

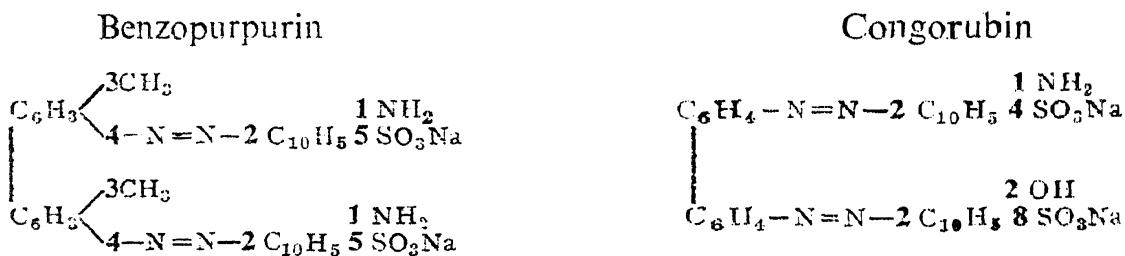
SURFACE CHEMISTRY OF CONGORUBIN SOLUTIONS*

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WHILE studying the effect of the electrical field on Tyndall scattering in aqueous solutions of dyes, it was noticed that the electric field affected Tyndall scattering in the case of benzopurpurin-6 B but not with congorubin. The difference in behaviour is rather surprising, as the two dyes appear to be similar in structure, each molecule having four hydrophilic groups as shown below:—



Evidently there seems to be some difference in spacial structure between the two dyes. To throw light on the phenomenon, the surface properties of congorubin solutions were studied. Some aspects of the surface behaviour of benzopurpurin have been studied by Doss.¹

EXPERIMENTAL

The congorubin used in this investigation was a Kahlbaum product and was purified by the sodium acetate method described by Robinson.²

The surface pressures were measured by the modified film technique described by Doss.¹ Measurements were made at a pressure of 0.9 dyne per cm. as the film would collapse at higher pressures.

For the study of the rate of accumulation, various concentrations (0.1% to 0.01%) of congorubin were employed. The effect of pH on the rate of accumulation was studied using 0.0125% solution of the dye. The pH of this solution was lowered by the addition of dilute acetic acid. The influence of foreign substances such as saccharose, amyl alcohol, Nekal Bx, sodium

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stearate and valeric acid on accumulation was also studied. The results are given in Table I. A glass electrode was employed to measure the pH of solutions.

TABLE I

Sl. No.	% Weight of congo- rubin in solution	pH	Foreign substance	Fraction of the surface occupied in				
				1 min.	2 min.	4 min.	8 min.	16 min.
1	0.10	6.8	..	0.101	0.122	0.158	0.216	0.320
2	0.05	0.061	0.079	0.100	0.146	0.186
3	0.025	0.043	0.057	0.079	0.102	0.145
4	0.0125	0.031	0.043	0.055	0.082	0.108
5	0.0125	4.7	Acetic acid to adjust pH	0.070	0.086	0.100	0.140	0.180
6	0.05	6.8	3% saccharose	0.037	0.043	0.059	0.091	0.128
7	0.10	..	0.17% amyl alcohol	0.070	0.102	0.141	0.201	0.310
8	0.10	..	0.002% Nekal Bx	0.572	0.703	0.902
9	Nil	..	0.002% Nekal Bx	0.137	0.154	0.174

Of the several methods available for the study of surface tension, only a few can be employed for investigating the variation of surface tension with time. As pointed out by Doss,³ the dynamic methods are unsuitable for this purpose. Venkatachala⁴ has used the ring method for the study of Nekal Bx solutions. When this method is employed for congorubin solutions, the surface tension measured corresponds only to that of water. Evidently this technique is inapplicable to the study of congorubin solutions, wherein condensed films are formed and the attainment of equilibrium is therefore exceedingly slow, while with Nekal Bx the film produced is of the gaseous type and the rate of accumulation is very high. The trough method was found to be suitable for the study of congorubin solutions. The strength of the rubin solution in this case was 0.2%. The results are represented in Graphs 1 and 2.

The area of cross-section of congorubin was determined in the following way. A paraffined barrier was kept on the trough, almost touching the float. For forming the fresh surface, the barrier was moved away from the float. The fresh surface thus formed between the barrier and the float was allowed to age for about two minutes, during which period, the rate of accumulation of the dye was relatively high. Then, the dye that had collected on the surface was enclosed between the barrier and the float by moving the barrier towards the float. With another barrier, a fresh surface was allowed to form, by repeating the above operation starting from the first barrier, instead of the float. This surface also was allowed to age for 2 minutes, and the accumulated dye pushed towards the float, after removing

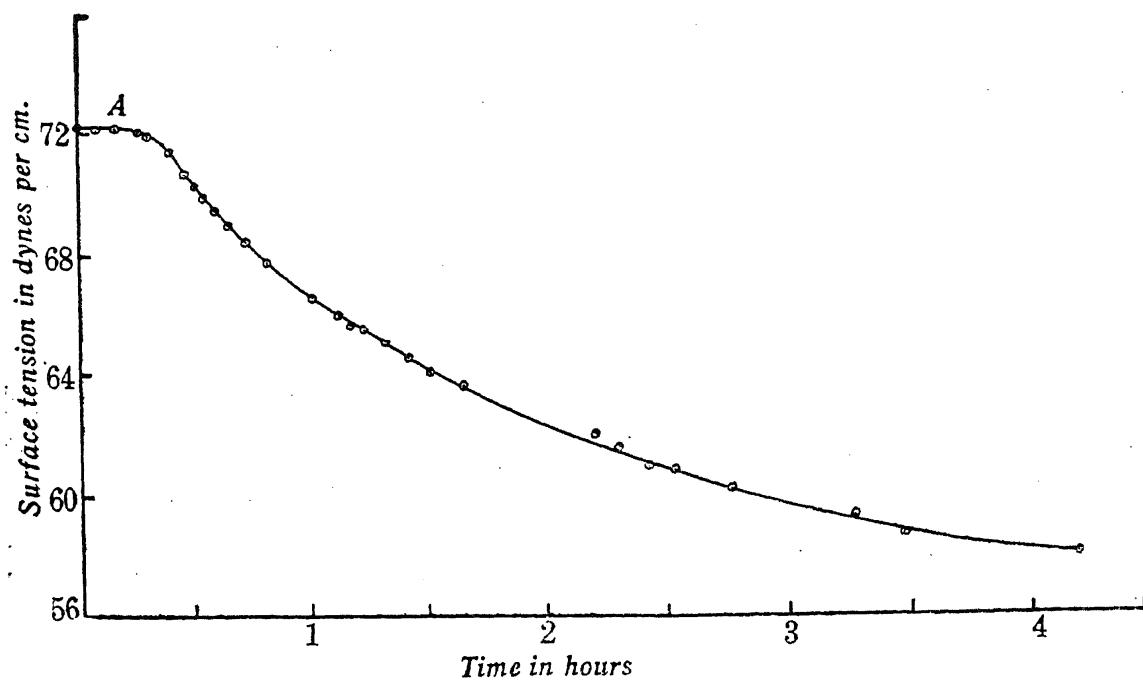


FIG. 1. Variation of surface tension with time of congorubin solution

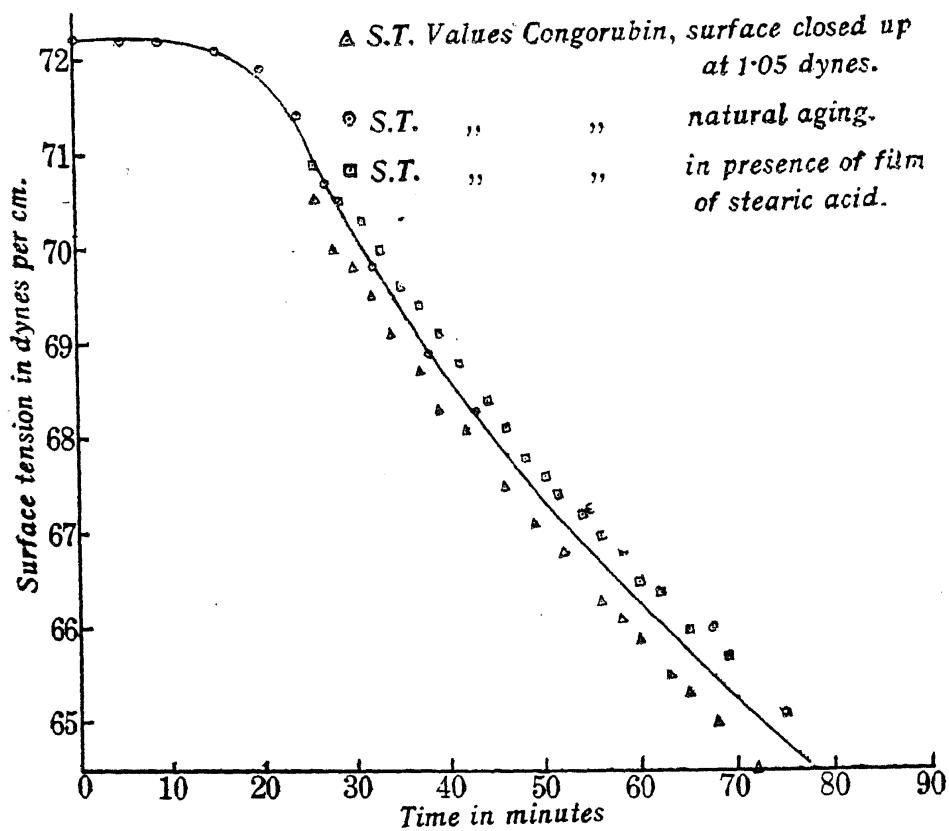


FIG. 2

the first barrier. This technique was repeated several times, so that about three-fourths of the surface of the trough was covered with the dye. In this way, the total time taken to form the film was reduced to about 20 minutes, while accumulation would normally have required several hours. The congorubin film trapped between the float and the barrier was allowed to age for about 40 minutes. This was found to be quite adequate for the attainment of equilibrium. The film was then swept, collected in a well at the end of the trough, and weighed.⁵ Its concentration was determined by comparing its colour with that of a standard congorubin solution in a colorimeter.

Very dilute solutions (0.0002 M) were employed in the trough. This secured adequate accuracy in the subsequent colour comparison. The area of cross-section of the congorubin molecule is equal to

$$\frac{A.M.}{W(x_2 - x_1) N},$$

where x_1 = No. of g. of dye in 1 g. of the original solution.

x_2 = No. of g. of dye in 1 g. of the sweepings.

W = Wt. of the sweepings.

M = Molecular weight of the dye.

N = Avogadro Number.

A = Total area occupied by the film.

The cross-section of the rubin molecule obtained by this method was

$$42 \times 10^{-16} \text{ sq. cm.}$$

DISCUSSION

Accumulation of congorubin from aqueous solutions

The data presented in the table indicate that congorubin molecules accumulate slowly at a water surface. Increase in concentration enhances the rate of accumulation. At lower concentrations (0.05% and below), for a given accumulation, the time is inversely proportional to concentration. Thus, at a concentration of 0.05%, two minutes are required to increase the surface covered from 7.9 to 10% while at 0.025% the time required is nearly four minutes to bring about the same effect. When the equation $\frac{dx}{dt} = K_1 c (1 - x)$

is applied to the values obtained, K_1 is found to be inconstant and to diminish with time. It is of interest to note, that when the pH of the solution was lowered by the addition of acetic acid, accumulation during the first minute

was nearly doubled (compare experiments 4 and 5). When lowering in pH of the same order was effected by the addition of valeric acid (instead of acetic acid) the effect was very slight, the accumulation in the acidified solution being 0.07 at the end of the first minute while in absence of the acid the value was 0.061. The addition of amyl alcohol or of sugar decreased the accumulation of the dye while Nekal Bx increased it. Sodium stearate, on the other hand, had very little effect.

Several theories,^{6, 7, 8, 9, 10} have been put forward to account for the phenomenon of slow accumulation. The most satisfactory explanation seems to be the one proposed by Doss.¹⁰ He suggests that the orientation of the molecules of the dye and the formation of an electrical double layer are responsible for slow accumulation. In the case of condensed films, slow accumulation is mainly due to the orientation effect. The electrical double layer is responsible for slowing down the accumulation in gaseous films.

Examination of the F-A relationship indicates that congorubin forms a condensed film at the surface of water. Owing to the four hydrophilic groups in its molecule, the dye is quite soluble in water. At each end of the hydrophobic chain the dye has two hydrophilic groups. When a molecule of the dye comes up to the air-solution interface the molecule may possibly orientate itself in two ways: (1) The molecule may bind itself in such a way that all four hydrophilic groups are anchored in the aqueous phase. (2) Only one hydrophilic end may be in the water and the other, out in the air. In the first case the molecule is very likely to be dragged into solution because of the predominant pull of the hydrophilic groups and there will thus be no accumulation at all at the surface. In the second way however, there will be an accumulation of the dye at the air-solution interface to form a condensed film. But, only molecules of the dye that have high translational energy can come up and orientate in this fashion. The number of such molecules must obviously be very small. This accounts for the slow accumulation.

It has been pointed out already, that in the case of congorubin, accumulation falls off with time. This effect seems to be due to the concentration of negative charges at the interface, due to the ionised hydrophilic groups of the dye anchored in the solution. This charged layer makes it increasingly difficult for molecules of the dye to come up and accumulate at the interface.

The effect of acetic acid on the accumulation can easily be accounted for. The lowering of pH brought about by the addition of the acid decreases the negative charge at the interface. It is noticed that valeric acid has far

less effect than acetic acid on the accumulation. This seems to be due to the formation of a complex between the valeric acid and the dye. Owing to the formation of this complex, the hydrophilic character of the dye is enhanced and it becomes more difficult for the dye molecule to take up the particular position resulting in accumulation. It may be pointed out that amyl alcohol, which does not affect the pH, also causes a diminution in accumulation. This is probably due to complex formation resulting in an increase in hydrophilic character, as with valeric acid. The decrease noticed with saccharose can be accounted for on the same basis.

When Nekal Bx is mixed with congorubin the combined accumulation is far greater than the sum of the accumulation of each component, as can be seen from Table I. Nekal Bx has a large hydrophobic group, and the complex of Nekal Bx with the congorubin, compared with the dye, will be more hydrophobic in character. The increase in hydrophobic character facilitates accumulation. In the case of sodium stearate however, the rate of accumulation is practically unaffected. The fraction of the surface covered with sodium stearate (0.0002%) in 1 min. was 0.150 and with congorubin 0.061. A mixture of rubin and stearate gave a value of 0.216, which is practically the same as the sum of the two individual accumulations, *viz.* (0.211). As has been shown later in this paper, the formation of a film of congorubin is not affected by the presence of stearic acid at the surface at which the film of the dye is produced.

Variation of surface tension with time

The variation of surface tension with time is plotted in Graph 1. It is seen that the surface tension of the rubin solution is practically the same as that of pure water during the first fifteen minutes. At this stage however (point A), a distinct fall in surface tension is noticed. This fall is rapid at first but slows down with time. These observations can be accounted for, on the basis of accumulation of congorubin. Up to the point A the congorubin molecules that come up to the surface, form only patches or islands of condensed film. At A however, there is practically complete union of the islands to form a compact film. Thereafter, the molecules of the dye that come up to the surface increase the surface pressure and cause a lowering of surface tension. This effect is marked in the beginning but progressively falls off. This is to be expected, as the rate of accumulation of rubin molecules rapidly diminishes with time.

In Graph 2 is illustrated the accumulation of congorubin under different experimental conditions: (1) natural ageing, (2) ageing when the surface is closed up at a pressure of 1.05 dynes, (3) ageing in presence of a film of

stearic acid. From Graph 1, it will be noticed that a period of 25 minutes is necessary to develop a surface pressure of 1.05 dynes. This period has been taken into account in determining the points for Graph 2. The three curves lie very close to one another and it may therefore be concluded that once a compact film has been formed on the surface of the congorubin solution, the lowering of surface tension due to further accumulation is the same in all the three cases. The presence of stearic acid does not affect the accumulation of congorubin. The area of 42×10^{-16} sq. cm. for the cross-section of the congorubin molecule obtained by the trough method indicates that the molecule of the dye orients itself on the surface of water with one end having two hydrophilic groups of the hydrophobic chain away from the water, while the other two hydrophilic groups of the chain are anchored in water.

SUMMARY

1. The rate of accumulation of congorubin molecules at an air-water interface has been investigated under varying conditions of concentration and pH. The rate of accumulation increases with the increase in the concentration of the congorubin solution. The rate is also enhanced by an increase in the hydrogen ion concentration. The results are explained on the basis of activated accumulation.
2. The effect of (a) acetic acid, (b) valeric acid, (c) saccharose, (d) amyl alcohol, (e) sodium stearate and (f) Nekal Bx, on the accumulation has been investigated. With (b), (c) and (d) a fall in accumulation is noticed while in (a) and (f) there is an increase. In (e) on the other hand, no change is observed. These results are explained on the basis of orientation of the molecule of the dye. Formation of a complex by the congorubin with valeric acid, saccharose, amyl alcohol and Nekal Bx is responsible for the departure from the normal behaviour of the dye.
3. The trough method is employed to study the variation of surface tension with time. The surface tension shows no variation during the first 15 minutes, but, after this period suffers a lowering with time. The lowering becomes less as ageing proceeds and tends to reach an equilibrium value.
4. The accumulation of congorubin is not affected by the presence of a stearic acid film on the surface of congorubin solution.
5. The area of cross-section of the congorubin molecule has been determined by the trough method. This value supports the view that there is orientation of the congorubin molecule at the air-water interface,

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