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The Use of the Streaming Current Detector for Determining Dye Adsorption Characteristics of Papermaking Fibers

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The Use of the Streaming
Current Detector for Determining
Dye Adsorption Characteristics
of Papermaking Fibers

by

Thomas Meersman

A Thesis submitted to the
Faculty of the Department of Paper
Technology in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

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Abstract

The purpose of this thesis was to study the dye adsorption characteristics of cellulose by means of the Streaming Current Detector. The influence of electrolytes on dye adsorption, and the electrokinetic phenomena of two-sided dyeing were areas of particular concentration.

Contrary to general belief, it was found the addition of sodium chloride was not necessarily beneficial to dye adsorption and in some cases it could actually be detrimental. The Streaming Current Detector was found to be a useful tool for predicting this effect.

The higher charge of fines was found to be an important factor in the increased dye adsorption by fines. Limited control of two sided dyeing could result from further studies relating fiber furnishes and dye materials by means of the Streaming Current Detector.

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Historical Background

Dyes as electrolytes and the cellulose surface potential The importance of the electrical surface potential of cellulose in interpreting dyeing behavior relates back to the early electrokinetic studies. Perrin, appears to have been the first to observe that cellulose in water acquires a negative charge.¹ Harrison carried out more quantitative measurements, determining the streaming potential developed when certain solutions were passed through a cotton plug held between perforated electrodes.² The electrokinetic potential of the cellulose fiber surface calculated from these measurements was -20 millivolts in water.

Pelet, Jolivet, and Wild concluded in 1909 that dyes behaved as electrolytes.³ Later that same year Knecht and Batey showed undoubtedly that solutions of benzopurpurine, chrysophenine, soluble blue, erika, and naphtol yellow are electrolytes.⁴

Harrison and Gee provided the first notable article in the area when their paper on "The Electrical Theory of Dyeing" appeared in 1910.⁵ The speed of various dyes, in the form of small particles when immersed in a liquid under electrical stress, were measured. Water suspensions were used in most cases and the speeds were expressed in centimeters per second per volt per centimeter. They also discussed to some extent the influence

of temperature on the potential difference between water and cellulose. Their work showed solutions of the direct dye Diamine Blue produced increasing negative potential with increasing concentration, as might be expected.

Lattermoser and Gansel studied the effect of anionic and cationic dyes on the surface potential of cellulose but arrived at no clear conclusion.⁶ The effect of salt solutions on the potential of cellulose was carefully studied by Briggs.^{7,8} All salt solutions were found to reduce the negative potential of the surface at high concentrations. Tri-basic cations being the most effective followed by dibasic cations then monobasic cations.

Neale and Peters found that the potential of oxidized cellulose fiber is less negative than that of normal cellulose.⁹ They also found that basic dyes decrease the negative zeta potential and may even give the fiber a positive charge. They found some anionic direct dyes such as Benzopurpurine 4B increases the negative charge as would be expected. Other anionic dyes, including Chlorazol Sky Blue FF, produce a reduction in zeta potential. They found cationic dyes such as Victoria Blue B rapidly decreased the zeta potential of cellulose.

The Effect of Sodium Chloride and Sodium Sulfate on Dye Adsorption Neale and Stringfellow found the adsorption of direct dyestuff from pure aqueous solution is negligible, but it increases rapidly with the addition of salts.¹⁰ Garvie, Griffiths, and Neale found that the amount of dye adsorbed at equilibrium is very roughly halved for thirty degree centigrade rise and the rate of adsorption is roughly doubled for twenty degree centigrade temperature rise.¹¹ Hanson and Neale found the amount of dye adsorbed increases with the concentration of dye but a proportionate increase in the concentration of salt proved more effective in increasing adsorption of the dye.¹²

Griffiths and Neale pointed out the chief factors governing the adsorption of dyes.¹³ For a given dyestuff the chief factors are:

1. The concentration of the dye
2. The amount of added electrolyte
3. The temperature of dyeing
4. The time of dyeing

Neale has pointed out the majority of the known dyes which have specific affinity for pure cellulose are of the anionic type, their molecules having been made soluble in water by di-, tri-, or tetra- sulphonation.¹⁴ Their adsorption increases the natural negative electrical potential of the fiber and is therefore

opposed by electrostatic forces. Neale believes this adsorption to be facilitated by the addition of any electrolyte to the solution because the ions of this electrolyte serve to reduce the thickness of the ionic atmosphere and so decrease the negative potential of the fiber.¹¹ The adsorption of such anionic "direct" dyes by cellulose is therefore increased in amount when a neutral electrolyte is added to the bath. Neale found on the other hand that any cationic dye with specific affinity for cellulose would be assisted by the electrostatic forces and adsorption would decrease on the addition of salt. This effect was shown to be true of the following cationic dyes: Janus Red (C.I. 225), and Victoria Blue B (C.I. 729).

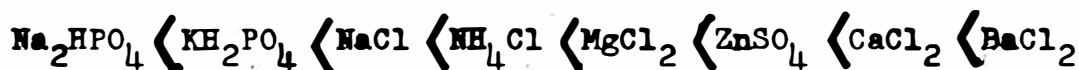
The effect of electrolytes other than sodium chloride on dyeing has been studied to some extent, although for economic reasons there is little likelihood of sodium chloride or sodium sulfate being displaced from practical usage. The alum present in paper systems is an exception to this and a very important one.

The Effect of Valence and Various Cations on Dye Adsorption Willis, Warwicker, Standing, and Urquhart studied the adsorption of Chrysophenine in presence of sodium chloride, sodium bromide, potassium chloride, potassium bromide, and sodium sulfate.¹⁶ The interchange of chloride and bromide ions produced no detectable difference in adsorption while the replacement of sodium chloride by the equivalent quantity of sodium sulfate produced only a very small reduction in adsorption.

The nature of the cation and particularly its valence may be expected to have a greater effect than the anion and its valence. The subject was first studied by Wictoroff, who measured the amount of dye adsorbed by cellulose in an arbitrarily fixed time from solutions containing various electrolytes. Using the sulfates he found the order of cations producing increasing adsorption of Benzo Pure Blue was:¹⁷



Neale and Patel examined the effect of several cations on the rate and equilibrium adsorption of Benzopurpurine 4B and Chlorazol Sky Blue FF.¹⁸ They found the order of effectiveness to vary somewhat with concentration. But in one tenth normal solutions of salt and Chlorazol Sky Blue FF the order was:



Adsorption, Precipitation, and Common Practices in Dyeing In the study of dyeing cellulose there are many different chemical and physical phenomena which must be considered. The monograph of Venkatarman and the book by Vickerstaff critically analyzes the work of many investigators who have attempted to explain the dyeing process.^{19,20} The actual process of dyeing with direct dyes is probably a combination of adsorption and precipitation (salting out). Precipitation in itself will not guarantee that the dyestuff will remain on the cellulose once it is removed from the dyebath, unless there exists an affinity between the dye and the adsorption medium.

In the case of direct dyes, there seems little doubt that the attraction of the azo ($-N=N-$) and amino (NH_2) groups for the hydroxyl (OH) or carboxyl ($COOH$) groups on the cellulose is the main affinity factor.

In samples where the cellulose is not essentially pure such as the pulps used in most paper mills the contaminants may have a much greater effect than the hydroxyl or carboxyl groups. These contaminants may be present in the form of sulfonic groups left from the pulping reactions or the initial lignin.

In order for the attractive forces to have their effect, the repulsive effects of the ionized sulphonate

($-SO_3^-$) groups of the dye must be overcome. The chief means by which a dye is made soluble is by its degree of sulphonation, so, although electrostatically the sulphonate groups may be a hinderance they are a necessity.

It has been reported that the addition of five to ten percent common salt to the beater will give greater retention of direct dyestuffs and heating the dyed stock in the beater up to 120° F will improve the retention of direct dyes.²¹ Not only would heating cause hydrolysis of cellulose in most systems it would seem to be quite uneconomical.

While most direct dyes may respond favorably in the above manner there are still many which do not and these generalizations which are found in paper books on the subject may lead to practices in which dye adsorption is actually hampered.

The effect of temperature on the adsorption of direct dyes by cellulose has been studied by a number of workers. There are two factors which influence adsorption with a rise in temperature. First, the rate of diffusion into the cellulose fiber will rise and second, the actual amount of dye adsorbed at equilibrium will decrease.

These factors play against each other when the dyeing conditions are not taken to equilibrium (which is seldom done in paper mills).

Different dyestuffs are adsorbed at different rates even under identical conditions of concentration and temperature, and with the same type of cellulose. Experience has indicated in technical practice that different dyestuffs are affected in opposite directions by temperature change, some showing increased adsorption with rising temperature and others decreased adsorption with rising temperature. The reason for the difference between the two types of dyes is that some dyes which are slow to adsorb are not carried to equilibrium thus, an increase of temperature increases the rate of adsorption thus causing a greater amount to be adsorbed after a relatively short time of dyeing. The dyes which will adsorb quickly are taken to equilibrium much faster and there is noticed a decrease in the amount of dye adsorbed.

The effect of the addition of up to ten percent common salt to the dye, cellulose system has been studied by various authors. Nearly all of their experiments show that anionic direct dyes have increased adsorption of dye with increasing salt concentration when the dyeing conditions are taken to equilibrium.

Dye Adsorption by Fines in Paper Systems Hinton and Quinn when studying the fiber surface characteristics as they affect two-sided dyeing of paper concluded that the larger zeta potential of fines was responsible for the greater uptake of dye by the fines.²² The zeta potentials recorded were: fines -28 millivolts and longs -7.5 millivolts for cellulose fibers. Thus, dyestuffs will be adsorbed more strongly by the fines than by the longs. It was found by Hinton and Quinn that both the naturally occurring short fibers and the short fibers produced by mechanical action in the beater or refiner will dye to a higher visual strength than will the long fibers. It was also demonstrated by the pair that the use of titanium dioxide (which has a high negative zeta potential) will minimize color two sidedness. This may be partially explained by the fact that the titanium dioxide and the anionic dye will repel each other.

The Streaming Current Detector The recent development of a new instrument known as the Streaming Current Detector (SCD) makes available a new technique to study adsorption of various additives on pulp.²³ The instrument has been found to be useful to determine the charge characteristics of pulps and pulp systems. The main part of the unit is a boot and piston constructed of a material with electrical insulation properties, such as polyethylene, epoxy, or glass. The boot consists of a sample reservoir and a deadended bore, in which the piston reciprocates to force fluid back and forth in the annular space between the bore and piston. Silver electrodes are located at the top and bottom of the bore. The piston is driven by a synchronous motor, which also drives a synchronous rectifier switch. A flow of ions in the fluid forced through the annular space past the electrode constitutes a current that is amplified and read directly on a microammeter calibrated in arbitrary units.

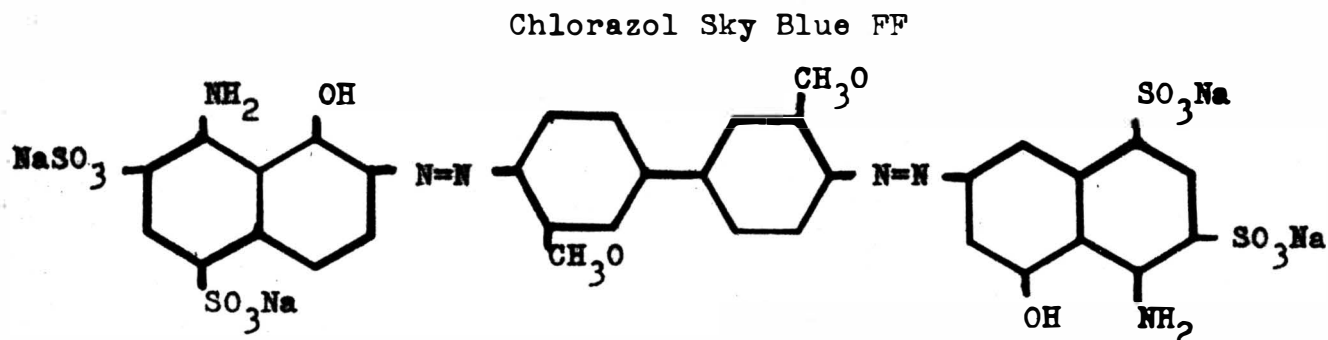
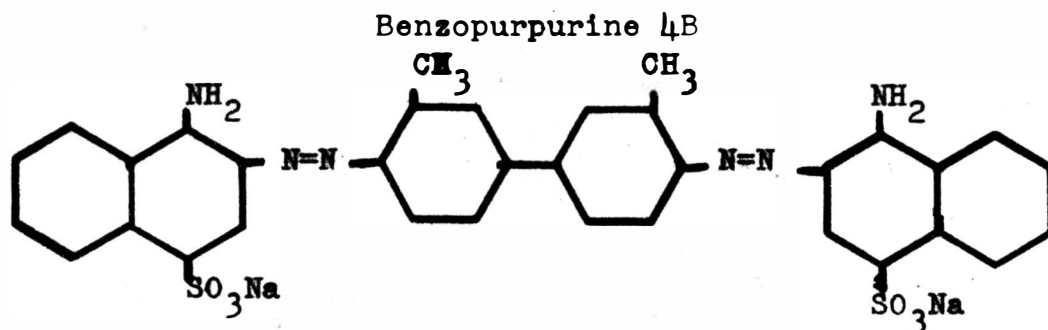
Operation of the instrument is based on the streaming phenomena. One of the discoveries which made the instrument possible was that the walls of a capillary quickly take on the charge characteristics of colloidal particles or of other charge influencing species present in the fluid. The capillary in the case of the Streaming Current Detector being the annular passage between boot

and piston. The streaming current results from the physical separation of counterions from charged surfaces, and this occurs only in the case of charges immobilized on the surface of the boat and piston.

The published articles on the use of the Streaming Current Detector point to the fact it can be very useful in the study of cationic materials and their effect on pulp suspensions.²⁴ As to date there has been no attempt to correlate SCD readings and their relationship to dye adsorption characteristics.

Experimental Design

Two direct dyes Chlorazol Sky Blue FF and Benzopurpurine 4B were chosen to study the relationship between direct dye adsorption and Streaming Current Detector readings. The two dyes have structures as follows:



Since the dyes purchased by paper mills rarely, if ever, are pure it was decided in practical interest to study the dyestuffs as they would be purchased. Most all direct dyes contain a small amount of either sodium sulfate or sodium chloride. These impurities can no doubt produce significant variations in dyeing properties, however, a study of pure dyes would not lend itself as readily to application in the dyeing of

pulp samples. It has been reported in the complete absence of electrolytes direct dyes have a very low affinity for cellulose. Thus the impurities (in the form of sodium salts) could help to increase the adsorption of the dyes.

The impurities are present in these dye samples because of two basic reasons. One, dyes are initially salted out of solution by addition of sodium chloride or sodium sulfate in commercial production and the preparation of pure dyes is a matter of considerable difficulty where often the salts cannot be further separated by ordinary production facilities. Two, diluents, such as the salts mentioned are often used to bring the dye to a standard tinctorial strength for convenience in use.

One consideration when choosing the dyes to work with was their chemical structure. It should be noted that Benzopurpurine 4B and Chlorazol Sky Blue FF have similar structures although different substituted groups. Chlorazol Sky Blue FF has two more substituted sulphonic acid groups per molecule and the presence of two phenolic groups. It should be noted for Chlorazol Sky Blue FF that there are methoxy groups in the positions where methyl groups are present in the Benzopurpurine 4B molecule. While there is considerable difference in the substituted structure these differences can be related to earlier work done by Boss.²⁵

The original intent of this thesis was to study dye adsorption on a first cut cotton linters sample. Due to errors in identification Hercules Grade PIHS-31 cotton linters was used in the research carried out on the first part of this thesis. Hercules Grade PIHS-31 of cotton linters is hydroxy ethylated with a medium range of substitution. Although this may have introduced another variable the conclusions derived from this thesis should not differ if a sample of first cut cotton linters were to be used in the same experiments.

Cotton linters were chosen for one basic reason, that is, their high negative zeta potential when dispersed in water. This is important because the Streaming Current Detector is not as sensitive to most pulp samples as it is to cotton linters. The Hercules sample PIHS-31 basically reduced this advantage since substitution of hydroxy groups by ethoxy groups reduced electrophoretic mobility.²⁶ The sample used also had the characteristic of being easily dispersed by a vibrational instrument known as Chem-Pac. This eliminated contamination which may have resulted due to some other type of mechanical dispersing of the cotton linters.

The Streaming Current Detector which was used was produced by Water Associates Incorporated and is their Model 65. The boot and piston material was polyethylene and the electrodes were silver. Prior to any testing

the instrument was calibrated and standardized and the procedure will be presented later in this paper.

The effect of dye concentration on SCD was studied for Chlorazol Sky Blue FF and also Benzopurpurine 4B. The effect of sodium chloride concentration versus SCD was also studied.

The effect of the concentration of cotton linters on SCD was studied with concentrations varying from one tenth to five tenths percent. Since headbox consistencies are closer to five tenths percent it was chosen as the consistency on which the experiments would be run. The effect of the concentration of Chlorazol Sky Blue FF and the concentration of Benzopurpurine 4B on the SCD of the solution and the absorbance of the dyed handsheets made from the five tenths percent cotton linters sample was studied.

After preliminary work had been performed the effects of various salts and sodium chloride concentration on SCD and dye adsorption were studied.

In studying two-sided dyeing as related to fiber surface characteristics the SCD of the solutions and the absorbance of handsheets were measured for a system of dye and fines and a system of dye and longer fibers.

Testing Procedures

Calibration and Standardization of the SCD When beginning the first thing which was done was to adjust the Streaming Current Detector to give a constant value of -50 for a sample of deionized water. This was done by adjusting the recorder signal adjust (gain system) located on the back of the instrument. The sensitivity selector switch located in the front of the electronic indicator was set at X10. All readings here and throughout the experimentation were taken after five minutes had elapsed. The resistance of the deionized water was initially two hundred and fifty thousand ohms.

The effect of temperature of the deionized water on the SCD reading was obtained by varying the temperature in increments of five degrees centigrade from fifteen to forty five degrees centigrade and recording the SCD. Since room temperature was approximately twenty five degrees centigrade it was decided to maintain the value for the SCD at -50 for this temperature on the remainder of the experimental work.

Experimental Procedures The two dyes were dispersed in deionized water and then allowed to come to equilibrium and room temperature. The effect of concentration of dye on SCD was later studied. The concentration of Chlorazol Sky Blue FF was varied from .125 grams per liter through 8 grams per liter. The concentration of Benzopurpurine 4B was varied from .01 grams per liter through 1 gram per liter.

A one molar sodium chloride solution in deionized water was made and the effect of concentration of the salt on the SCD was recorded. The sodium chloride concentration varied from .001 molar through one molar.

In studying dye adsorption on cellulose the SCD readings were recorded for five tenths percent cotton linters with varying degrees of dye concentration. For Chlorazol Sky Blue FF concentrations between .05 grams per liter and 2 grams per liter were used. For Benzopurpurine 4B concentrations varying between .0125 grams per liter and 1 gram per liter were used.

Three runs at each concentration were made. Each was made up to fifty milliliters and after the five minutes (allowed for adsorption on boot and piston) small handsheets were made. These were made on a small wire (sixty mesh) which had been fitted to a buchner funnel. The samples were couched off the wire with blotter paper and allowed to dry at room temperature. The adsorption of dye on these handsheets was tested

using the Hitachi Perkin Elmer Spectrophotometer.

The absorbance of Chlorazol Sky Blue FF was measured at six hundred millimicrons and the absorbance of Benzo-purpurine 4B was measured at five hundred and forty millimicrons. They were measured at these values after curves for the dyed cotton handsheets (dyed from a bath with a concentration of one gram per liter) through the range four hundred millimicrons through seven hundred millimicrons had been obtained. Five hundred and forty millimicrons and six hundred millimicrons were chosen as they were the peaks in the absorbance curves for the two dyes respectively.

Two runs were made with various levels of sodium chloride added to solutions of 1) five tenths percent cotton linters and five hundredths grams per liter Chlorazol Sky Blue FF; 2) solutions of five tenths percent cotton linters and .0125 grams per liter of Benzo-purpurine 4B. From these runs handsheets were made and analyzed to see the effect of sodium chloride on dye adsorption.

With five tenths percent cotton linters and .0125 grams per liter of Benzopurpurine 4B various .125 normal salt solutions were tested to see their effect on SCD reading and dye adsorption. The salts used were: Na_2SO_4 , CaCl_2 , and AlCl_3 .

To study the effect of the fines and their charge

on the two sided dyeing effect the Streaming Current Detector was used. One tenth percent solutions of fines (prepared from screening softwood kraft pulp through a sixty mesh screen) and longs (the residual fibers left on the sixty mesh screen) were made up and their SCD values were recorded. A solution of fines and a solution of longs at one tenth percent was made up with a dye concentration of .0125 grams per liter Benzopurpurine 4B and a sodium chloride concentration of one hundredth normal. The SCD values for these solutions and the absorbance of handsheets made from these solutions as measured by the Hitachi Perkin Elmer Spectrophotometer were recorded.

Results & Discussion

The effect of the addition of sodium chloride on dye adsorption was one of the areas studied in this thesis by means of the Streaming Current Detector and the Hitachi Elmer Spectrophotometer. Before these results are discussed the results on the preliminary work must be brought out.

Graph I shows the relationship which was found to exist between the SCD reading of deionized water and temperature. With an increase of temperature there is an increase in the negative SCD reading. Within the temperature range which all of the tests were carried out the change in SCD was minimal (50 ± 1).

Graph 2 shows the relationship between SCD reading and concentration of sodium chloride. It should be noticed that at very low concentrations there is a steep rise in SCD. This could partially explain why many dyes have a much greater adsorption or a lesser adsorption with only a very small addition of common salt.

Graph 3 shows the variation in SCD with varying concentrations of Chlorazol Sky Blue FF. The cotton linters gave a reading of -16 and on the addition of dye the SCD initially decreased rapidly. Although the SCD decreased it should be noted that it did not cross the value of -50 at any point with increasing

concentration. Graph 5 helps to explain this, since with increasing dye concentration in deionized water the SCD reading is steadily increasing for Chlorazol Sky Blue FF.

Graph 4 is similar to Graph 3 only the effect of the addition of Benzopurpurine 4B is studied. In Graph 4 the curve readily drops below the -50 value and stays below it once the line is crossed. As Graph 5 helped to explain Graph 3, Graph 6 helps to explain Graph 4. On the addition of Benzopurpurine 4B to deionized water a steadily decreasing curve is obtained.

From these graphs one can now get an understanding of Graphs 7 and 8 which are concerned with the effect of sodium chloride on dye adsorption. Graph 7 shows the effect on SCD of increasing salt concentrations in a system containing .05 grams per liter of Chlorazol Sky Blue FF and five tenths percent cotton linters; it also shows the effect of salt on absorbance of dye on the handsheets made at the various salt concentrations.

Likewise Graph 8 shows the effect on SCD of increasing salt concentrations in a system containing .0125 grams per liter of Benzopurpurine 4B and five tenths percent cotton linters; and also the effect of salt on absorbance of dye on the handsheets made at the various concentrations. The curves of SCD versus salt concentration in the two systems are quite similar, however, when one looks at

the absorbance of dyes in these two systems he will easily notice that there is decreasing absorbance with rising salt concentration for the Chlorazol Sky Blue FF. In Graph 8 the increase of salt concentration resulted in the increased absorbance of the dyed sheet and thus the increased adsorption of Benzopurpurine 4B.

If the curves for Graph 7 and Graph 5 are compared, with rising concentration of Chlorazol Sky Blue FF it should be noted in Graph 5 there is an increasing SCD curve; and in Graph 7 there is decreased absorbance with increasing salt concentration.

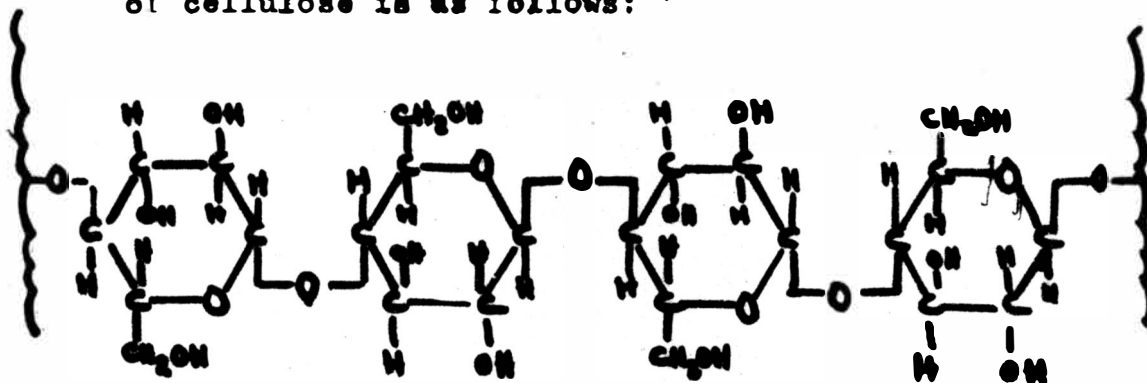
If the curves for Graph 8 and Graph 6 are compared one will notice an opposite tendency. With rising concentration of Benzopurpurine 4B a decreasing SCD value is obtained in Graph 6, and in Graph 8 there is increased absorbance with increasing salt concentration.

While the SCD reading of the dye dispersed in deionized water could in the case of these two dyes be used to predict whether the addition of common salt will help or hinder adsorption of the dye this observance was not carried out over a wide range of direct dyes.

The testing of many direct dyes would be necessary before any test could be immediately applied to know whether dye adsorption would be hindered or helped by the addition of sodium chloride. If one compares the molecular structure of the two dyes studied and tries

to explain the results by the different degrees and different substitution groups he may easily suspect that the basis for the use of SCD in analysis of this type may be quite valid.

The purest form of cellulose is found in cotton. Pure cellulose is a carbohydrate and may be hydrolyzed almost quantitatively to glucose. The Haworth Structure of cellulose is as follows:²⁷



The xray evidence of Meyer and Mark, and Meyer and Misch shows that in crystalline cellulose the long chains are arranged parallel in with a unit cell structure repeated many times.²⁸ The orientation of the cellulose is important in consideration of dyeing.

Meyer suggested that if a dye possesses a long, chain-like molecule it can lie close up to the cellulose molecule and the residual valency forces will thus be more effective in holding the two together than would be the case if the dye was not linear, and deviations from linearity would generally lead to a loss in the effective holding power. From this consideration a

dye molecule with many substituted groups (not a consideration here of what types) would deviate more from linearity and would not have the effective holding power of a more linear dye.

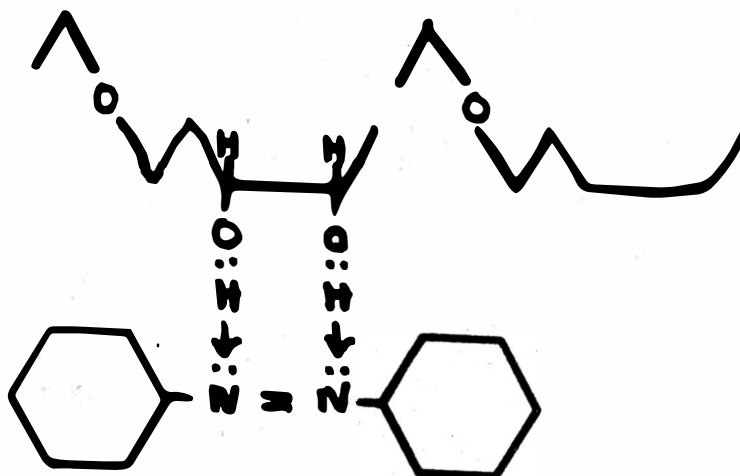
This could be considered to be the case electrostatically as well with the addition of sodium chloride we are decreasing the thickness of the ionic atmosphere of the cellulose and thus, allowing the more linear molecules to get closer. The non linear molecules are not helped to the same degree. This is not the most important factor when we consider the action of sodium chloride on Chlorazol Sky Blue FF and Benzopurpurine 4B dye adsorption but it is one factor which helps to explain the opposite action sodium chloride causes. Since Chlorazol Sky Blue FF has many substituted groups it would behave more like a non linear molecule.

Another factor which must be taken into account is the action of the solubilizing groups. The dyes must be soluble in water, and this is achieved by the introduction of sulphonic acid groups. An increase in the number of solubilizing groups in a molecule must reduce its adsorption even in the absence of any further effect. Such groups give the dye a more negative charge, and, since cellulose in water is itself negatively charged, this leads to electrical repulsion

between dye and fiber. Chlorazol Sky Blue FF is a tetrasulphonic acid, and Benzopurpurine 4B is a disulphonic acid. This is one of the very important reasons why Benzopurpurine 4B is much more active (substantive) in the dyeing of cellulose than is Chlorazol Sky Blue FF.

Hydrogen bonding both intramolecular and intermolecular is responsible for the attraction which still exists between the negative fiber and the negative dye molecule. Hydrogen bonding may occur between cellulose and azo groups present on the dye molecule (Figure I). Hydrogen bonding may occur between cellulose and ethereal oxygen of a methoxy group on a dye molecule (Figure II). Hydrogen bonding may occur between a hydroxyl group on a dye molecule and a hydroxyl group on cellulose (Figure III). Hydrogen bonding may occur between cellulose and the amine groups on the dye molecule (Figure IV).

Figure I



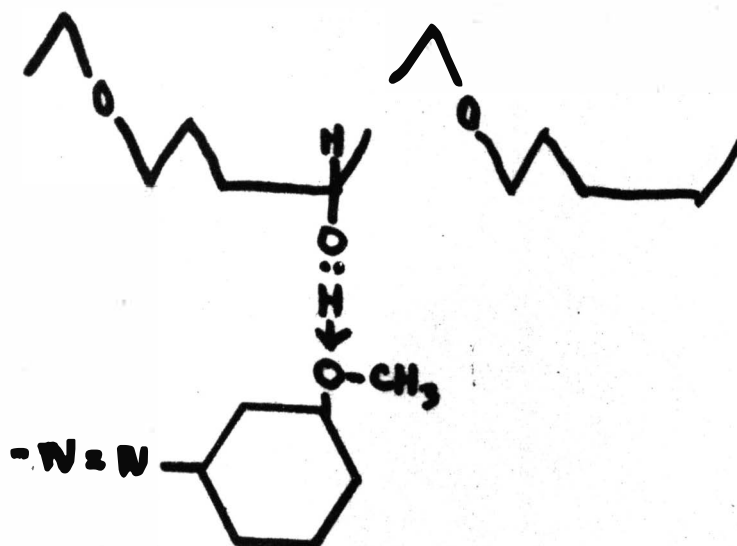


Figure 2

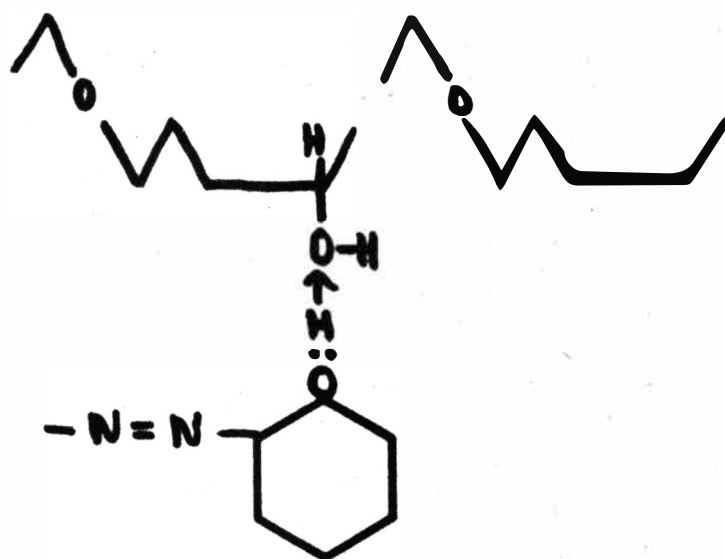


Figure 3

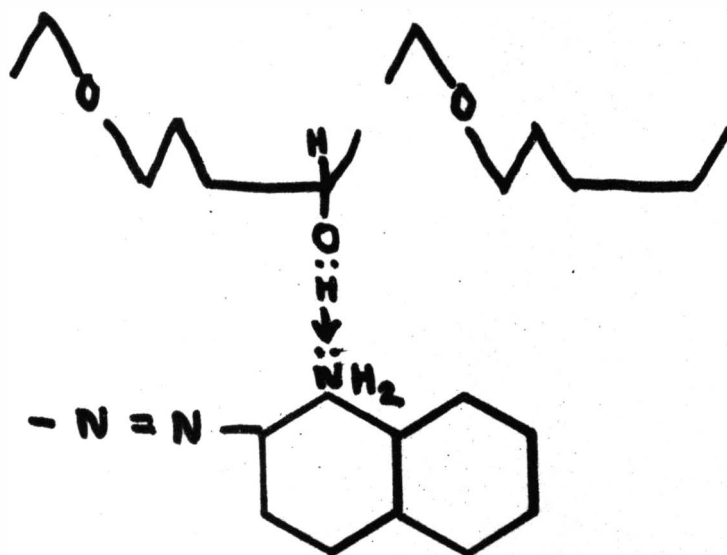


Figure 3

It would be reasonable to assume the more favorable groups such as; amino, azo, phenol, and methoxy when present would help dye adsorption; and the presence of sulphonic acid groups would hinder dye adsorption. Since one group would tend to make the readings more positive with the SCD and the other would produce a more negative SCD the instrument may be capable of determining the effect salts will have on dye adsorption as mentioned earlier.

Besides these considerations there is also the effect of precipitation (salting out). This is probably what is happening with Chlorazol Sky Blue FF and once it precipitates there is little affinity between the cellulose and the dye. This would be especially true for Chlorazol Sky Blue FF since it is a tetra-sulphonated dye.

The salting out effect also appears to be the case for the calcium and aluminum chloride causing reduced adsorption of dye in .125 normal solutions of the salts. This data supporting this may be found in Table 3.

In studying the fiber surface characteristic it was found that fines had a greater charge than longs (for the softwood kraft pulp studied). Fines gave a SCD of -59 while the SCD value for the longs was -51.5. When comparing the dye adsorption of Benzopurpurine 4B it was found that the fines adsorbed considerably more

dye and this has been widely reported. One might expect that by finding the SCD values of the fines and longs he could determine whether the dye would be strongly or weakly two sided with the pulp being used. The data for this part of the thesis may be found in Table 4.

Conclusions

The process of dyeing with direct dyes is a combination of adsorption and precipitation. Adsorption of direct dyes may be helped or hindered by the addition of sodium chloride and other salts such as alum.

On the addition of salts the dye may be precipitated and if the dye is highly negatively charged there will be little attraction between it and the negatively charged cellulose fiber. If the molecular structure of the dye contains many sulphonated acid groups it will be highly negatively charged.

It is hard to determine whether sodium chloride will be beneficial or harmful to dye adsorption. Since the Streaming Current Detector is sensitive to the charge of the various substitution groups present on the dye molecule the instrument may be able to predict the behavior of the dye. By dissolving the dye in deionized water and watching the direction of the curve it may be possible to predict the effect of sodium chloride on dyeing. If the SCD reading tended to go positive dye adsorption may not be helped by the addition of salt. However, if the SCD went negative one could almost be assured the addition of sodium chloride would be beneficial to dye adsorption.

The alum present in pulp suspensions could be expected to act in the same way as the salt only with

much greater effect due to the tri basic aluminum cation. It has been noticed for many dyes that in the absence of rosin and alum very little dyeing takes place. This is due primarily to the effect of the alum present.

The dyeing process is aided by groups on the dye molecule which can hydrogen bond with the cellulose. These include azo ($-N=N-$), amino ($-NH_2$), methoxy ($-OCH_3$), and hydroxyl ($-OH$) groups of the dye. These groups will produce a rise in SCD.²⁹

The sulphonate groups hinder dye adsorption and will produce a more negative dye and thus a more negative SCD reading.

The practice of adding up to ten percent sodium chloride to the beater and the practice of heating a beater up to 120° F to increase dye adsorption should be studied more completely for the present dyes being used since it may be quite possible these procedures are hindering dye adsorption and are uneconomical. The extra cost of heating up the beater and the additional cost of sodium chloride may not be needed. It may even cause the use of more dye to get to the tintorial strength desired.

Since the Streaming Current Detector is sensitive to the charge on various cellulose samples it may be possible to predict dye adsorption potential of various pulp samples by using the instrument.

This was successfully done to some extent with the study of the surface charge of fines as compared with that of longs. The charge of the fines was noticed to be greater and also produced a sheet with greater absorbance at the wavelength being used.

It may be possible by use of the SCD to better control dye two-sidedness in paper. This however would require further investigation.

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Appendix

Table I

.5% Cotton Linters and
Varying Degrees
Chlorazol Sky Blue FF

Concentration in (grams/liter)	Absorbance of Handseets
2	1.45
1	1.40
.2	1.15
.1	.96
.05	.74

Table II

**.5% Cotton Linters and
Varying Degrees
of Benzopurpurine 4B**

Concentration in (grams/liter)	Absorbance of Handseets
1	1.22
.5	1.35
.2	1.35
.1	1.40
.05	1.28
.025	1.15
.0125	1.05

Table III

.5% Cotton Linters

.0125 Grams/Liter Benzopurpurine 4B

.125 Normal Solutions of:

Absorbance of Handsheets

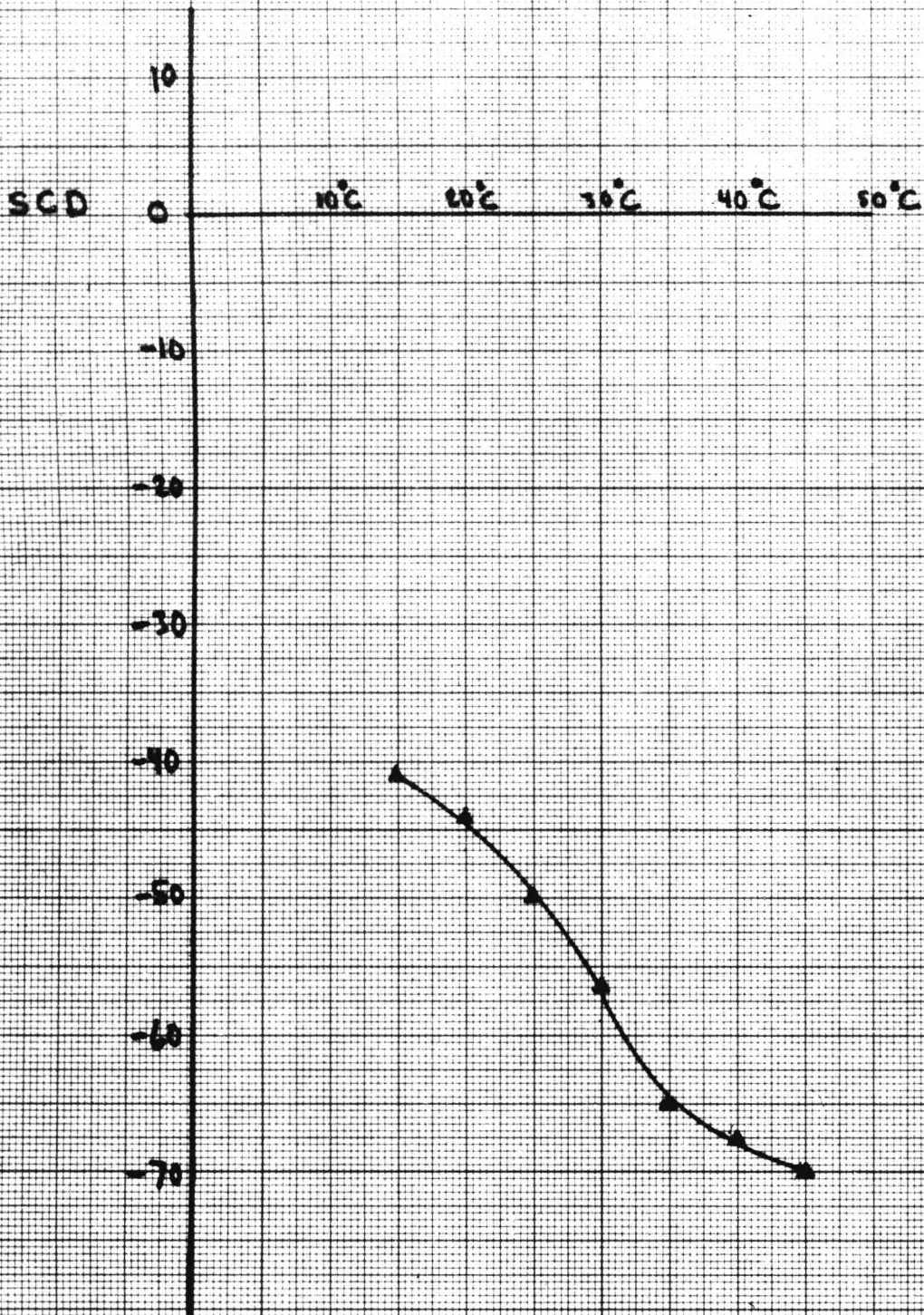
NaCl	.86
Na ₂ SO ₄	.90
CaCl ₂	.84
AlCl ₃	.74

Table IV

		SCD
.1% Fines (S.W. Kraft)		-59
.1% Longs (S.W. Kraft)		-51.5
.1% Fines, .0125 g/l Benzopurpurine 4B, .01N. NaCl		
SCD	-22.3	Absorbance 77
.1% Longs, .0125 g/l Benzopurpurine 4B, .01N. NaCl		
SCD	-17.7	Absorbance 58

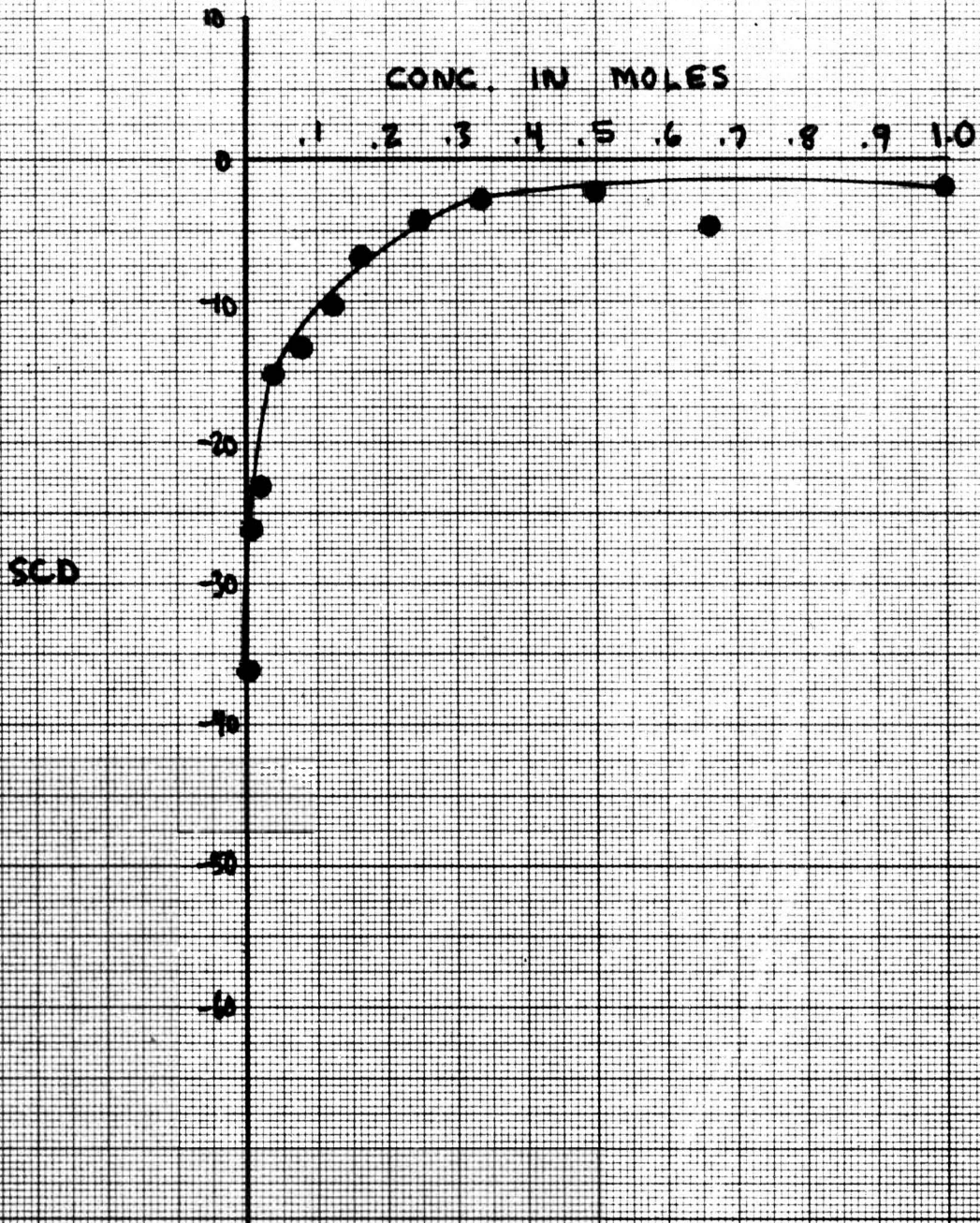
GRAPH 1

SCD VS. TEMP. OF D.I. WATER



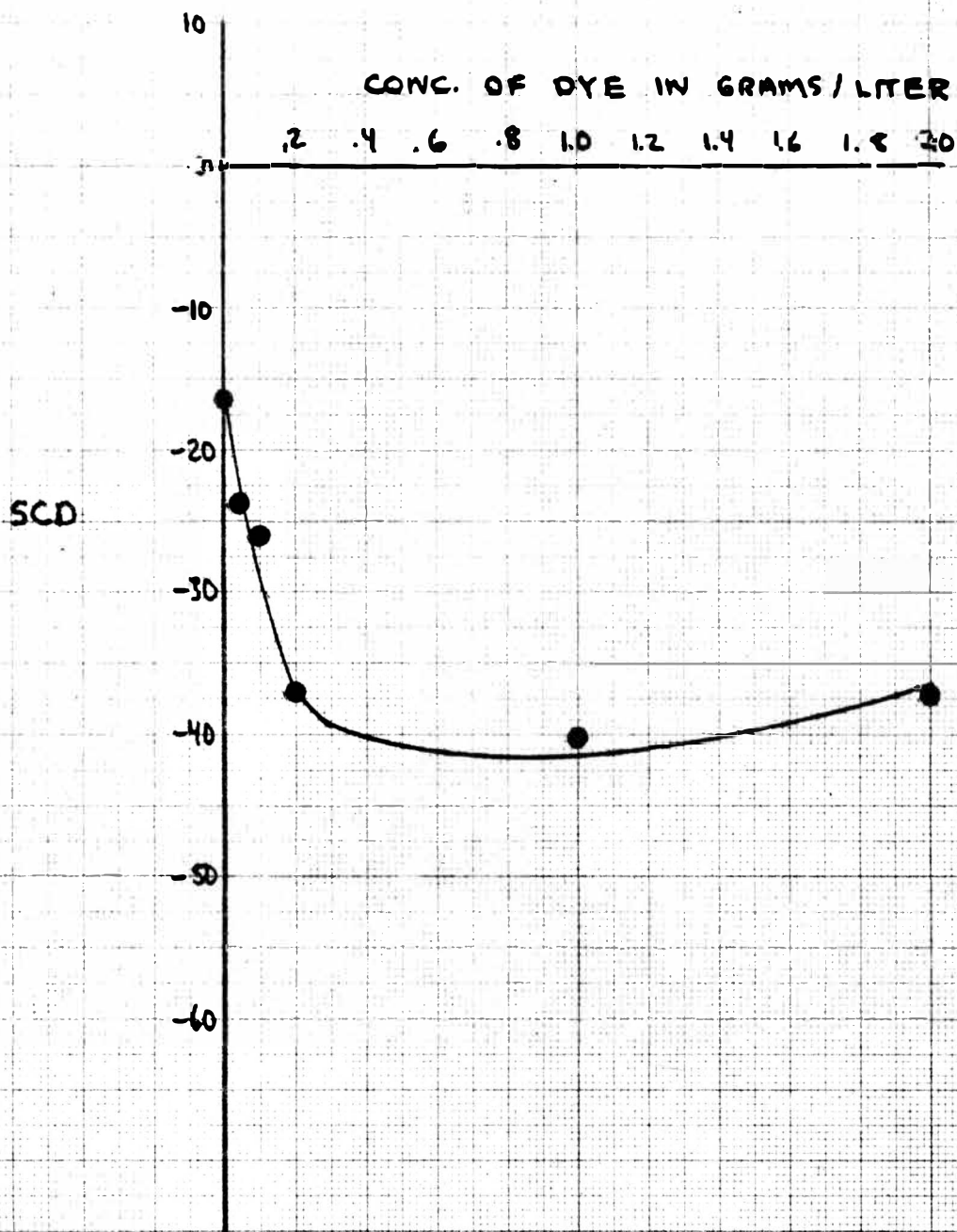
GRAPH 2

SCD VS CONC. OF
 NaCl



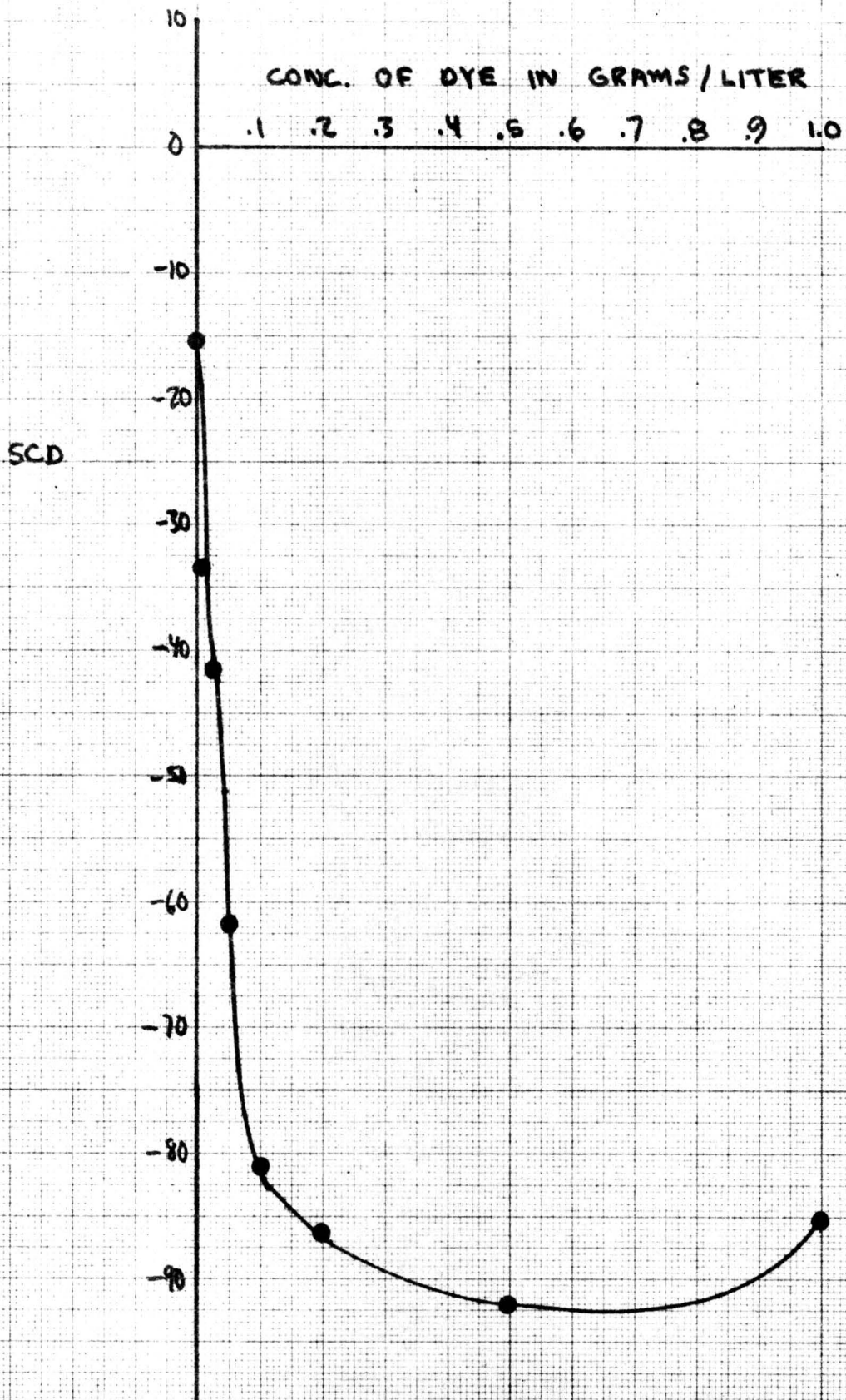
GRAPH 3

SCD OF .5% COTTON LINTERS
VS. VARIOUS CONC. OF CHLORAZOL
SKY BLUE FF



GRAPH 4

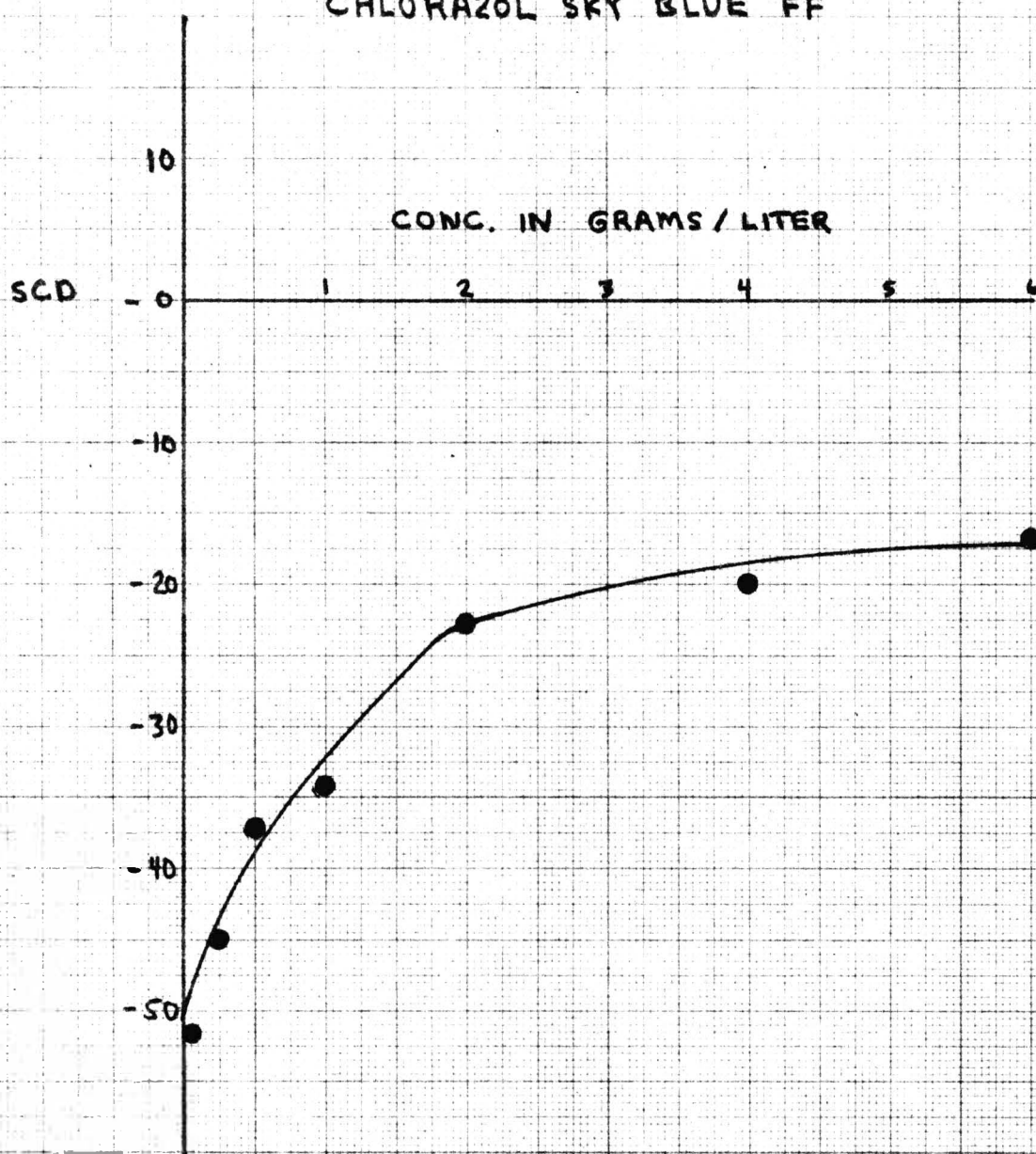
SCD OF .5% COTTON LINTERS
VS. VARIOUS CONC. OF
BENZOPURPURINE 4 B



GRAPHS

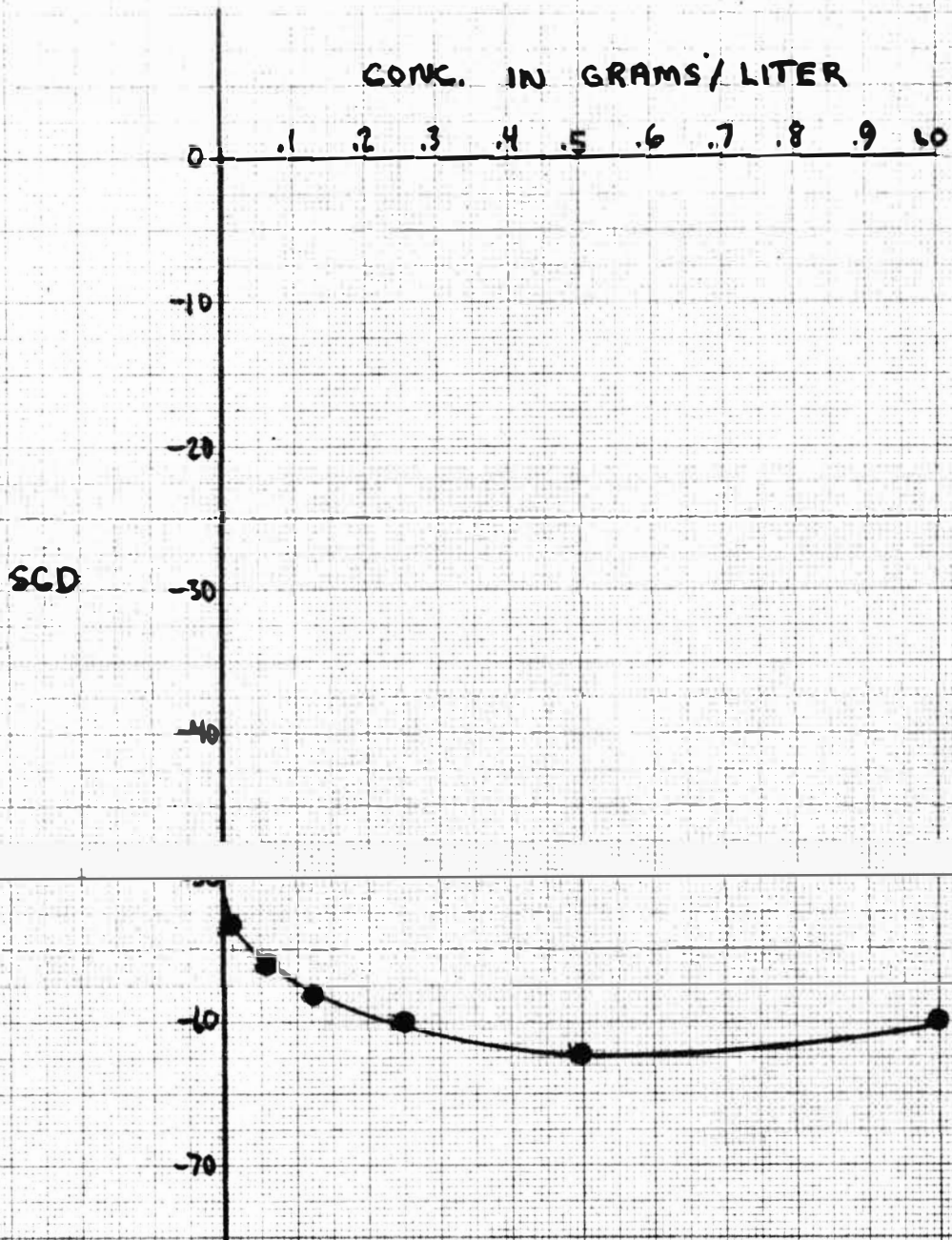
SCD VS. CONC. OF

CHLORAZOL SKY BLUE FF



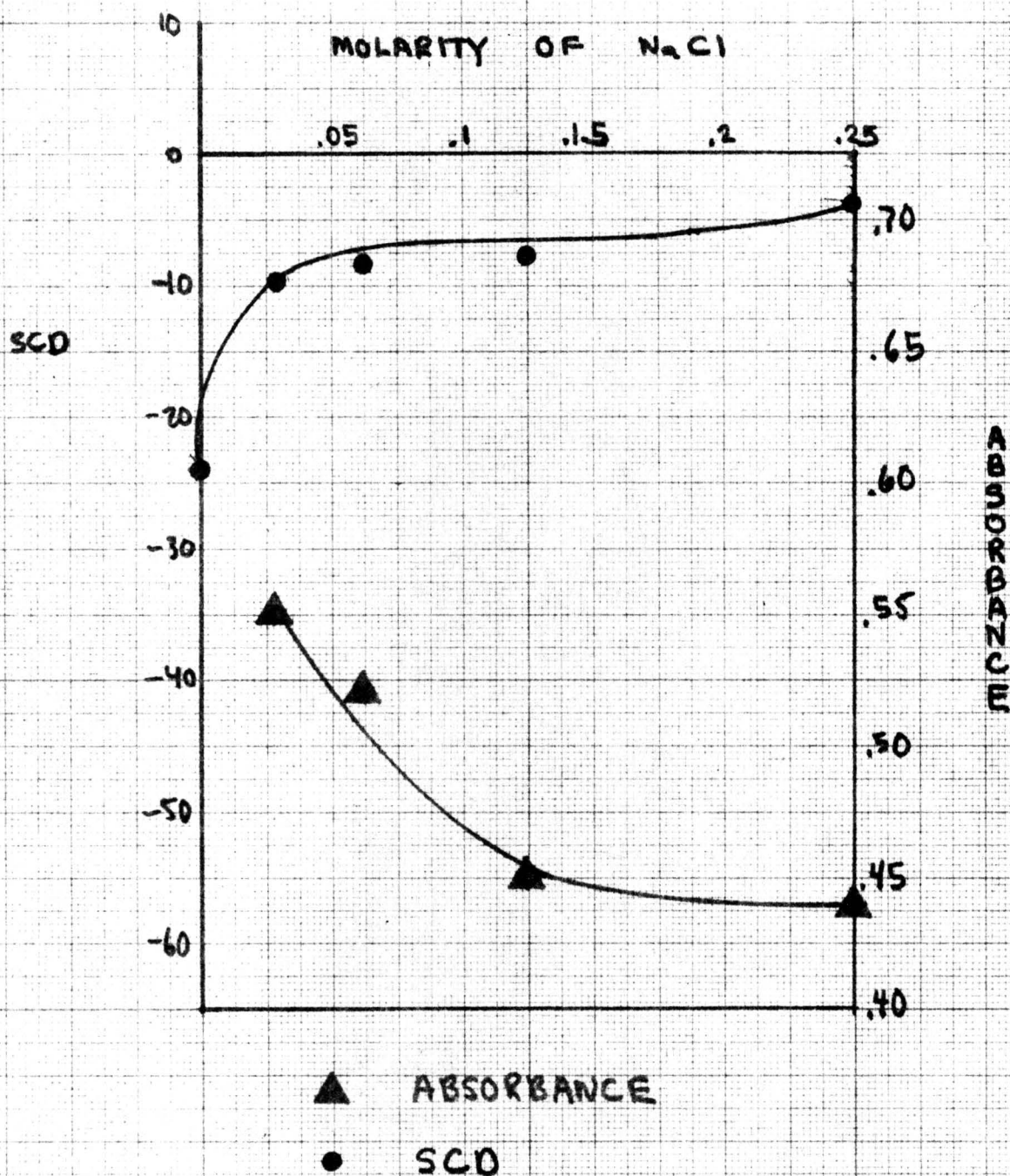
GRAPH 6

SCD VS. CONC. OF
BENZOPURPURINE 4B



GRAPH 7

SCD OF .5% COTTON LINTERS
.05 GRAMS/LITER OF CHLORAZOL SKY BLUE FF
VS. VARIOUS CONC. OF NaCl



GRAPH 8

SCD OF .5% COTTON LINTERS
.0125 GRAMS/LITER OF BENZOPURPURINE 4B
VS VARIOUS CONC. OF NaCl

