

CONDUCTIVITY AND CATAPHORETIC SPEED MEASUREMENTS OF BENZOPURPURIN 4B, CONGO RED AND SKY BLUE F.F.

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ALTHOUGH the dyeing of cotton by direct dye-stuffs has been practised for a long time, their action on the fibres has not been clearly understood. The substantive dye-stuffs have very high molecular weights and in aqueous solutions, they exist in the form of colloidal electrolytes.¹ In view of the colloidal chemical nature of the solutions of the direct dyes and the necessity of the presence of salts while dyeing, many investigators have studied their coagulation by and diffusion in the presence of different electrolytes. Benzopurpurin 4B, Congo Red and Sky Blue F.F. have already been the subject of numerous physico-chemical investigations and it was therefore decided to determine their conductivity and cataphoretic speed to see if these particular results can throw any light on the mechanism of dyeing by the substantive dye-stuffs.

Experimental.

It is a well-known fact that the technical dye-stuffs contain electrolytic and organic impurities, and for any investigational work, it is of fundamental importance to use the dyes in their purest form. Their purification is however not very simple as they are of complex nature and may contain their isomerides and homologues which are difficult to remove. Many methods which have been used for purification are open to objection as the dye is produced in a different state. The method adopted by Robinson and co-workers² was used for the precipitation of the dyes employed in this investigation as it is free from objections. The relative viscosity at 30° C. and the pH of solutions of the dyes so purified were as given below :—

Dye	Concentration	Relative Viscosity	pH
Benzopurpurin 4B ..	0.5%	1.039	7.10
Congo Red ..	0.4%	1.096	7.18
Sky Blue F.F. ..	0.4%	1.044	7.00

Conductivity water was used for preparing all the solutions.

The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer,³ the details of the method being the same as those given by Desai and co-workers.⁴

The cataphoretic speed was measured in the same way as done by Desai and Borkar.⁵ The upper liquid in these measurements consisted of a solution of sodium chloride having the same conductivity as the dye solution.

Benzopurpurin 4B was also subjected to dialysis in parchment paper bags and its cataphoretic speed measured at different stages of dialysis.

All the measurements of conductivity and cataphoretic speed were carried out in an air thermostat at a temperature of 30° C.

Results.

The results of these experiments are given in the tables below. The cataphoretic speed readings have been corrected for viscosity by taking the viscosity of water as unity. The concentration of the electrolyte is expressed in mols per litre of the mixture.

TABLE I. *Benzopurpurin 4B.*

Dye Conc. %	Cataphoretic speed $\times 10^5$						
	Period of dialysis						
	0	4 days	8 days	12 days	16 days	20 days	24 days
0.025	17.54	30.50	28.32	25.20	17.01	16.45	15.89
0.05	19.62	33.61	30.19	27.18	18.12	17.51	16.91
0.10	26.39	36.63	33.21	27.78	27.18	27.00	26.15
0.20	32.57	39.25	39.66	30.80	28.01	27.78	26.70
0.30	38.04	42.33	44.39	36.54	32.24	29.68	27.18

TABLE II. *Benzopurpurin 4B.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed $\times 10^5$
0.1795	125.65	17.54
0.3592	107.75	19.62
0.7184	99.30	26.39
1.4368	92.75	32.57
2.1552	85.05	38.04

TABLE III. *Benzopurpurin 4B.*
(Conc. 0.7184 N).

Conc. of NaCl	Cat. speed $\times 10^5$
0.000	26.39
0.684	33.81
1.368	30.19
2.052	22.64
2.736	21.74

TABLE IV. *Congo Red.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed $\times 10^5$
0.3453	116.20	22.64
0.6906	102.90	23.54
1.3812	97.30	36.23
2.0718	90.65	40.76
2.7624	90.15	45.50

TABLE V. *Congo Red*.
(Conc. 0.6906 N).

Conc. of NaCl	Cat. speed $\times 10^5$
0.000	23.54
0.342	25.60
0.684	27.50
1.368	36.23
2.052	30.53
2.736	23.54

TABLE VI. *Sky Blue F.F.*

Conc. of dye gram equivalent per litre	Equivalent conductivity	Cat. speed $\times 10^5$
0.063	342.5	17.21
0.126	342.0	18.57
0.252	342.3	27.09
0.504	342.3	33.06
0.756	342.3	36.69
1.008	280.3	..

TABLE VII. *Sky Blue F.F.*
(Conc. 0.252 N).

Conc. of BaCl ₂	Cat. speed $\times 10^5$
0.0	27.09
0.2	31.57
0.4	41.93
0.6	31.73
0.8	14.49

Discussion.

(a) *Changes in cataphoretic speed during dialysis.*—It will appear from Table I that with the progress of dialysis (horizontal rows) the cataphoretic speed first increases and then decreases in all the cases. It will also be noticed that there is a tendency for the cataphoretic speed to remain constant when the dye solution is subjected to dialysis for long periods. The changes in the cataphoretic speed with the progress of dialysis are similar to those observed by Desai and co-workers in the case of colloidal gold,⁶ ferric hydroxide,⁵ thorium hydroxide⁷ and Prussian blue.⁸

As stated before, the pH of the pure Benzopurpurin 4B dye solution was 7.1; the dye therefore does not hydrolyse in aqueous solution. Matters, however, become different when the solution of the dye is dialysed against pure water. As a result of the influence of the parchment membrane the dye will hydrolyse⁹ and some NaOH pass out in the dialysate. The solution in the parchment bag will contain the undissociated dye [if the dye (salt) is not completely dissociated], the dye ions, Na-ions and H-ions.

For spherical particles obeying Stokes' law the following equation holds good :—

$$U_0 = \frac{E}{6\pi\eta r}$$

where U_0 = Cataphoretic speed under unit potential gradient.

E = Total charge on the particle.

r = Radius of the particle.

and η = Viscosity.

The total charge being proportional to the total surface area, *i.e.*, the square of the radius, the cataphoretic speed would be greater for the larger particles assuming that the shape of the particles does not change materially during aggregation and the frictional resistance does not increase with aggregation at the same rate as the total surface charge. The initial increase in the cataphoretic speed with the progress of dialysis is therefore due to the formation of large ionic micelles. The turbidity of the dye solution was found to increase during dialysis thus showing that aggregation of the dye ions to form ionic micelles had taken place.

In view of the increase of turbidity (*i.e.*, of the size of the ionic micelles) of the dye solution with the progress of dialysis, the cataphoretic speed should have continuously increased instead of only upto a certain stage of dialysis. The subsequent decrease of cataphoretic speed may probably be due to the following causes :—

(1) The increase in the hydration of the ionic micelles during dialysis will decrease the cataphoretic speed to a certain extent.

(2) The 'inclusion effect,'¹⁰ *i.e.*, the inclusion of the gegenions (oppositely charged ions) will increase on standing during dialysis and the cataphoretic speed will decrease. This inclusion effect can be taken to mean preferential adsorption of the oppositely charged ions (gegenions).

It is considered that the influence of the second factor is mainly responsible for the subsequent decrease of the cataphoretic speed.

In the early stages of dialysis the inclusion effect will also be there but the cataphoretic speed increases because the effect of aggregation is more pronounced than that of inclusion.

The tendency for the cataphoretic speed to remain constant on dialysing the solution for long periods is probably due to effect of aggregation and inclusion being about the same.

It may be mentioned that the explanation which Desai and collaborators^{5,6,7,8} have advanced for the Λ -shaped cataphoretic speed-dialysis curves for the hydrophobic sols cannot be utilised in the present instance because in the former case the charge on the particles is due to preferential adsorption of the ions of the peptising electrolyte whose amount continuously decreases during dialysis, while in the latter case the dye ion itself represents the micelle ion.

(b) *Changes in conductivity and cataphoretic speed with dilution.*—It will appear from Tables II and IV that in the case of Benzopurpurin 4B and Congo Red the equivalent conductivity continuously decreases, while the cataphoretic speed continuously increases on increasing the concentration of the dye solution. In the case of Sky Blue F.F. (Table VI) on increasing the concentration of the dye solution the equivalent conductivity remains more or less constant at first and decreases later while the cataphoretic speed continuously increases as in the case of the other dyes.

In his extensive researches on soap solution McBain¹¹ observed a remarkable increase of equivalent conductivity with increasing concentration in the aqueous solutions of soaps at about N/10 and higher concentrations. He ascribed the increase in equivalent conductivity to the aggregation of ions of one kind to form ionic micelles. As discussed by Moilliet, Collie, Robinson and Hartley¹⁰ if ' m ' ions aggregate to form ionic micelles, their velocity will be multiplied by $m^{\frac{2}{3}}$ and as they carry the same amount of electricity as before their contribution to the conductivity will be multiplied by the same amount. The above arguments however apply only in the case of very dilute solutions in which the 'inclusion effect' of Robinson and

others and the 'atmosphere effect' of Debye, Hückel-Onsager theory are both negligible. It is likely that even in most dilute dye solutions multivalent ionic micelles will be there and the 'inclusion effect' and the 'atmosphere effect' will be very large as compared with the ordinary electrolytes. Thus the increase in conductivity due to Stokes' law effect of aggregation—termed primary effect—will be levelled out by the inclusion and atmosphere effects—termed secondary effects—which will decrease the conductivity. The decrease of conductivity due to the secondary effects will increase with the increase in the number of ions aggregating to one micelle, *i.e.*, with concentration. The dye solutions tried here are generally moderately concentrated and the conductivity has decreased with increase in concentration probably due to the fact that the secondary effects are more pronounced than the primary effect. In the case of Sky Blue F.F. the conductivity has remained constant between concentrations 0.063 N and 0.756 N; this is probably due to the fact that the primary effect and the secondary effects balance each other. For the same equivalent concentration the conductivity of Sky Blue F.F. is greater than that of either Benzopurpurin 4B or Congo Red; this perhaps indicates relatively high mobility of the dye ion in the case of Sky Blue F.F.

From Tables II, IV and VI it will appear that the cataphoretic speed has increased with concentration for all the three dye solutions. In view of the arguments discussed in section (a) the increase in the cataphoretic speed is due to aggregation of the dye ions to form ionic micelles. The cataphoretic speed results thus show that the size of the particles increases with concentration for Benzopurpurin 4B, Congo Red and Sky Blue F.F.

The next question to be considered is why the conductivity results do not give evidence of aggregation although the cataphoretic speed results definitely indicate formation of large micelles. Moilliet, Collie, Robinson and Hartley¹⁰ have discussed the difficulties of obtaining information regarding aggregation from conductivity measurements as a result of secondary effects mentioned above. They have also pointed out that the secondary effects might be less marked if mobilities or transport numbers of the ionic micelles are determined instead of conductance. They have shown that the atmosphere effect will decrease both mobility and transport number as conductance; the inclusion effect though tending to decrease the mobility slightly and conductance greatly will actually increase the transport number quite markedly. The transport number will not however increase due to aggregation to the same extent as mobility and conductance. Robinson¹² observed that the mobility of *meta*-Benzopurpurin increases with increase in concentration in dilute solutions although the conductivity measurements

under the same conditions did not give evidence of aggregation. He also found that the mobility of Benzopurpurin 4B decreases with increase in concentration from 0.004 N to 0.01 N. Moilliet, Collie, Robinson and Hartley¹⁰ however determined transport numbers of the 4B dye and found evidence of aggregation with increase in concentration from about 0.001 N to 0.012 N. From the present results (Table II) it will appear that the cataphoretic speed gives evidence of aggregation with increase in concentration from 0.1795 N to 2.1552 N. The cataphoretic speed determinations would thus appear to be more important than the transport number measurements for getting an idea about aggregation of ionic micelles.

The fact that ionic micelles aggregate on increasing the concentration of the 4B dye is further supported from stability determinations. It is found that the flocculation value with NaCl decreases as the concentration of the dye is increased. If aggregation of ionic micelles had not taken place, the amount of NaCl required to produce a given degree of turbidity in a certain time would be greater for a concentrated than for a dilute solution.

(c) *Changes in cataphoretic speed in the presence of salts.*—It will appear from Tables III, V and VII that on adding small increasing amounts of salts to the dye solutions the cataphoretic speed increases in the beginning but decreases later. Robinson and Moilliet¹³ also found an increase in the cataphoretic speed of the particles of Benzopurpurin 4B on the addition of electrolytes.

The initial increase in the cataphoretic speed on the addition of salt can be due to (i) preferential adsorption of the similarly charged ions and (ii) aggregation of the ionic micelles. It is considered that the increase in the cataphoretic speed is mainly due to the second factor. The increase in the turbidity of the dye solution on the addition of salt would also support aggregation of the particles. It is likely that some oppositely charged ions might also be preferentially adsorbed but the decrease in the cataphoretic speed on account of this is not perceptible owing to the marked effect of aggregation.

As the dye solution actually coagulates (increase in the size of the particles) on the addition of large amounts of salt one would expect an increase in the cataphoretic speed throughout. It will however appear that the cataphoretic speed has actually decreased on adding relatively large amounts of salts. This is probably due to the marked preferential adsorption of the gegenions which does not allow the effect of aggregation to be noticed at all.

These results are similar to those obtained by Valkó¹⁴ who determined the diffusion coefficients by the porous plate method of the 4B dye, Congo

Red and Chicago Blue 6B (identical with the Sky Blue F.F.) in the presence of different small amounts of NaCl and found that the particles aggregate in all the cases.

(d) *Bearing of the present results on the mechanism of dyeing by direct dye-stuffs.*—A very interesting and important discussion on the various theories on dyeing by direct dye-stuffs took place at London in September 1934 under the auspices of the Faraday Society, and it is proposed to examine some of the views expressed there in the light of the present results and conclusions. Morton¹⁵ has stated that in the presence of small amounts of NaCl the degree of dispersion of pure dye increases although on adding relatively large amounts of salt the degree of dispersion decreases. Our results do not support the view that the degree of dispersion of the dye particles increases in the presence of salt. The results of diffusion experiment of Valkó¹⁴ also show that the degree of dispersion of the ionic micelles does not increase on raising the salt concentration.

Neale and others¹⁶ have measured the adsorption of the dye-stuffs by fibres and observed that it increases with increase of salt concentration at least upto a certain concentration. They have calculated the rate of diffusion by the application of Hill's¹⁷ equation and found that the rate of diffusion first increases, reaches a maximum and then decreases. Their diffusion coefficients so calculated do not therefore agree with the results of Valkó.¹⁴ according to whom the diffusion coefficients continuously decrease on adding increasing amounts of salt. It must however be stated that the adsorption results of Neale and co-workers¹⁶ can be easily understood even on the basis of continuous increase in the size of the dye ions on the addition of increasing amounts of salt. Greater adsorption of the dye with the increase in salt concentration might probably take place in spite of a decrease in the diffusion coefficient, because relatively larger ionic micelles will be adsorbed instead of smaller ones (with little or no salt) as long as the ionic micelles are not bigger than the capillary pores of the cellulose. Once the micelles become of the same size as or larger than the capillary pores, further aggregation will not increase adsorption. Thus there will be an optimum concentration of salt for dyeing at which maximum dye can be adsorbed; smaller or larger amounts of salts than the optimum will mean less adsorption of the dye. The experience of the practical dyer that too much of the salt causes a waste of dye is to be explained on the basis that some of the ionic micelles reach such a large size that they cannot be adsorbed by the fibre.

Robinson¹⁸ has suggested that the effect of the negative charge in the viscose capillaries, which will oppose the passage of the dye whose ionic micelles are also negatively charged, will be almost completely suppressed

by the presence of the salt and hence the dye will be allowed to pass freely. According to him the effect of salt on the degree of dispersion of the dye is only of secondary importance. It may however be stated that increased adsorption of the dye in the presence of salt can easily be explained, as pointed out above, on the basis of aggregation and that it is not necessary to consider the effect of charge on the viscose capillaries on the adsorption of the dye whose micelles are also negatively charged.

Neale¹⁹ has also stated that it is difficult to be dogmatic with regard to the importance of aggregation in dyeing with direct cotton colours. His view is that there is only slight aggregation and that at the elevated temperatures (usually 90° C.) used in his experiments aggregation of the dye is of little or no importance except at exceptionally high concentrations of the added salts. We would like to mention that although there will be considerably less aggregation of the dye at 90° C. than at ordinary temperatures, it has been shown by Morton¹⁵ that the direct dyes are dissolved colloiddally to some extent even at 75° C. In view of this it is highly probable that even at the "boil" the addition of small amounts of salts would produce appreciable aggregation of dye micelles, although certainly less than at ordinary temperatures.

It is now possible to explain in a simple manner the process of dyeing by substantive dye-stuffs in the presence of salts on the basis of aggregation of dye ions. If salt is not added to the bath, the size of the dye ions may be so small (amicronic size or even smaller) that they may come out from the fibre on washing, *i.e.*, the colour will not be fast to wash. If too much of salt is added, the size of the ionic micelles will become very large and only a small amount of the dye will be adsorbed, some dye actually remaining in the bath as stated before. The advantage of dyeing at higher temperatures instead of at ordinary temperatures is that as a result of the swelling of the fibre relatively large sized dye micelles are adsorbed in the presence of salt in the former case and when the ordinary temperature is attained the dye becomes so fixed in the fibre due to shrinking of the latter that it cannot be washed out easily (colour fast to washing). If salt is not present in the dye bath only small sized micelles will be adsorbed at relatively high temperatures as the degree of dispersion of the dye increases with temperature and the fastness to washing will be less unless a very large amount of the dye is added to increase the size of the micelles adsorbed, but a considerable amount of dye will be wasted in that case. Dyeing at ordinary temperatures even if salt is present in the bath will also not give desired fastness as the micelles adsorbed will be easily washed out due to absence of shrinking of the fibre.

Summary and Conclusions.

Measurements of conductivity and cataphoretic speed of pure Benzopurpurin 4B, Congo Red and Sky Blue F.F. have been made and it is found that on increasing the concentration of the dye solutions although the equivalent conductivity continuously decreases the cataphoretic speed increases regularly. The cataphoretic speed of Benzopurpurin 4B first increases and then decreases with the progress of dialysis. On adding small increasing amounts of sodium chloride to Benzopurpurin 4B and Congo Red and barium chloride to Sky Blue F.F. the cataphoretic speed first increases and then decreases. The changes in conductivity and cataphoretic speed are explained on the basis of aggregation of the dye ions to form ionic micelles. It is shown that the process of dyeing of cotton fibre by substantive dyestuffs in the presence of salt can be easily understood on the basis of aggregation of dye ions.

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