VARIATION OF MICELLAR SIZE OF BENZOPURPURINE 4B DURING THE DYEING OF COTTON

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SUMMARY

An investigation of the variation of micellar size in aqueous solutions of Benzopurpurine 4B for different salt concentrations and at 26° and 75° C. during the dyeing of cotton, has been carried out by a measurement of light scattering. In the presence of electrolytes the micelles remain unaltered in size during dyeing. But in the pure dye solutions and also in the presence of a detergent, the dyeing is non-uniform and there is a change in micellar size. These and the other experimental facts have been discussed in the light of the kinetics of aggregation and dyeing mechanism.

1. INTRODUCTION

Extensive investigations on diverse physical properties such as diffusion, osmotic pressure, conductivity, etc., of aqueous solutions of many dyes lend support in classifying them with the soaps as 'colloidal electrolytes' (Hartley, 1948). As such, all these methods of study of dyes suffer from severe limitations due to the very nature of the solutions of the dyes. Consequently, it would be advantageous to carry out light scattering measurements which provide a measure of the molecular weight in a static system (P. Debye. 1944, 1947). Measurements could be made both in the absence and presence of salt and since readings are instantaneous, the kinetics of aggregation could be followed. Such studies have been made by Sivarajan (1952), by Alexander and Stacey (1952) on aqueous solutions of four dyes and more recently by Banderet and Meyer (1953). Since no study has so far been made on the change in micelle size during the actual dyeing process utilising light scattering, it was felt desirable to carry out such measurements on a number of substantive dyestuffs.

Benzopurpurine 4B (Colour Index 448) which has been very widely investigated by other methods (Robinson, Valko, 1935; Lenher and Smith, 1935) and also by light scattering (Sivarajan, *loc. cit.*; Alexander and Stacey, *loc. cit.*) was chosen first since it is known to form stable micelles after a certain period and measurements were carried out on the pure dye solution and dye solutions containing sodium chloride at two different temperatures, *viz.*, 26° C. and 75° C. as well as on dye solutions in the presence of a detergent such as sodium dodecyl sulphate. The results are presented below.

2. EXPERIMENTAL DETAILS AND RESULTS

All solutions were made in dust-free double distilled water using a Kahlbaum pure sample of Benzopurpurine 4B and stored in resistance glass flasks. All the stock solutions were carefully filtered through sintered glass funnels. These filtered solutions of different dye concentrations and added sodium chloride were stored for 24–36 hours before use, since the turbidity is initially time dependent and equilibrium sols containing stable micelles and of constant turbidity are obtained only after this time interval.

The method of dyeing is as follows.—Pure surgical cotton which had been thoroughly washed and dried was used as the dyeing material. Weighed pads of cotton were closely wound round a motor-driven resistant glass stirrer dipped in the dye bath, so that the dye diffused radially into the cotton. The ratio of cotton weight to dye-bath volume was kept constant at 1 : 100. The volume of dye-bath solution used was large so that the removal of small portions of it at different time intervals did not result in any appreciable change in the experimental conditions. For measurements at the higher temperature, *i.e.*, 75° C. the dye-bath vessel was kept immersed in an electrically heated water-bath whose temperature could be maintained constant at 75 ± 1° C. Suitable precautions were taken to avoid evaporation losses. Both the concentration and the turbidity were measured at different time intervals during the dyeing process. The concentration of the solutions was determined spectrophotometrically using a Beckman spectrophotometer. The turbidities were measured as described below.

In the Debye method of determining the molecular weight of substances forming colloidal solutions, the relation between the turbidity and molecular weight is given by (P. Debye, *loc. cit.*)

$$\frac{\mathrm{H}c}{\tau} = \frac{1}{\mathrm{M}} + \frac{2\mathrm{B}c}{\mathrm{RT}} \tag{1}$$

where H is a constant, τ the turbidity, c the concentration in grams per c.c. and B the interaction constant. In the above equation

$$\mathrm{H} = \frac{32\pi^3}{3\lambda^4\mathrm{N}}\left(\frac{n-n_0}{c}\right)^2 n_0^2 \tag{2}$$

where N is the Avogadro's number, λ the wavelength, n the refractive index of the solution and n_0 that of the solvent. So a determination of the molecular weight using these equations involves a measurement of the intensity of scattering in a transverse direction for different concentrations and a knowledge of the refractive increment ratio $(n - n_0)/c$. It may be mentioned also that this method presupposes that the particles are small compared to wavelength of light ($< \lambda/20$), the solution is transparent to the wavelength λ at which measurements are made and that the refractive index increment is a linear function of the concentration. Under these conditions, a plot of Hc/τ *versus* c is linear and on extrapolation to zero concentration gives an intercept on the co-ordinate axis equal to the reciprocal of the molecular weight M.

In the present investigation the turbidity measurements were made at a mean wavelength of λ 6500, the absorption of the dye solution being extremely small in this region. The light from a 500 C.P. pointolite lamp was condensed on a slit 3 mm. × 6 mm. and the light emerging from this aperture was focussed by means of lens of long focal-length on to the centre of the cell containing the solution. By means of a suitable red filter interposed in its path a fairly intense beam of narrow band width having a mean wavelength of 6500 A°U was isolated. The rest of the arrangement used by the author for the measurement of turbidities has been fully described elsewhere (Sivarajan, 1953). Suitable corrections for refraction and volume effects were made using the formulæ of Carr and Zimm (1950) and for absorption by the method due to Putzeys and Dory (1940).

For measurements at 75° C. the rectangular cell was replaced by a uniform thin-walled cylindrical cell which was surrounded by an electrically heated coil. Suitable precautions were taken to eliminate all stray light. No refraction correction was made.

The value of the refractive index increment for Benzopurpurine 4B was taken from the data of Alexander and Stacey (*loc. cit.*).

Before studying the changes that occur during the dyeing process, a measurement of the turbidities at different concentrations of salt and dye was made and the results are given in Fig. 1 and Table I. The molecular weights given in Table I have been evaluated by determining the intercept on the co-ordinate axis corresponding to zero concentration by an extrapolation of the straight line passing through the experimental points.

As described earlier in order to study the variation of micellar size during the dyeing process, the turbidity and concentration of the solutions extracted from the bath at different time intervals were measured and the values of Hc/τ were plotted against c for different salt concentrations and at 26° C.

TABLE 1. *Temperature* 26° C.

Dye Solution	NaCl Concentration in gm./litre	Molecular Weight
1	4	10^6
2	3·75	154,000
3	3·33	121,000
4	3	51,300
5	2·5	21,000
6	2·0 + ·004% detergent	18,500

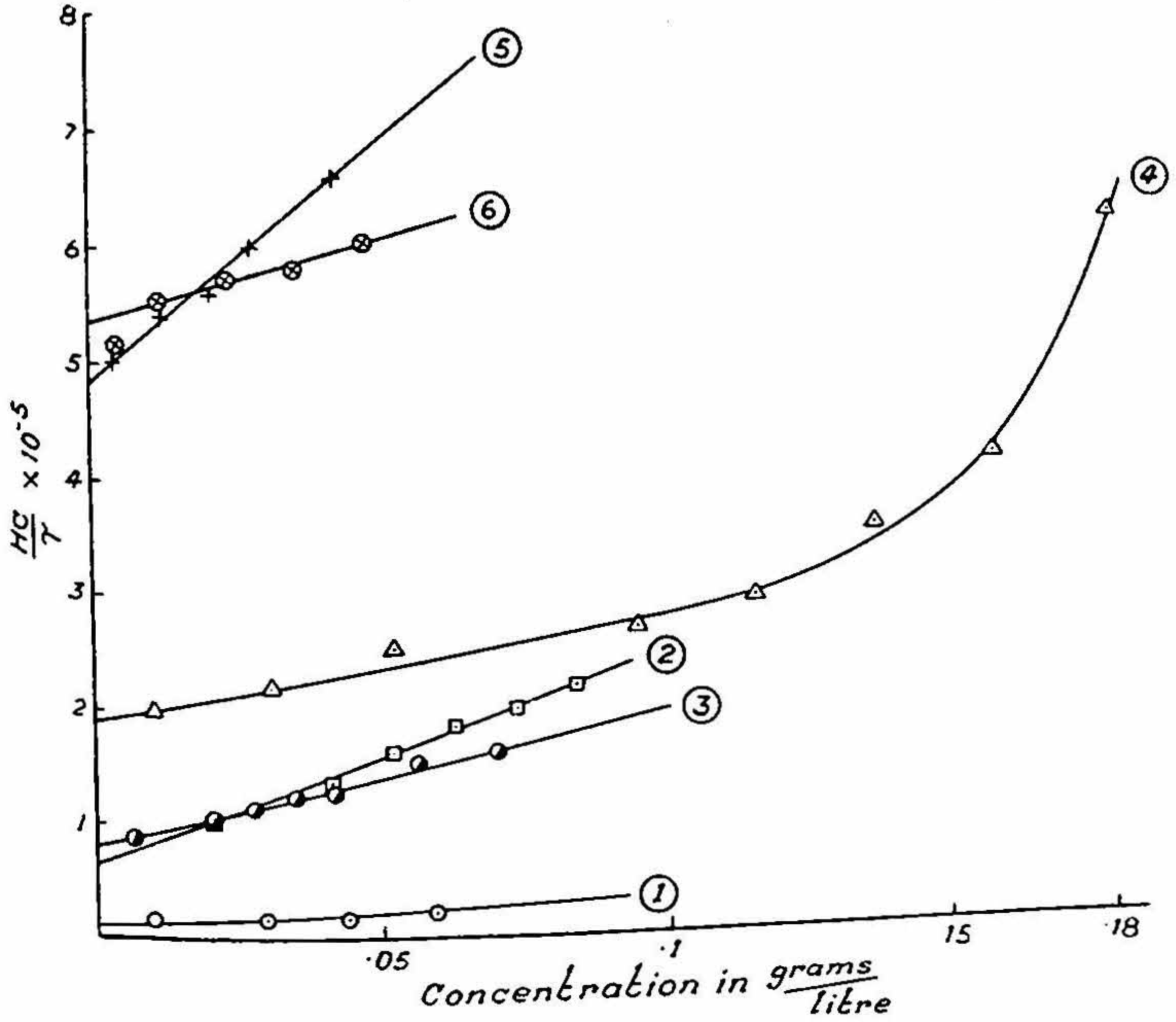

FIG. 1. Variation of $\frac{Hc}{T}$ with the Concentration.

TABLE II

Dye Solution	NaCl Concentration in gm./litre	Initial Molecular Weight	Final Molecular Weight
1	4	833,000	833,000
2	3	540,000	540,000
3	2·5	80,000	80,000
4	2 +·013% detergent	22,000	11,000
5	0	50,000	15,000

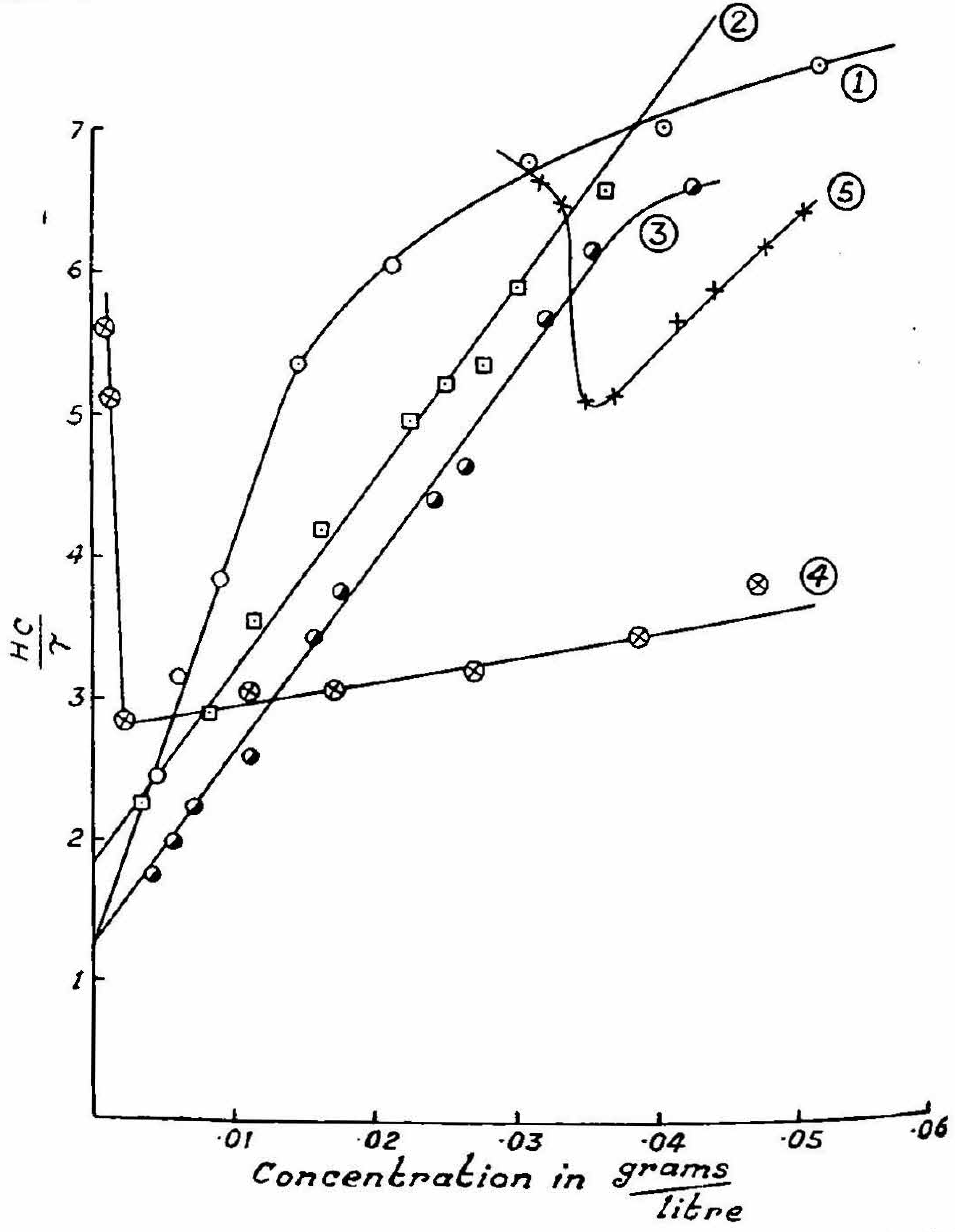

FIG. 2. Variation of $\frac{Hc}{\tau}$ with dye-bath Concentration at 26° C. Values on vertical axis are $\frac{Hc}{\tau} \times 10^{-6}$ for curves 1 and 2. For the rest they are $\frac{Hc}{\tau} \times 10^{-5}$.

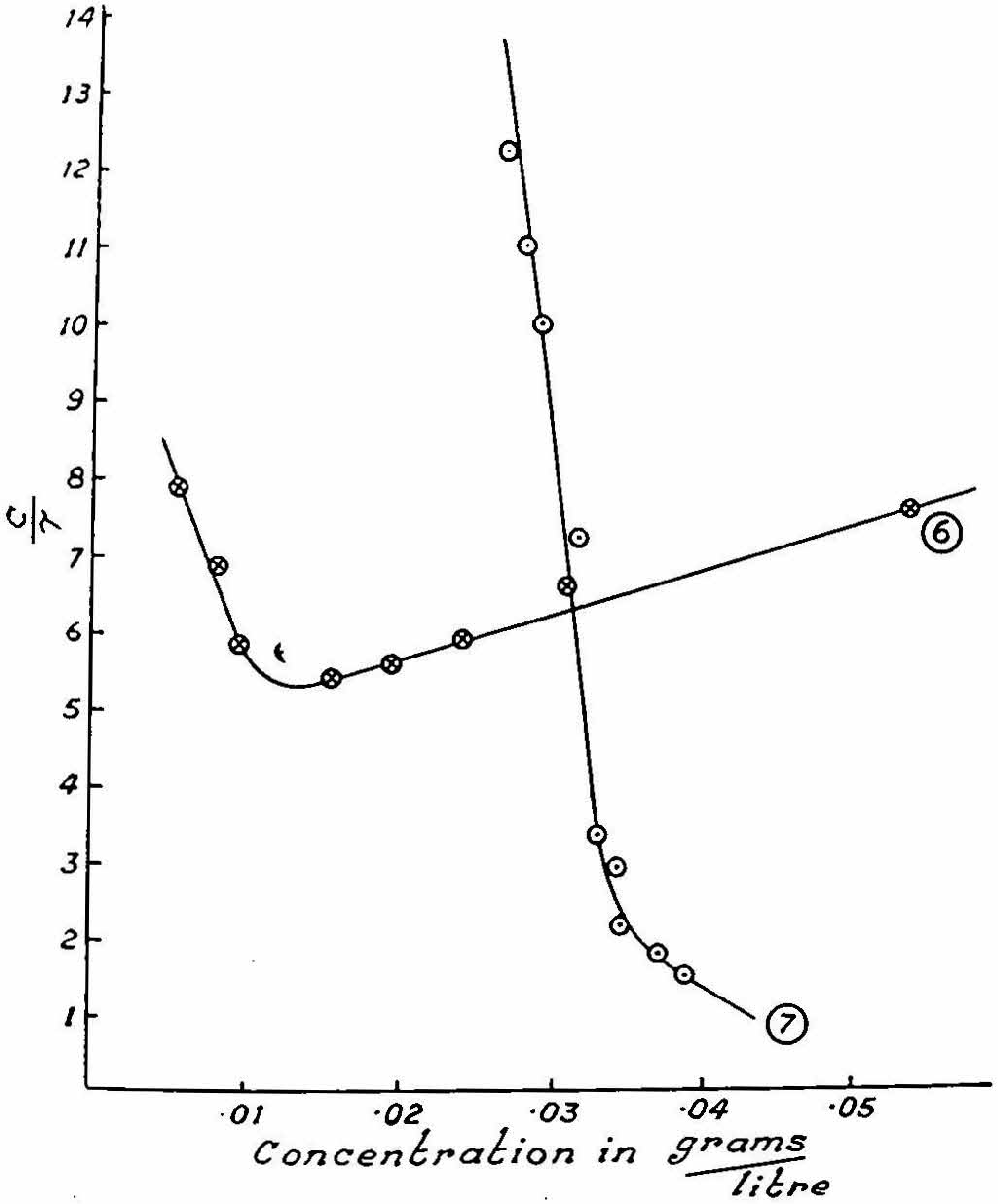

FIG. 3. Variation of $\frac{c}{\tau}$ with Concentration of dye-bath, at 75° C. The vertical scale gives the values of $\frac{c}{\tau} \times 10^{-1}$ for curve 7 and $\frac{c}{\tau} \times 5 \times 10^{-1}$ for curve 6.

The effect of the detergent was studied for only one particular salt concentration. The results are given in Table II and Fig. 2. In Table II the final molecular weights have been calculated from the experimentally observed values of Hc/τ for the lowest concentration. It was not possible to adopt a similar procedure for examining the results at the higher temperature since an accurate value of $(n - n_0)/c$ is not known at that temperature. Consequently in Fig. 3 only c/τ values have been plotted against c. In Fig. 5

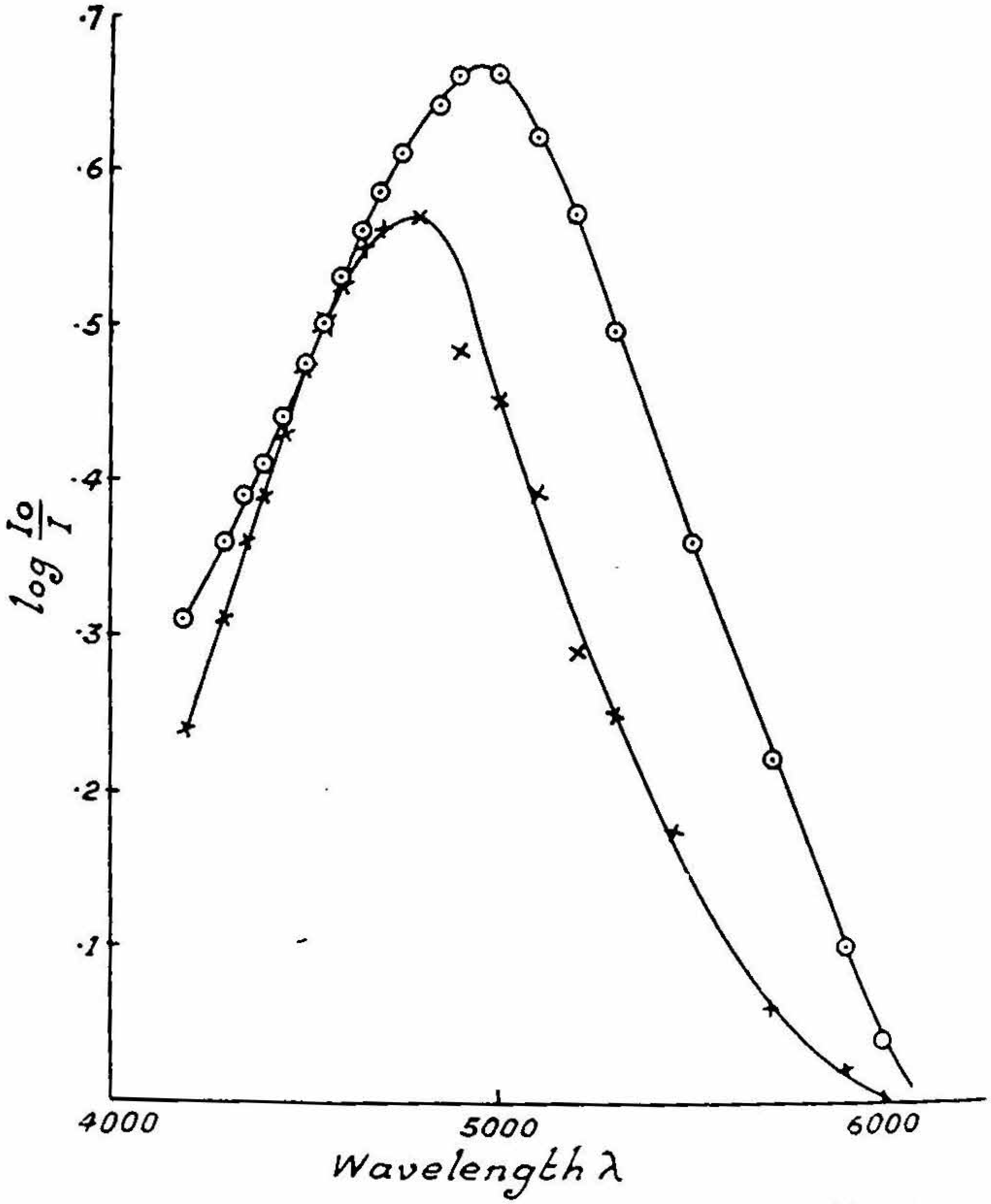

FIG. 4. Absorption spectra of Benzopurpurine 4B solution with and without detergent.

the variation of turbidity with time has been shown. Finally the absorption spectra of two solutions, one containing the dye and sodium chloride and the other containing the dye, sodium chloride and sodium dodecyl sulphate were also measured with a Beckman spectrophotometer in order to observe the effect of the change in micelle size on the spectrum.

3. DISCUSSION

From Fig. 1 it is easily seen that in all cases except 4 Hc/τ is linear with concentration though the intercepts and hence the molecular weights are different for the different salt concentrations. The slope of the curves, which

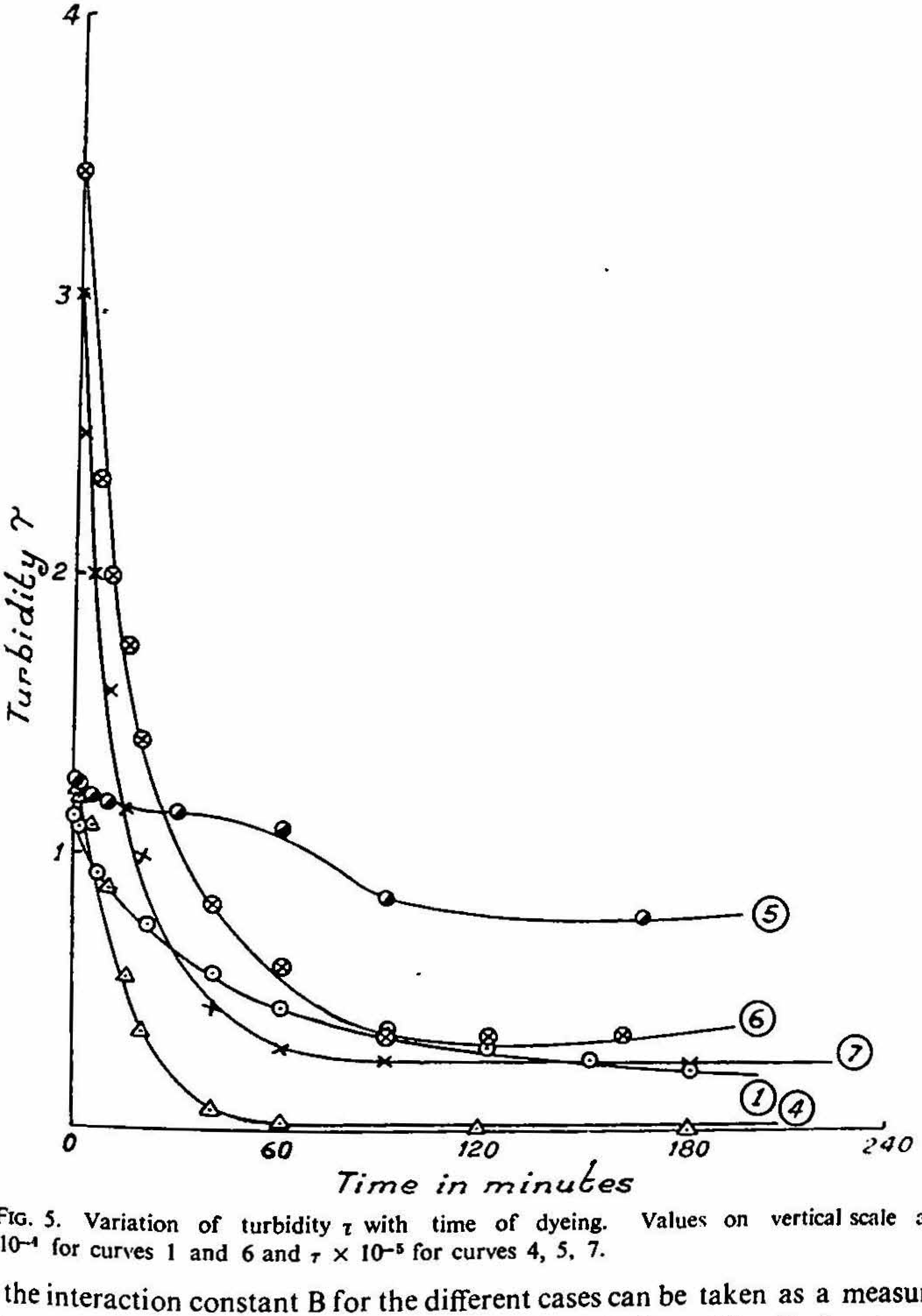

FIG. 5. Variation of turbidity τ with time of dyeing. Values on vertical scale are $\tau \times 10^{-4}$ for curves 1 and 6 and $\tau \times 10^{-5}$ for curves 4, 5, 7.

give the interaction constant B for the different cases can be taken as a measure of the repulsive forces that exist between the micelles. Usually large and positive values of B indicate a good solvent, *i.e.*, one in which there is greater solute-solvent interaction than solute-solute interaction. Small and negative values of B show the contrary behaviour and are characteristic of bad solvents. In case 4 alone there is a distinct deviation from linearity at higher concentrations and one may find an explanation for this by considering the charge effects on light scattering in association colloids (Mysels, 1954). When the ratio of salt concentration to dye concentration is not large, *i.e.*, the salt cannot be viewed as a 'swamping electrolyte' the ionic charge present in the solution producing a deviation from linearity.

In the presence of ·004% of sodium dodecyl sulphate the intensity of scattering is reduced and for the same dye and salt concentration the ratio of intensities with and without the detergent is 1 : 1·3. The micelles are not so large in the presence of the detergent (see Table I). But on examining the absorption curves given in Fig. 4 it is seen that the detergent reduces the maximum extinction coefficient to a small extent and the maximum also shifts towards the violet. This behaviour is quite contrary to what happens when the aggregation of Benzopurpurine 4B decreases since the work of Martin and Standing (1949) shows that with decreasing aggregation the maximum extinction coefficient increases and the peak shifts towards the red. It is possible that in the case of the detergent added, a complex formation between the dye and the detergent occurs.

From the curves showing the variation of turbidity with time during the dyeing process (Fig. 5) it can be seen that the change is more rapid in the presence of electrolytes and at higher temperatures, *i.e.*, the rate of dyeing is more. Also in the absence of electrolyte the dyeing is not uniform. The curve 1 which shows the variation at 26° C. in the presence of 4 gm./litre sodium chloride has a more gradual slope than 4, 6 or 7. This is because the micelle size in these cases is much smaller than in 1 and also the dyeing corresponding to 7 and 6 occur at 75° C. It is observed that the dye-bath exhaustion is more rapid in the presence of detergent; but the dye appears to be loosely bound to the cotton and the colour of the dyeing is light pink and not deep orange red as is the case in the absence of the detergent.

Our present view of the dyeing process is that initially the dye is adsorbed on the cotton surface and then diffuses into the bulk of the cotton to give a uniform dyeing. The dyeing units are the single dye molecules, the micelles supplying these, however, without a change in size, only the number of micelles decreasing with the time of dyeing. The extent of this initial adsorption as well as the eventual uniform rate of dyeing are factors dependent on temperature, dye concentration, and concentration of added electrolyte. The existence of a potential at the cotton-water interface, the charge on the micelle, the presence of carboxyl groups in the cotton, etc., are also factors which determine the rate, fastness, and the other dyeing properties. Now experimentally we find that in the presence of the electrolyte the Hc/τ *versus* c

curves at 26° C. (1, 2, 3 of Fig. 2) are linear. The deviation at higher concentrations in 1 is, as stated earlier probably due to initial changes in micelle size or to some charge effects. The curve 4 for the pure aged dye solution at 26° C. is linear up to a concentration ·0345 gm./litre and then there is a sharp increase in the Hc/τ value. In the presence of the detergent at 26° C. the behaviour is somewhat similar but the slope of the linear portion is much less than for the pure dye curve.

At the higher temperature, with pure dye (Fig. 3, 7) the size of the micelle decreases very rapidly with time of dyeing even from the beginning. In the presence of electrolyte however up to a concentration of ·015 gm./litre the micelle size remains the same and beyond this it decreases very rapidly. From these it is clear that the size of the micelle in dye solutions containing electrolyte does not alter much during the dyeing process and this view is in keeping with the idea of an equilibrium existing between the dye micelles and single dye molecules which are the dyeing units. One finds that the initial points on these curves are not so close to the linear plot as those at an advanced time of dyeing. This is because the changes in concentration are more rapid initially and also because the effect of the zeta potential, etc., is greater at this early stage of unsaturation. These two factors can cause initial changes in the micelle size but once uniform dyeing sets in no further change in size occurs. In the case of the pure dye and in the presence of detergent, where the dyeing is non-uniform and not so fast beyond a certain concentration the micelle size decreases rapidly. This is evident on a perusal of Table II where the molecular weights obtained using the Hc/τ values corresponding to the final concentration are also given.

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