.0500	4.6

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 18. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.0
0.0250	0.0050	68.2
0.0500	0.0100	47.3
0.1000	0.0200	23.5
0.1500	0.0300	12.5
0.2000	0.0400	7.2
0.2500	0.0500	4.6

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 19. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.5
0.0250	0.0050	68.6
0.0500	0.0100	47.7
0.1000	0.0200	24.0
0.1500	0.0300	13.2
0.2000	0.0400	7.8
0.2500	0.0500	4.9

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 20.   Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Rubidium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.9
0.0250	0.0050	68.0
0.0500	0.0100	46.8
0.1000	0.0200	23.5
0.1500	0.0300	12.6
0.2000	0.0400	7.6
0.2500	0.0500	5.1

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 21. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Cesium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.9
0.0250	0.0050	67.9
0.0500	0.0100	46.6
0.1000	0.0200	23.0
0.1500	0.0300	12.4
0.2000	0.0400	7.1
0.2500	0.0500	4.6

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 22. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Thiocyanate (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.4
0.0250	0.0050	68.5
0.0500	0.0100	47.3
0.1000	0.0200	23.2
0.1500	0.0300	12.6
0.2000	0.0400	7.2
0.2500	0.0500	4.3

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 23. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Fluoride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.0
0.0250	0.0050	68.4
0.0500	0.0100	47.5
0.1000	0.0200	23.9
0.1500	0.0300	13.0
0.2000	0.0400	7.9
0.2500	0.0500	4.8

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 24. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Bromide (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.8
0.0250	0.0050	67.8
0.0500	0.0100	46.8
0.1000	0.0200	23.2
0.1500	0.0300	12.3
0.2000	0.0400	7.0
0.2500	0.0500	4.9

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 25. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Iodide (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.2
0.0250	0.0050	67.5
0.0500	0.0100	46.6
0.1000	0.0200	23.2
0.1500	0.0300	12.8
0.2000	0.0400	7.4
0.2500	0.0500	5.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 26. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Nitrate (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.1
0.0250	0.0050	68.2
0.0500	0.0100	47.2
0.1000	0.0200	23.3
0.1500	0.0300	12.3
0.2000	0.0400	7.2
0.2500	0.0500	4.3

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 27. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Lithium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.6
0.0250	0.0050	68.4
0.0500	0.0100	47.2
0.1000	0.0200	23.4
0.1500	0.0300	12.5
0.2000	0.0400	7.2
0.2500	0.0500	4.4

pH of the Dye Solution: 3.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 28. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Sodium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.3
0.0250	0.0050	68.3
0.0500	0.0100	47.1
0.1000	0.0200	23.6
0.1500	0.0300	12.5
0.2000	0.0400	7.4
0.2500	0.0500	4.5

pH of the Dye Solution: 3.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 29. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Potassium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	81.8
0.0250	0.0050	68.4
0.0500	0.0100	47.5
0.1000	0.0200	24.6
0.1500	0.0300	13.6
0.2000	0.0400	8.2
0.2500	0.0500	5.4

pH of the Dye Solution: 3.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 30.   Light Transmission for

Caleodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Rubidium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.0
0.0250	0.0050	68.5
0.0500	0.0100	48.0
0.1000	0.0200	25.1
0.1500	0.0300	14.1
0.2000	0.0400	8.6
0.2500	0.0500	5.8

pH of the Dye Solution: 3.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 31. Light Transmission for

Calcodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Cesium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.5
0.0250	0.0050	68.9
0.0500	0.0100	48.0
0.1000	0.0200	25.0
0.1500	0.0300	14.2
0.2000	0.0400	8.8
0.2500	0.0500	6.0

pH of the Dye Solution: 3.0

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

Table 32. Light Transmission for

Caleodur Resin Fast Grey 2G

Concentration of Dye (grams/liter)	Concentration of Ammonium Chloride (moles/liter)	Per Cent Transmission
0	0	100.0
0.0125	0.0025	82.2
0.0250	0.0050	68.3
0.0500	0.0100	47.3
0.1000	0.0200	23.7
0.1500	0.0300	12.6
0.2000	0.0400	7.3
0.2500	0.0500	4.5

Monochromatic Filter Used in Colorimeter:

Blue 460 millimicrons

Scale Ratio Used on Colorimeter:

25 Galvanometer Graduations to

10 Transmission Dial Graduations

BIBLIOGRAPHY

LITERATURE CITED

1. Vickerstaff, Thomas, <u>The Physical Chemistry of Dyeing</u>. New York: Interscience Publishers, Inc., 1950, p. 123.

2. <u>Ibid</u>., p. 241.

3. <u>Ibid</u>., p. 241.

4. Boulton, J., and other, "Quantitative Research on the Dyeing of Viscose Yarns", <u>Journal of Textile Institute</u>, 24 (1933), pp. 113.

5. Neale, S.M., and Patel, A.M., "Adsorption of Dyestuffs by Cellulose. Part V. The Effect of Various Electrolytes Upon the Absorption", <u>Transactions of the Faraday Society</u>, 30 (1934), pp. 905.

6. Vickerstaff, T., and Lemin, D.R., "Aggregation of Dyes in Aqueous Solution", <u>Nature</u>, 157 (1946), pp. 373.

7. Vickerstaff, <u>op</u>. <u>cit</u>., p. 89.

8. Neale, S.M., and Stringfellow, W.A., "The Absorption by Cellulose of Mixtures of Direct Cotton Dyes", <u>The Journal of the Society of Dyers and Colourists</u>, 59 (1943), pp. 241.

9. Speakman, J.B., and Clegg, H., "Some Relationships between the Chemical Constitution and Levelling Properties of Acid Dyes as Applied to Wool", <u>The Journal of the Society of Dyers and Colourists</u>, 50 (1934), pp. 348.

10. Holmes, F.H., and Standing, H.A., "The Dyeing of Cellulose with Direct Dyes. Part III.- The Aqueous Diffusion of Direct Dyes", <u>Transactions of the Faraday Society</u>, 41 (1945), pp. 542.

11. Millson, H.E., "The Anomalous Behavior of Direct Dyes", <u>American Dyestuff Reporter</u>, 47 (1958), pp. 221-234.

12. Vickerstaff, <u>op</u>. <u>cit</u>.

13. Hunt, C.M., and others, "Submicroscopic Structure of Cellulose from Nitrogen Sorption Measurements", <u>Journal of Research of National Bureau of Standards</u>, 43 (1949), pp. 547.

14. Vickerstaff, op. cit., p. 183.

15. Valko, E.I., Colloid Chemistry, Theoretical and Applied, Alexander, J., New York: Reinhold Publishing Company, 1946, p. 595

16. Royer, G.L. and others, "Studies in Viscose Rayon Dyeing: Applications of the Dyeometer", The Journal of the Society of Dyers and Colourists, 63 (1947), pp. 254.

17. Crank, J., "The Diffusion of Direct Dyes into Cellulose III - The present State of the Theory and its Practical Implications", The Journal of the Society of Dyers and Colourists, 66 (1950), pp. 366.

18. Neale, S.M., and Stringfellow W.A., "The Absorption of Dyestuffs by Cellulose. Part I.- The Kinetics of the Absorption of Sky Blue FF on Viscose Sheet, in the Presence of Various Amounts of Sodium Chloride", Transactions of the Faraday Society, 29 (1933), pp. 1167.

19. Boulton, J., "The Importance of Dyeing Rate an Interpretation for the Practical Dyers of Recent Research on Direct Dyeing", The Journal of the Society of Dyers and Colourists, 60 (1944), pp. 5.

20. "Report of the Committee Appointed by Council to Discuss the Dyeing Properties of Direct Cotton Dyes", The Journal of the Society of Dyers and Colourists, 62 (1946), pp. 280-83.

21. Standing, H.A., and others, "The Dyeing of Cellulose with Direct Dyes. Part II. The Absorption of Chrysophenine by Cellulose Sheet", Transactions of the Faraday Society, 41 (1945), pp. 506.

22. Crank, J., "An Absorption Isotherm for Direct Dyes", The Journal of the Society of Dyers and Colourists, 63 (1947), pp. 293.

23. Vickerstaff, T., "The Adsorption of Direct Dyes on Cellulose", Proceedings of Royal Society of London, 192A (1948), pp. 292.

24. Marshall, W.J., and Peters, R.H., "The Heats of Reaction and Affinities of Direct Cotton Dyes for Cuprammonium Rayon, Viscose Rayon and Cotton", The Journal of the Society of Dyers and Colourists, 63 (1947), pp. 446.

25. Neale, S.M., and Peters, R.H., "Electrokinetic Measurements with Textile Fibers and Aqueous Solutions", <u>Transactions of the Faraday Society</u>, 42 (1946), pp. 482.

26. Robinson, Conmar., and Mills, Harold A.T., "Colloid Chemistry of Dyes: The Aqueous Solutions of Benzopurpurine 4B and its Isomer Prepared from m-Tolidine.- Part I.", <u>Proceedings of Royal Society of London</u>, 131A (1931), pp. 567.

27. Kielland, J., "Individual Activity Coefficients of Ions in Aqueous Solutions", <u>Journal of the American Chemical Society</u>, 59 (1937), pp. 1675.

28. Daniels, F., and Alberty, R., <u>Physical Chemistry</u>. New York: John Wiley and Sons, Inc., 1955, p. 392.

29. Jirgensons, B., and Straumanis, M., <u>A Short Textbook of Colloid Chemistry</u>. New York: John Wiley and Sons, Inc., 1954, p. 98.

30. Cohen, Manasseh, "The Action of Mineral Acids upon Cotton", <u>The Journal of the Society of Dyers and Colourists</u>, 31 (1915), pp. 162.

31. Klotz, I.M., <u>Chemical Thermodynamics</u>. New York: Prentice-Hall, Inc., 1950, p. 329.