

ADSORPTION OF NAPHTHOLS IN THE PRESENCE OF DIFFERENT ELECTROLYTES AND PEPTISING AGENTS AND AT DIFFERENT TEMPERATURES

BY J. A. NABAR, P. M. BARVE, A. M. PATEL AND B. N. DESAI
(From the Physical Chemistry Laboratory, Wilson College, Bombay 7)

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IN spite of considerable experimental work which has been done to understand the mechanism of dyeing, we are still uncertain about the same. The main cause of this is that the different dyestuffs and fibres have widely different physical and chemical properties. One should therefore limit the application of one's results to only a particular class of dyestuffs and fibre for a proper understanding of the mechanism of dyeing. The present work was undertaken with an idea to study the colloidal nature of the dyestuffs of the Naphthol AS series and the process of dyeing cotton fabric with those dyes by estimating adsorption of the dyes by cotton cloth in the presence of alcohol, sodium hydroxide, sodium chloride, sodium sulphate, sodium phosphate, soap, agar-agar and gum tragacanth and at different temperatures.

Experimental

Purification of the dyes.—The Naphthols are the aryl amine derivatives of B-hydroxy Naphtholic acid. Five Naphthol AS series dyes of varying substantivity were selected for the work. Arranged in the increasing order of substantivity,¹ they are (1) Naphthol AS-G, (2) Naphthol AS, (3) Naphthol AS-TR, (4) Naphthol AS-BO, and (5) Naphthol AS-SW. The dyes kept on the market by I. G. Farbenindustrie were purified in the manner given below:—

Water-soluble impurities were first removed by stirring the dye in boiling distilled water for a few minutes in a boiling water-bath and filtering while hot. The filtrate, which was deep brown in colour and smelling of phenol, gave a reddish substance on evaporation, which gave violet coloration with ferric chloride and white precipitate with silver nitrate solution, thus showing the presence of substances of phenolic character. This process of removing water-soluble impurities was repeated till the filtrate was colourless and gave no reaction with ferric chloride or silver nitrate, and had the same conductivity as that of distilled water. The dye was then dried on a steam-bath at 100° C. for several hours and the last traces of water were removed by further heating in a hot air oven at about 105° C. till its weight remained constant. It was then stocked in air-tight glass stoppered bottles.

In order to see if any further impurities were left in the dye purified in the above manner, a further test of purification was made. Some of the purified dye was pasted up with absolute alcohol and sodium hydroxide was added and the mixture stirred. The solution was filtered and the filtrate treated with hydrochloric acid in excess to precipitate the original dye. This was filtered and washed free from chloride and dried as before. Two solutions of the same concentration were prepared from the two samples of the same dye in two stages of purification. 5 c.c. of each solution were treated with the same amount of developer solution (Trivasol Red TR—it is a hydrochloride of 5-chloro-O-toluidine diazotized and stabilized) and the dye so produced dried on a water-bath. It was then dissolved in the same volume of chloroform and the two solutions thus obtained were compared by means of a colorimeter. They were found to be quite identical. The second stage of purification was thus found to be unnecessary.

Cloth used for dyeing.—The adsorbing material used was the thin cotton cloth 'Malmal' No. 3948 manufactured by the Finlay Mills, Ltd., Bombay. The cloth was cut into small pieces, each six inches square and weighing 0.8 to 0.1 gm. One such piece was used for each adsorption reading. Starches and pectinous matter in the form of sizing material contained in the cloth as available in the market were removed before using the cloth for dyeing by treating it in the following manner:—

The pieces of cloth were first boiled with N/20 solution of sodium hydroxide and washed with water till completely free from alkali. They were then boiled with a 0.2% soap solution and washed with water till free from soap. Afterwards they were squeezed out and dried in air at room temperature for several hours. The pieces were then folded and further dried in a hot air oven at about 105° C. and stocked in a desiccator over anhydrous granular calcium chloride for a day or two until their weight was constant (complete dehydration).

Preparation and estimation of the dye in solution.—The dye solutions were prepared by the 'hot' process as the solutions so prepared could be employed conveniently for adsorption at any temperature between 0° C. and the temperature at the boil. A 10% solution of sunlight soap was used as a protective colloid. The proportions of the dye, protective colloid (10% soap solution), sodium hydroxide and formaldehyde used for the preparation of the various dye solutions were the same as those recommended by I. G. Farbenindustrie in their recipes. Formaldehyde was not added in the case of Naphthol AS-G as it destroys the dyeing power of the dye.

Several methods were tried for the estimation of the concentration of the Naphthol dye solutions prepared as above. The method devised by

E. Jungmichl and D. Kimovec² was found to be the most suitable and convenient from all points of view. Various experiments were tried to find out a suitable dye salt (developing salt) which could be used for the estimations by this method. Trivasol Red TR was found to be the most suitable from the point of view of stability of the solution and sharply defined end point. 0.5% solution of this developer salt was used and every time a fresh solution was prepared as soon as the one prepared previously was 4 hours old. Actual experiments showed that after 8 hours of the preparation of the solution of the developer salt Trivasol Red TR, there could be an error only of 0.5% in determining the end point with its help. Finally worked out the method of estimation of the dye in solutions is as follows:—

10 c.c. of a 0.5% solution of Trivasol Red TR are taken in a beaker and titrated against the solution, the concentration of dye in which is to be determined, using a 2% Naphthol AS solution as an external indicator. The solution of the dye is allowed to run from a burette into the beaker containing the developer salt solution continuously till near the end of the reaction (determined previously by a preliminary titration) and drop by drop thereafter until the red coloration does not appear any more at the point where the two drops (one of the mixture in the beaker and the other of the 2% Naphthol AS solution used as external indicator) run together. Repeating the experiment with a solution of a known concentration, the concentration of the dye left in the solution, after the cloth is allowed to adsorb the dye under the conditions of the experiment, was calculated. It may be mentioned that some sodium chloride was added to the developer salt solution in order to quicken the coupling reaction.

Method of studying adsorption of the dyes by the cloth—'Malmal' No. 3948 (Finlay).—The dye solutions were prepared by the 'hot' process as mentioned above. If the adsorption was to be studied at a particular concentration of the dye, a solution of higher concentration (generally double the required concentration) was prepared. A definite volume of this solution was taken in measuring cylinders, varying amounts of absolute alcohol or sodium hydroxide, sodium chloride, sodium sulphate or sodium phosphate and soap, agar-agar or gum tragacanth were added as necessary to these cylinders in increasing amounts and the volume made up to 25 c.c. with distilled water so that requisite strength of the dye was reached in each case. The pieces of 'Malmal' cloth mentioned above were accurately weighed. Since the amount of the dye adsorbed depends on the proportion of the amount of the material (cotton cloth) to that of the dye solution, the proportions were so adjusted that the volume of the dye solution measured in c.c. was twenty times the weight of the material measured in grams. The

volume of the dye solution proportional to the amount of the material to be immersed was measured out into hard glass test tubes which were used as dyeing vessels. The tubes were kept in a water-bath at temperature of 30° C. till they attained the temperature of the bath and the cloth pieces were then immersed in the dye-baths noting the time of immersing. The pieces of cloth were kept immersed in the dye-bath for exactly two hours at the end of which they were taken out, squeezed by hand and subsequently thoroughly dried by pressing between filter papers. Each piece was then treated with 25 c.c. of a 0.5% solution (excess) of the developer salt—Trivasol Red TR. A measured volume of this developer solution was taken in a beaker and titrated against a 0.05% solution of the same dye as used for dyeing, using a 2% Naphthol AS solution as an external indicator.

The endpoint was noted as mentioned before. From this titration the volume of the 0.05% of the dye solution equivalent to 25 c.c. of the developer solution used, after developing the dye adsorbed, was calculated. A blank titration was carried out using 5 c.c. of the same developer solution against the same dye solution using the same indicator and in the same manner (but without developing any adsorbed dye previously) for calculating the volume of a 0.05% dye solution equivalent to 25 c.c. of the developer solution. The difference between the blank titration and the first titration thus gave the amount of the dye adsorbed by the corresponding amount of the cloth in terms of c.c. of a 0.05% dye solution. From this the amount of the dye in grams that would be adsorbed by one kilogram of the cloth in presence or absence of the added substances, mentioned above, was calculated in each case.

The electrolytes used were Merck's extra pure products.

The 'Sunlight' soap was used in the experiments. The cake was cut into thin chips, which were dried in a hot air oven at 100° C. till their weight remained constant. Fresh solution of soap so dried was prepared every time before the experiment.

Agar-agar manufactured by Merck and specified 'extra pure' and free from moisture was used. A weighed amount of this substance was stirred with distilled water and kept for 24 hours. It was then diluted to the required volume and hydrolysed by keeping in a boiling water-bath for one hour and then cooled to 30° C. A fresh solution was prepared in this manner every time.

Ordinary commercial sample of gum tragacanth was used. It was finely powdered, sieved through a fine cloth and kept in a dry place. Necessary solutions for experiments were prepared from this powder each time exactly in the same manner as in the case of agar-agar.

For experiments at different temperatures, the test tubes containing the dye solutions were kept in a water-bath, the temperature of which was regulated by means of a thermo-regulator. In the case of higher temperatures the volume of the dye solution in the test tubes was kept constant by adding requisite amounts of distilled water from time to time to make up for the loss of water due to evaporation. The adsorption experiments were performed in the same manner as before, the time for which the cloth was kept immersed in the dye bath being however different in each case.

Results and Discussion

A. *Effect of alcohol and sodium hydroxide on the adsorption of Naphthols by cotton fibre.*—A typical set of results with Naphthol AS-TR in the case of alcohol and Naphthol AS in the case of sodium hydroxide is given in Figs. 1 and 2 respectively.

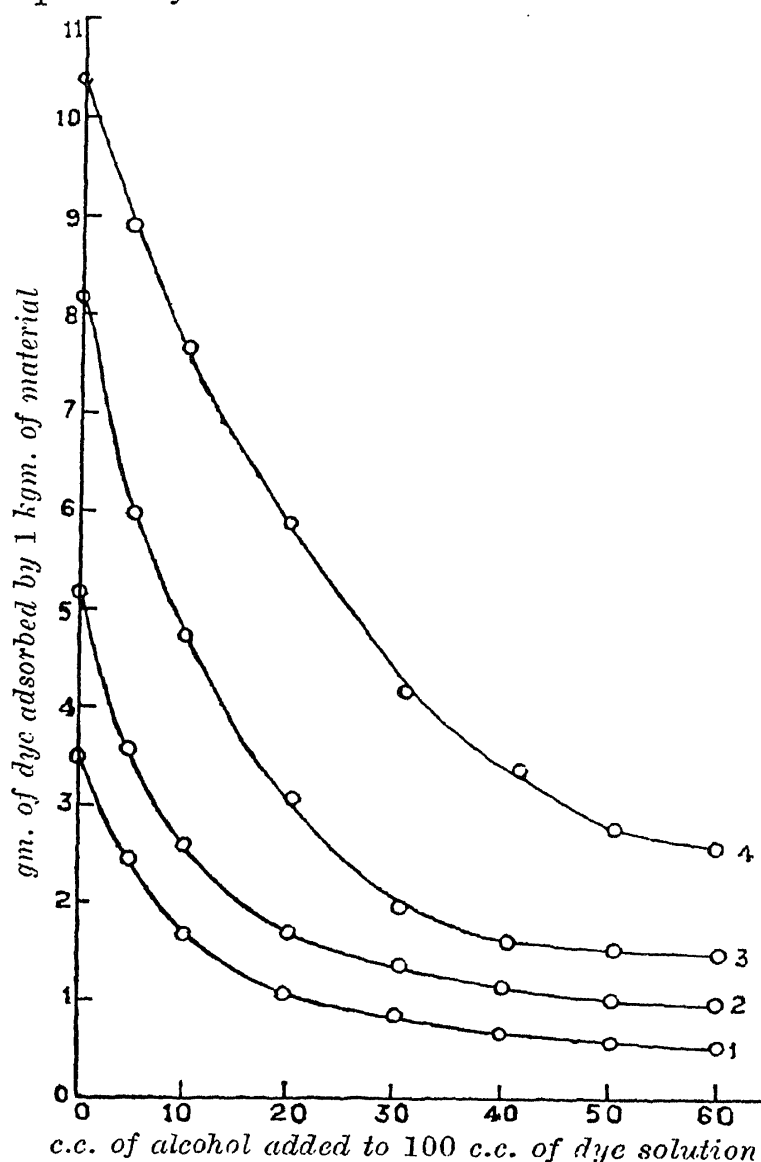


FIG. 1

Naphthol AS-TR

- | | |
|------------------|------------------|
| 1. 0.2% solution | 3. 0.8% solution |
| 2. 0.4% ,, | 4. 1.0% ,, |

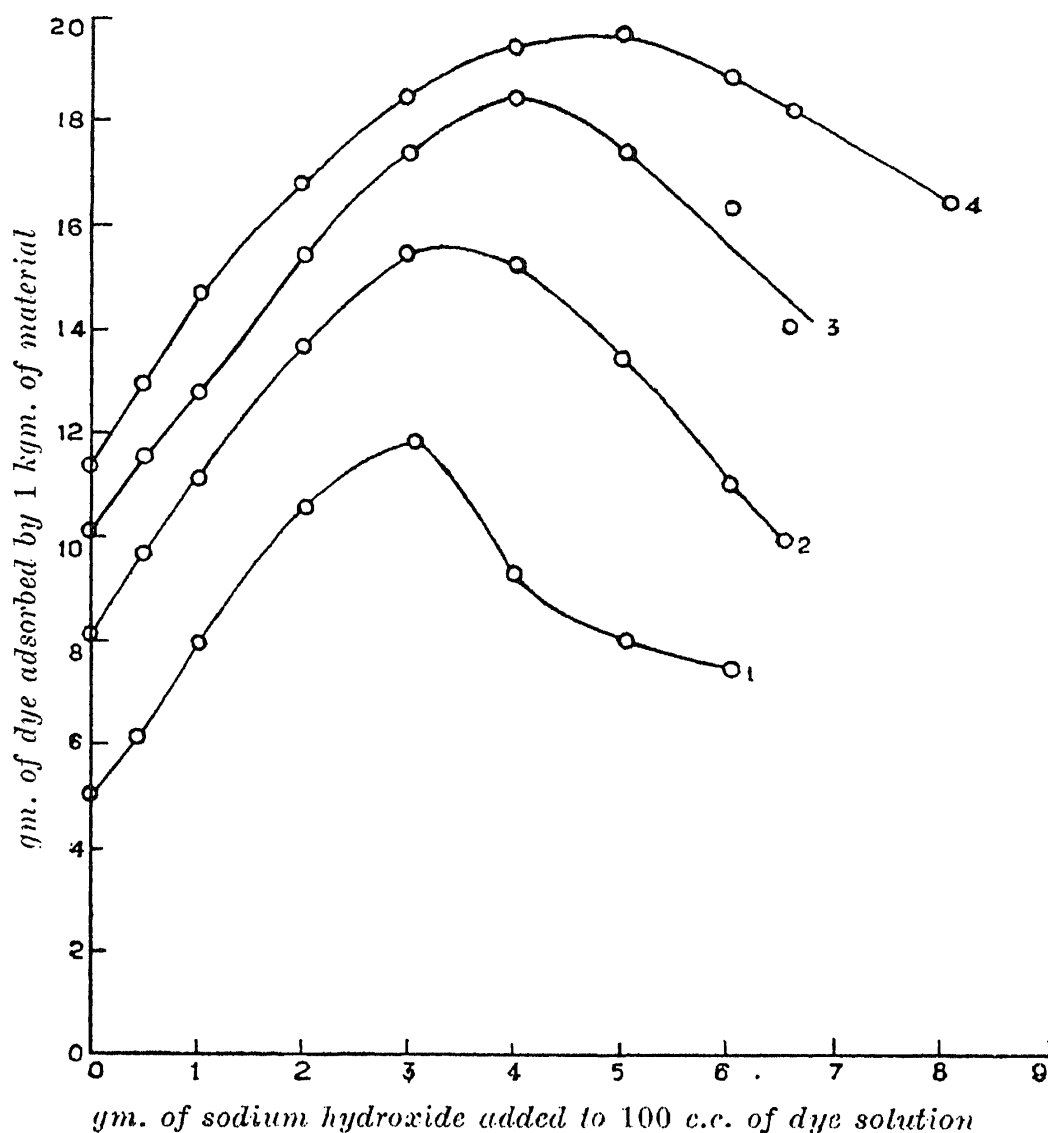


FIG. 2
Naphthol AS

- | | |
|------------------|------------------|
| 1. 0.5% solution | 3. 1.5% solution |
| 2. 1.0% ,, | 4. 2.0% ,, |

It has been observed that the adsorption of the dye decreases with increasing amounts of alcohol in the dye-bath (Fig. 1). Alcohol serves to clear the solution of the dye of its turbidity. This is probably due to its increasing the degree of dispersion of the dye micelle. If the degree of dispersion of the dye micelles increases, the adsorption of the dye by cotton fibre will decrease as the dye particles can come out of the pores of the fibre more easily than when they are large (*cf.* Acharya, Patel and Desai).³ The adsorption of the dye should therefore decrease with the increasing amounts of alcohols in the dye-bath. Further as a result of increase in the degree of dispersion of the dye micelle, the adsorption of sodium hydroxide by the dye particles will increase. If OH' ions are preferentially adsorbed to Na' ions, the charge on the particles will increase and this will prevent

coalescence or the formation of bigger micelles, thus decreasing adsorption of the dye.

The effect of addition of sodium hydroxide is invariably to increase the adsorption of the dye at first (Fig. 2) ; with increasing amounts of the alkali, the adsorption reaches a maximum, and any further addition of the alkali thereafter results in decreasing the adsorption of the dye. Similar results have been obtained with all the Naphthol dyes tried. The final decrease in adsorption however is particularly more marked in the use of highly concentrated dye solutions and of dyes of higher substantivity. When this effect of sodium hydroxide is compared with that of alcohol, it is clear that the two substances affect the dye particles differently. It is recognised that the dyes exist in the form of colloidal electrolytes having negatively charged ionic micelles.⁴ We know that on adding small increasing amounts of the electrolytes having univalent coagulating ions to colloidal solutions the charge on the particles first increases due to preferential adsorption of similarly charged ions and then decreases due to preferential adsorption of the oppositely charged ions.⁵ If the initial increase in charge on the particles means increase in the degree of dispersion of the dye micelles, one would expect adsorption to decrease in the beginning. The adsorption has however not decreased in the beginning in the present case. This would mean that the size of the dye micelles has continuously increased. If the size of the dye particles continuously increases on adding increasing amounts of NaOH, the adsorption of dye by cotton fibre would increase upto a certain stage and decrease thereafter as soon as the size of the dye particles becomes so large that they are bigger than the pores of the fibre ; once the particles become larger than the pores of the fibre, they cannot be adsorbed, and the adsorption will decrease with any further addition of alkali. The particles which are bigger than the pores of the fibre will either be adsorbed on the fibre (these can be washed out or detach as scales on drying) or remain in the dye-bath.

B. Effect of sodium chloride, sodium sulphate and sodium phosphate on the adsorption of Naphthols by cotton fibre.—It will be seen from Table I that with all the dyestuffs tried the adsorption of the dye by cotton in the absence of salts increases with concentration of the dye solution. This is to be expected according to adsorption equation of Freundlich.

As regards the influence of the salts on adsorption it is found that generally on adding small increasing amounts of the same, there is first an increase in adsorption followed by a decrease (Figs. 3, 4 & 5). It is necessary that adsorption experiments are tried with smallest amounts of salts possible in order to get initial increase in adsorption. The final decrease

TABLE I

Dye	Grms. of dye adsorbed by 1 kgm. of cloth (' Malmal ' No. 3948—Finlay) from solutions of dye having concentrations		
	0.5%	1.0%	1.5%
Naphthol AS-G ..	4.394	6.920	8.430
Naphthol AS ..	5.042	8.130	10.130
	0.4%	0.8%	1.2%
Naphthol AS-TR ..	5.233	8.110	..
Naphthol AS-BO ..	6.769	9.663	..
	0.25%	0.50%	0.75%
Naphthol AS-SW ..	7.473	11.58	..

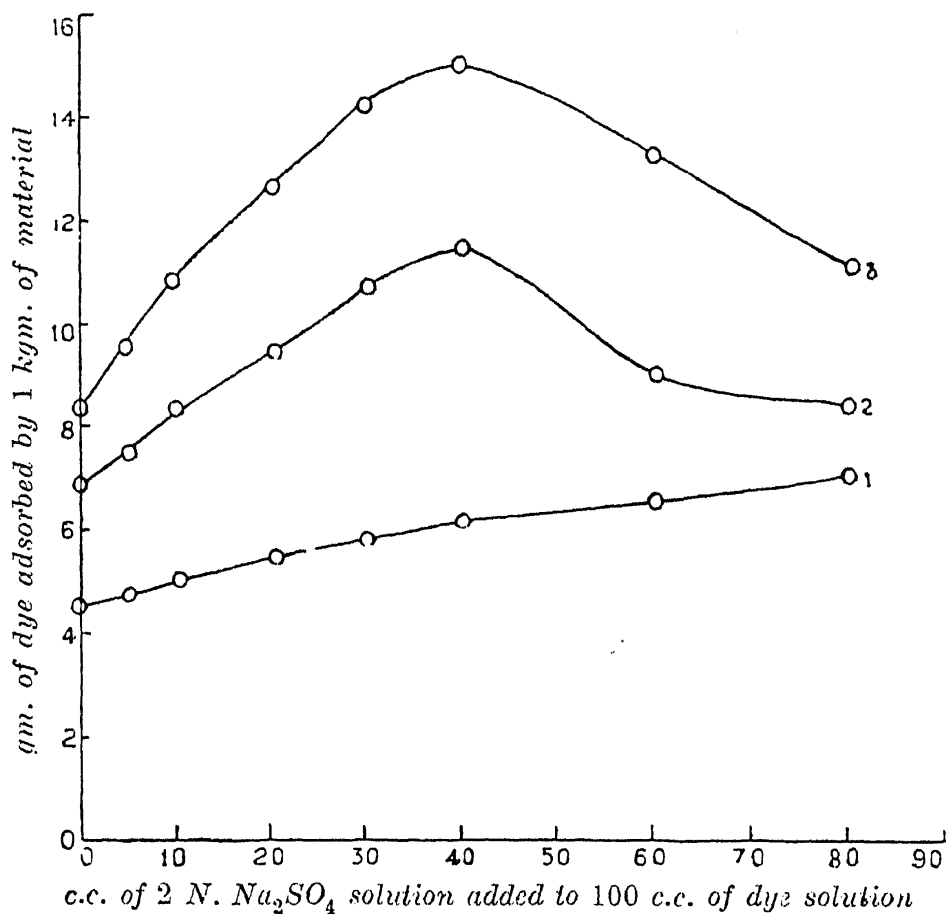


FIG. 3
Naphthol AS-G

- 1. 0.5% solution
- 2. 1.0% ,,
- 3. 1.5% solution

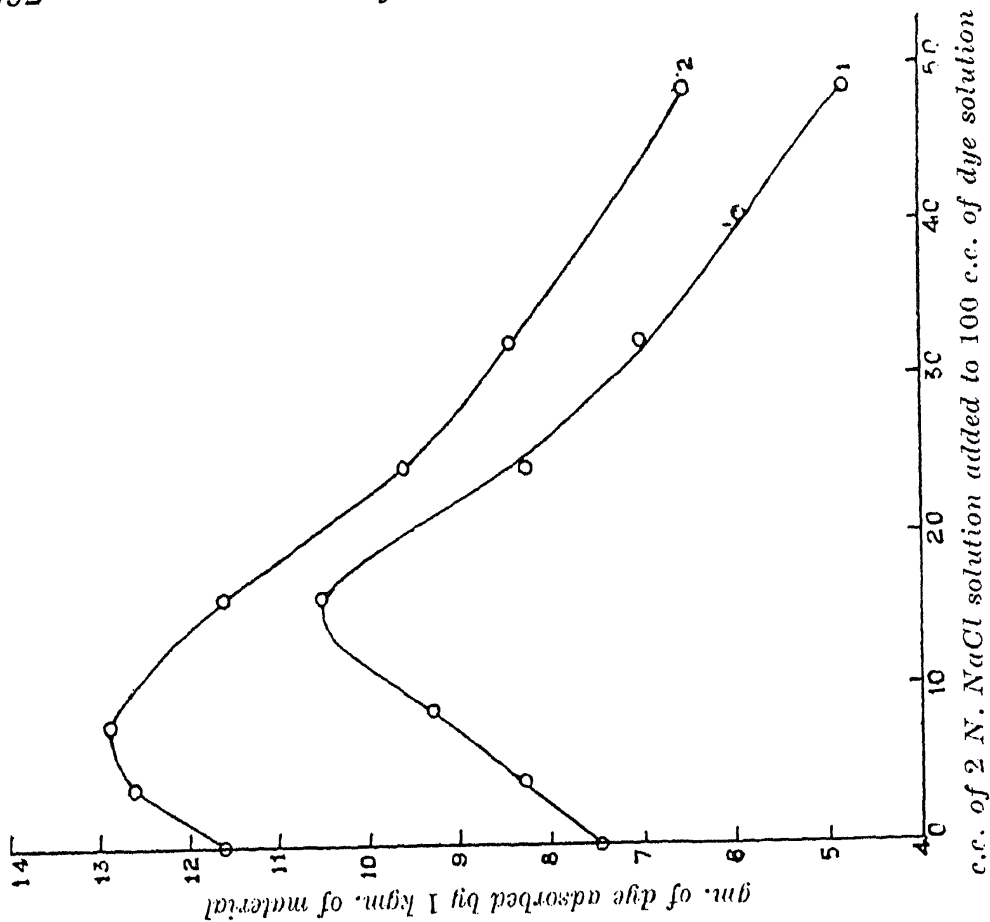


FIG. 5
Naphthol AS-SW
1. 0.25% solution 2. 0.50% solution

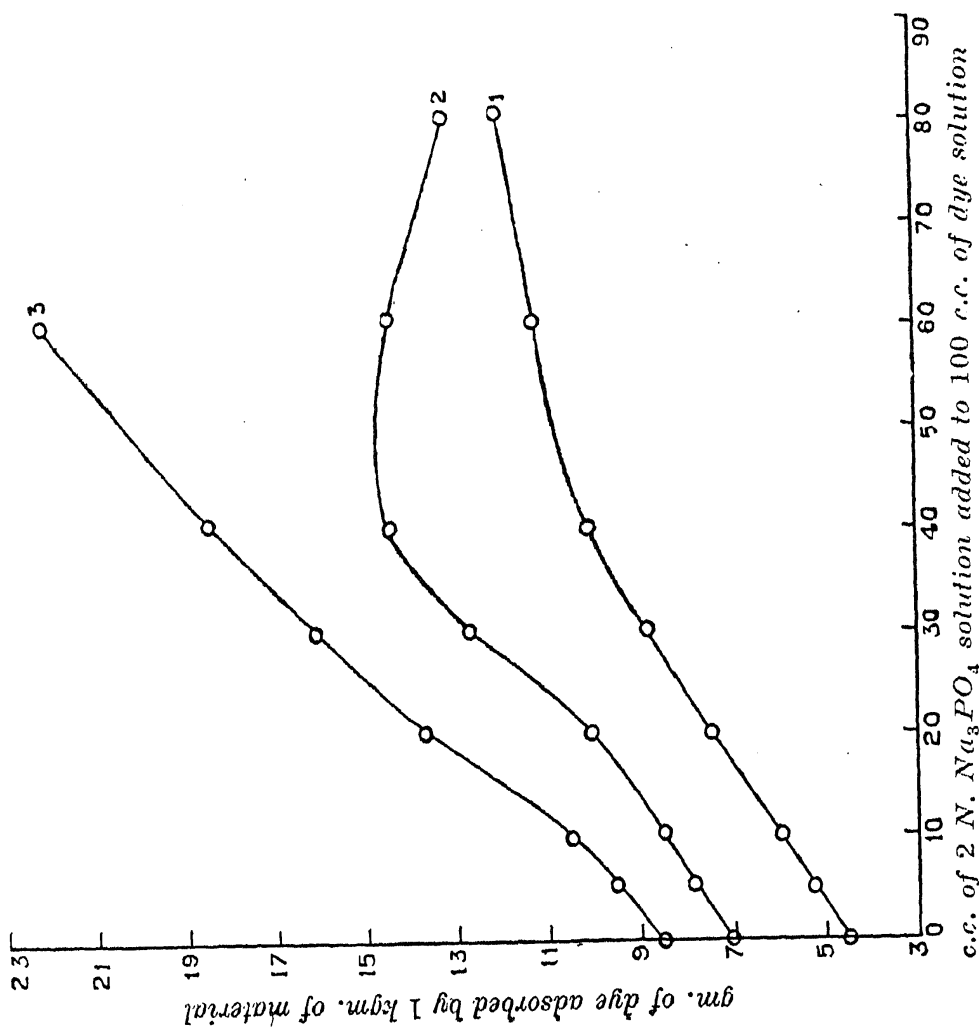


FIG. 4
Naphthol AS-G
1. 0.5% solution 2. 1.0% 3. 1.5% solution

in adsorption may not be noticed in some cases due to impossibility of adding very large amounts of salts on account of their solubility limit.

Many other investigators have also observed in agreement with our results that in the presence of small amounts of electrolytes the adsorption of dye increases. The increase has been explained on the basis that dyes exist in solution in colloidal condition. The present adsorption results can be explained in the same manner as those obtained with sodium hydroxide and discussed in the previous section.

C. Effect of soap, gum tragacanth and agar-agar on the adsorption of Naphthols by cotton fibre.—A typical set of results is given in Figs. 6, 7 and 8.

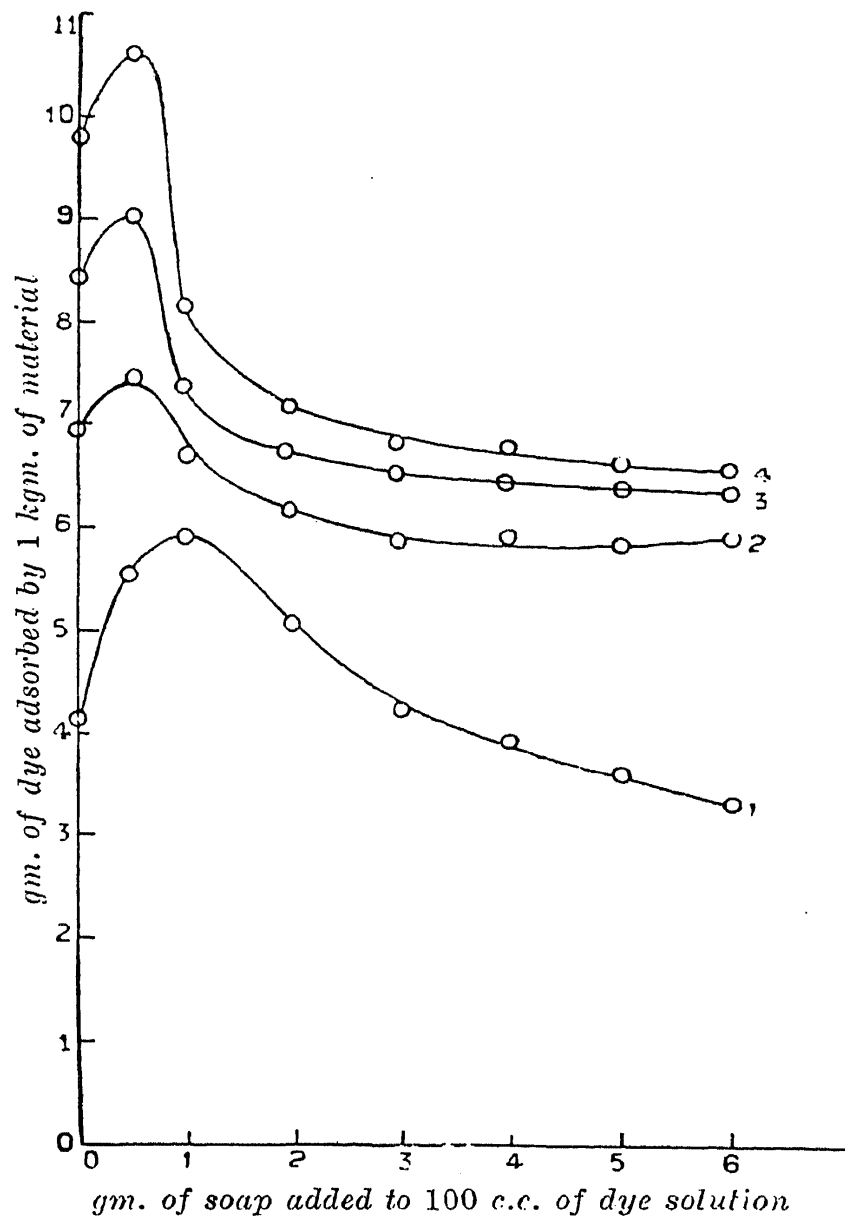


FIG. 6

Naphthol AS-G

- | | |
|------------------|------------------|
| 1. 0.5% solution | 3. 1.5% solution |
| 2. 1.0% ,, | 4. 2.0% ,, |

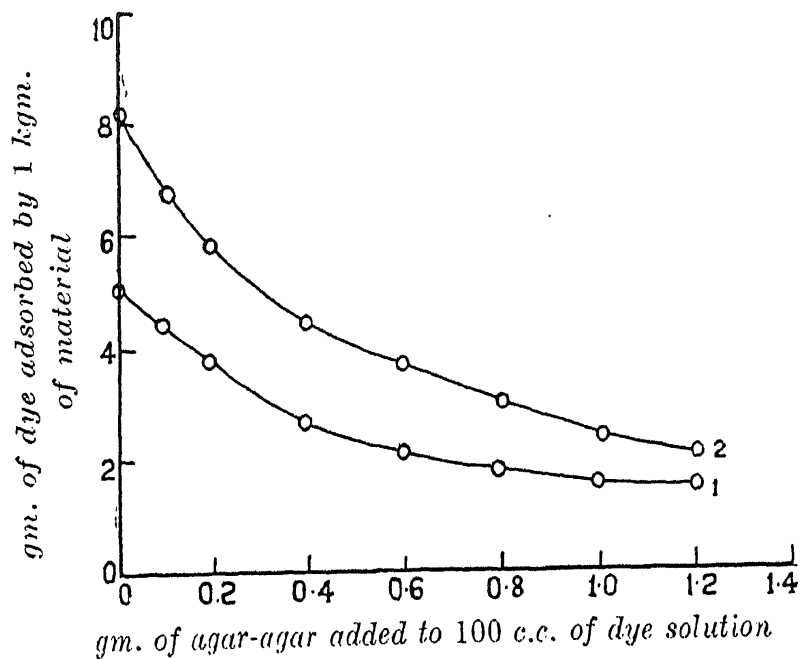


FIG. 7

Naphthol AS

1. 0.5% solution

2. 1.0% solution

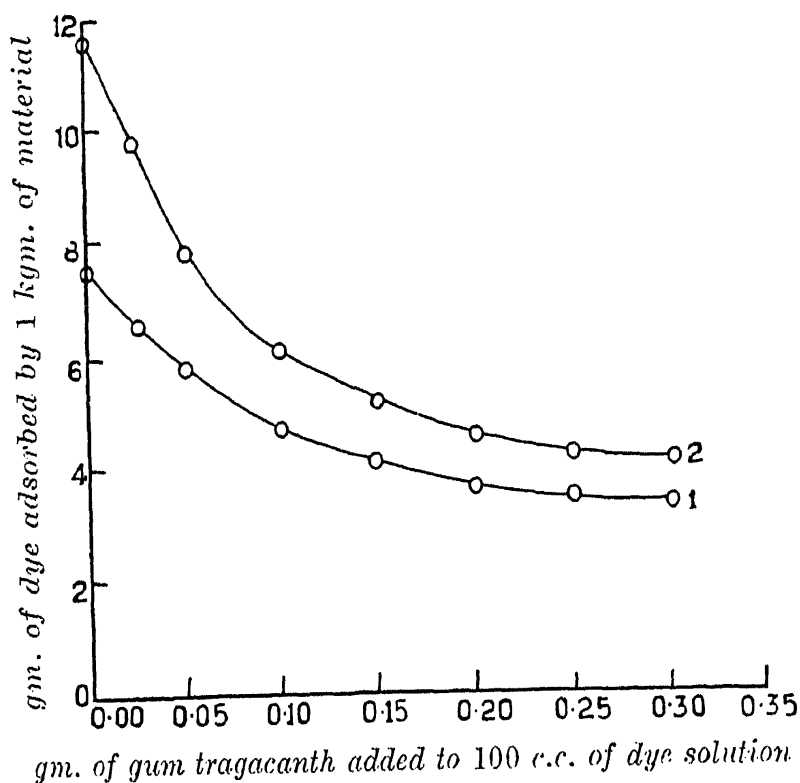


FIG. 8

Naphthol AS-SW

1. 0.25% solution

2. 0.50% solution

It is found that for all the dyestuffs investigated, the adsorption of the dye by cotton fibre in the presence of soap solution first increases, reaches a maximum and then decreases (Fig. 6). These results are similar to those obtained with sodium hydroxide and salts. If we look at the chemistry of

soap solution, we find that it is a sodium salt of some fatty acid. It is known that soap solutions are hydrolysed in dilute solutions giving rise to sodium hydroxide and the fatty acid.⁶ In dilute solutions the concentration of sodium hydroxide will increase upto a certain stage and the increase in adsorption of dye by fibre can be explained in the same manner as in the case of sodium hydroxide in section A. In concentrated soap solutions the fatty acid molecules will aggregate to form -vely charged colloidal particles. If these colloidal aggregates form film round the dye particles, they will prevent coalescence of the latter to form larger particles which may be retained by fibre on squeezing the cloth; the dye particles thus remaining small, the adsorption will be small. With increasing amounts of soap the adsorption will decrease. The final decrease in adsorption is considered to be mostly due to this effect.

In the case of gum tragacanth (Fig. 7) and agar-agar (Fig. 8), it is found that the adsorption continuously decreases on adding increasing amounts of these substances. These substances are protective colloids and they will surround the dye particles in the same manner as the colloidal aggregates in soap solutions. The adsorption of the dye will thus decrease with an increase in their concentration.

It is thus clear that although the presence of soap may upto its certain concentration limit help to clear the dye-bath by increasing adsorption, large quantities of soap and of protective colloids in any amounts will decrease the adsorption of dye instead of increasing it.

D. Effect of temperature on the rate of adsorption of Naphthols by cotton fibre.—It has been observed for all the Naphthol dyes studied in this investigation that the amount of the dye adsorbed increases at first with the increase of time interval for which the adsorption is to take place, reaches a maximum value and finally becomes constant. The time for the attainment of equilibrium, *i.e.*, the time corresponding to the maximum adsorption, decreases as the temperature increases and at the 'boil' the equilibrium is attained very quickly or almost instantaneously (see Fig. 9 for example).

We have noticed that at a particular temperature the time required for the attainment of equilibrium is maximum with Naphthol AS-SW and minimum with Naphthol AS-G. In general the effect of temperature on the rate of adsorption seems to be more marked in the case of dyes of higher substantivity.

It is observed that the equilibrium adsorption increases with the rise of temperature (Fig. 10). The rate of increase, however, decreases with increase

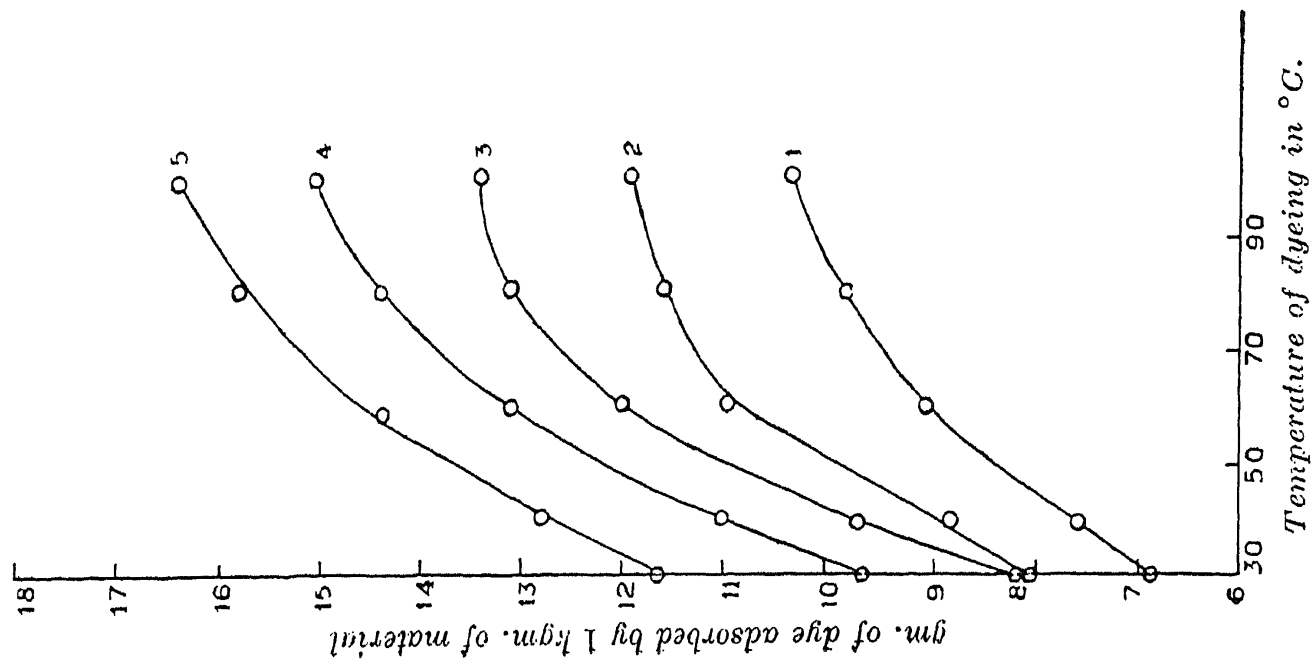


FIG. 10

1. 1.0% Naphthol AS-G solution
 2. 1.0% " AS "
 3. 0.8% " AS-TR "
 4. 0.8% " AS-BO "
 5. 0.5% " AS-SW "

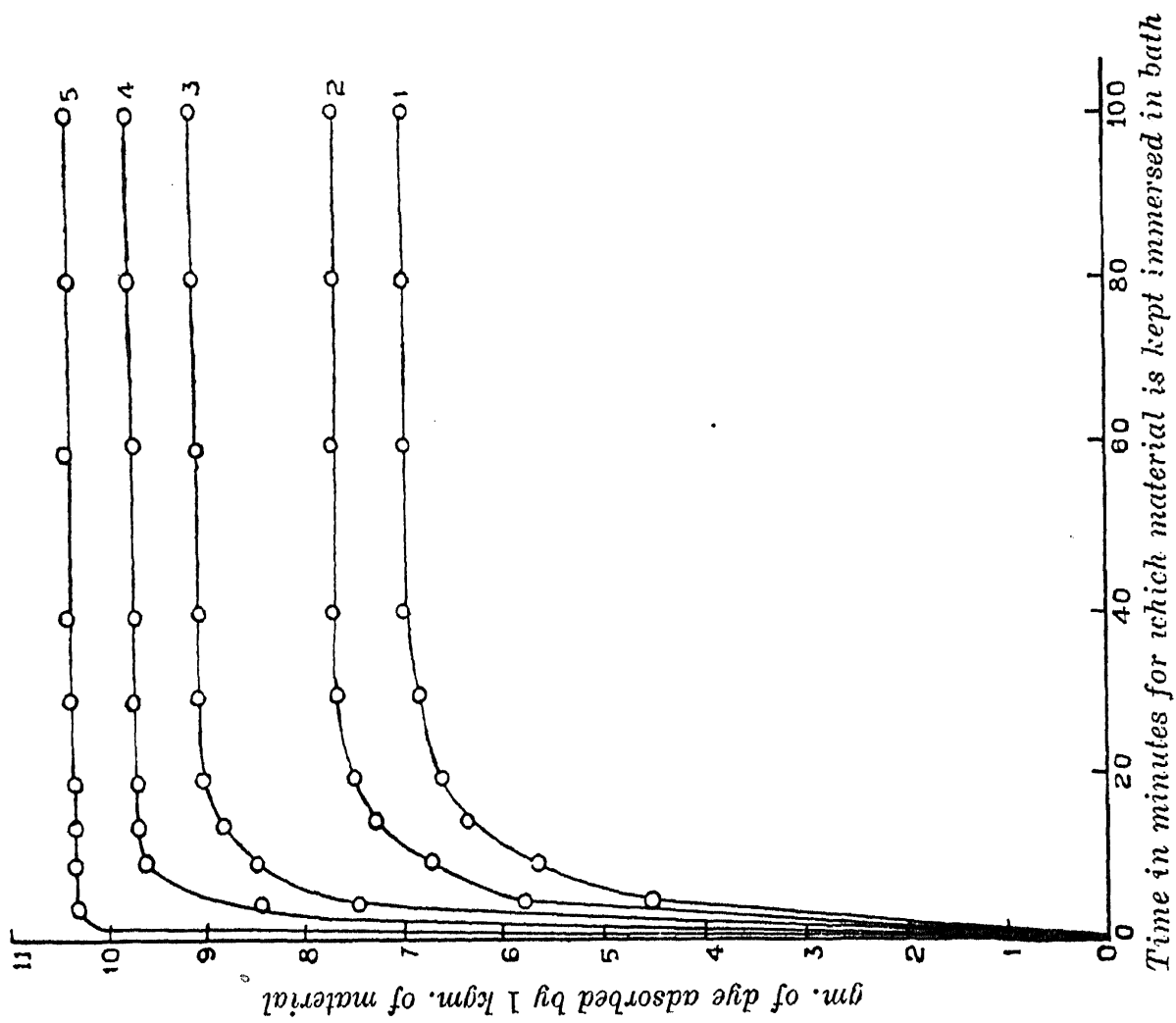


FIG. 9

- 1.0% Naphthol AS-G solution
 1. At 30° C.
 2. " 40° C.
 3. " " boil
 4. At 80° C.
 5. " " boil

of temperature. The effect of temperature is thus more marked with all the Naphthol studied at lower than at higher temperatures.

The attainment of equilibrium very quickly or instantaneously at the 'boil' is probably connected with the marked decrease in colloidalness of the dye micelles, *i.e.*, increase in the degree of dispersion, and the increase in the size of the pores of the fibre at that temperature.⁷ The increase in the number of collisions between the different micelles and the fibre with increasing temperature would also slightly decrease the time of the attainment of equilibrium at the 'boil'. The increase in the adsorption with the rise of temperature might probably be due to one or more of the following reasons:—

(a) If the size of the pores of the fibre through which the dye particles are adsorbed increases as a result of rise of temperature, the adsorption of the dye will increase due to relatively larger dye particles being adsorbed. As soon as the temperature is brought down, the size of the pores will again decrease and the large dye particles already adsorbed will not be squeezed out due to their then being larger than the pore size.

(b) As a result of the rise of temperature it is likely that the dye particles may be broken up in smaller units. This will mean that the dye particles which were large enough not to be adsorbed at low temperatures will be adsorbed at high temperatures and the adsorption will increase.

(c) The protective power of the substances which are present in the dye-bath may be more marked at higher than at lower temperatures.⁸ This will mean that the dye particles will not become so large at high temperatures due to aggregation as they would do at low temperatures, and consequently the adsorption will increase as in (b).

The processes (a) and (b) referred to above, *i.e.*, the increase in the size of the pores of the fibre and the decrease in the size of the particles with increase in temperature, cannot go on indefinitely, and therefore effect for a particular increase of temperature should be more marked at lower than at higher temperatures.

Summary and Conclusions

Adsorption of some dyestuffs of the Naphthol AS series by cotton fibre has been studied in the presence of alcohol, sodium hydroxide, sodium chloride, sodium sulphate, sodium phosphate, soap, gum tragacanth and agar-agar and at different temperatures to understand the mechanism of the process of dyeing.

It is observed that adsorption of the dyestuffs decreases with increasing amounts of alcohol, gum tragacanth and agar-agar, while it first increases,

reaches a maximum and then decreases on adding increasing amounts of sodium hydroxide, sodium chloride, sodium sulphate, sodium phosphate and soap solutions. Regarding the effect of temperature on adsorption, it is found that (1) the rate of adsorption is greater at higher than at lower temperatures, (2) the equilibrium adsorption increases with the rise of temperature, and (3) the amount of increase of adsorption for a particular range of temperature is greater at lower than at higher temperatures.

The results obtained become easily intelligible if it is assumed that the dye particles exist in colloidal condition and the process of dyeing is interpreted from that point of view.

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