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" Studies on Absorption, Conductivity and polarised Fluorescence
of Dyestuffs in solution."

Thesis
for
the degree of Doctor of Philosophy.

GIFT

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Submitted by
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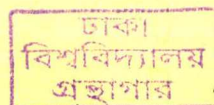
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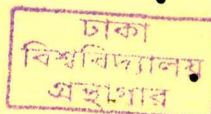
STUDIES ON ABSORPTION, CONDUCTIVITY AND POLARISED FLUORESCENCE
OF DYESTUFFS IN SOLUTION.

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C O N T E N T S.

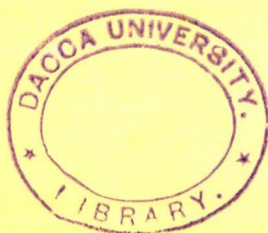
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I N T R O D U C T I O N .

It is well known that the intensity of fluorescence of most of the Dyestuffs in solution at first increases with increase in concentration of the emitting molecules, reaches a maximum and with higher concentrations the fluorescence gradually disappears. Two principal hypotheses are generally put forward to explain concentration-quenching: (1) quenching by collisions of the second kind in which there is an abnormally large effective radius for like molecules, (2) the formation of associated molecules, which themselves are non-fluorescent and have a somewhat modified absorption spectrum. The second hypothesis does not really represent quenching in the true sense of the term as quenching is always accompanied with a diminution of the average life-period. F. Perrin (1931) has however combined it with the hypothesis of quenching by collision of the second kind in such a way that there is a transfer of energy from the excited molecules to the associated molecules which cannot reconvert into radiation the energy taken up.

The problem of the Kinetics of quenching has been examined by Frank, Wawilow (1931) and Svesnikov (1936). By taking into account the Brownian movement and the properties of the medium and the collision of the second kind, Frank and Wawilow arrived at the following form :-



$$\frac{L_0}{L} = e^{\omega N c} \left[1 + \frac{T_0 N c k T_z (\sigma_1 + \sigma_2)^2}{3 \eta \sigma_1 \sigma_2} \right]$$



where $\frac{L_0}{L}$ is the ratio of unquenched to quenched fluorescence, w is the volume of the sphere of action, r its radius, z is the ratio of effective to kinetic collisional distances ($z = \frac{r + \sigma_1}{\sigma_1 + \sigma_2}$) σ_1 and σ_2 are the radii of the dyemolecule and the added molecule, c is the concentration of the latter (quencher) in gm./c.cm.; N is the Avogadro number, T is the mean life of the fluorescent molecule, T the absolute temperature and η the viscosity of the quencher. It has been shown that when Nc is somewhat small, the quenching formula takes the form

$$\frac{L_0}{L} = 1 + \frac{T_0 N c k T z (\sigma_1 + \sigma_2)^2}{3 \eta \sigma_1 \sigma_2} + w N c$$

In this case, therefore, $\frac{L_0}{L}$ is a linear function of c in agreement with experiment, provided the kinetic sphere and the effective sphere of the collision of the second kind are not very different. Deviations from Wawilow's formula, however, occur for higher concentrations; collisions of the second kind do not, therefore, completely explain the quenching of ^{fluorescence of} liquids.

The diminished fluorescence in concentrated dye solutions is largely due to aggregate formation as shown by the fact that they do not obey Beer's law (1935) as well as by other observations on mean life and depolarisation (1929)(1930). Mitra (1938) observed a close parallel between the change of molar absorption co-efficients with concentrations and the change of fluorescence yields. It is interesting to note that in very dilute solutions where Beer's law seems to hold, the fluorescence yield remains constant. Further increase in concentration diminishes the yield as well as absorption capacity per molecule.

It is difficult to explain on purely collision hypothesis the change of the absorption co-efficient to the extent observed by Mitra. Lewschin (1927) found modified absorption spectra of dyestuffs at fairly high concentrations. He studied the effect of temperature on specific fluorescent capacity in concentrated solution. Though temperature increases the number of collisions, the fluorescence yield increases at the same rate. Bouchard (1936) has confirmed the above observations which go against the collision of the second ^{kind} as means of quenching. Banov (1933) has further shown that increase of temperature has, sometimes, a decreasing effect on the quenching of fluorescence by salts. All these facts go against the theory of the collision of the second kind and we are thus inclined to look for the explanation in the micelle formation of the ions of the dyestuffs to which the greater part of the effect may be due. In order to gain insight as to the mechanism of micelle formation and its bearing on the mechanism of quenching it is proposed to study the association of the dyestuff molecules with and without foreign substance.

The deformation of the absorption ~~spectra~~ spectra of dyes at high concentrations shows that changes occur in the molecule. The absorption spectra of dyestuffs in solution therefore furnish a method of studying the mechanism of formation of associated molecules. It is rather difficult to study the absorption spectra of dyes at high concentrations. The Sector photometer method and the Hydrogen discharge tube method are practically unsuitable for the purpose. The Sector photometer method can, however, be conveniently utilised for studying the absorption spectra of dyes with foreign neutral salts.

The mechanism of micelle formation can be best studied from measurements on conductivity of dyestuffs. It is a well known fact that the equivalent conductivity of an electrolyte generally increases with dilution and tends to a limiting value at infinite dilution. It was pointed out by McBain(1913) that the equivalent conductivity of an electrolyte would be increased by the aggregations of ions of one kind to form ionic micelles and the remarkable increase of equivalent conductivity with increasing concentration has been attributed to association of solute molecules. Robinson(1934) and his co-workers determined the transport number as well as the equivalent conductivities of some of the rigorously purified dyestuffs. The equivalent conductivities of dyesolutions when plotted against square root of concentrations, give curves similar in nature to those obtained by Howell and Robinson(1936). The departure of the conductivity curve from the perfect straight line can only be explained on the assumption that ionic micelles are formed with increase in concentration.

The present investigations have been carried out to gain some insight as to the ionic states of dyemolecules. The measurements of conductivity of dyes is, however, beset with difficulties. The Kohlrausch method of determining resistances of electrolytes is generally employed using electrodes coated with platinum black. The Platinum black coating eliminates the disturbing effect of polarisation but it has certain inherent disadvantages. It adsorbs the solute molecules and acts as a catalyst in the oxidation of certain substances, particularly dyestuffs. In our observations the coating has therefore, been avoided altogether and a method has been devised to measure electrolytic resistance using bright platinum electrodes. The method gives quite satisfactory results.

The mean life of the fluorescing molecules in the excited state has a direct bearing on quenching. If quenching molecules are added to a dye-solution, the excited molecules will be deactivated before they have time to emit according to their natural life-period τ_0 . Therefore, when we increase the concentration of the dyestuff, either the effective value of the life-period will remain unaltered or probably due to increase in the number of collisions, the excited molecules will have a tendency to dissipate their energy in the form of kinetic energy of translation of the molecules. This would be equivalent to diminishing the mean period of duration of the molecules in the excited state. *The life-time of the excited state* is intimately connected with polarisation of the emitted light. On the basis of Perrin's theory (1929) the diminution in the mean life τ of the molecules in the excited state amounts to an increase in the value of polarisation. The polarisation of the fluorescent light has therefore been measured in certain cases and the value of τ has been calculated from Perrin's theory. The effect of temperature, viscosity and concentration on the average life-period has been investigated as well. According to Wawilow's theory τ_0/τ should be a linear function of C/η or T/η . The measurements show that this holds only within a limited range. It is expected therefore, that the measurement of τ and its dependence on temperature, viscosity and concentration will throw additional light on the mechanism of quenching.

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PART - 2.

ON THE ULTRAVIOLET ABSORPTION OF THE DYESTUFFS IN SOLUTION AND
THE INFLUENCE OF NEUTRAL SALTS ON THE SAME.

ON THE ULTRA-VIOLET ABSORPTION OF THE DYESTUFFS IN SOLUTION AND THE INFLUENCE OF NEUTRAL SALTS ON THE SAME

BY KRISHNADAS CHOWDHURY

AND

CHITTARANJAN BOSE

(Received for publication, August 12, 1942)

ABSTRACT. The paper deals with the ultra-violet absorption of a large number of fluorescent dyestuff solvents, namely, succinyl eosin, pinakryptol yellow in glycerine, acriflavine in alcohol, pinaflavol in alcohol, aniline orange in alcohol, 'rose Bengal' in alcohol, pinakryptol green in alcohol, succinyl fluorescein in glycerine. The absorption curves for each of these dyestuff are given. The effect of quenching element, namely, potassium iodide, has also been studied for acriflavine, succinyl fluorescein and pinakryptol yellow. With this particular type of quenching element it has been found that practically there is no change in the nature of absorption curves.

INTRODUCTION

A large amount of experimental work has been done by the different workers on the absorption of the dyestuff in different solvents. The existing literature on the subject reveals that the great majority of the investigators in that particular domain confined their investigations in the visible region of the spectrum. Very few quantitative measurements have been made in the ultra-violet region of the spectrum. It is well known that a quantitative measurement of absorption spectra of solutions of pure compounds can be made relatively easily, and it not only furnishes a method of identification of the substances but also serves as a basis of a theoretical treatment of their molecular structure, as is evident from the recent investigations of Mayneord,¹ Fisher² and others.

Mitra³ and Grisebach⁴ measured the absorption coefficient of a few dyestuffs in solution in the ultra-violet region and tried to establish a relation between the absorption curves in the near ultra-violet and polarisation curves of the fluorescent radiations emitted by these dyestuffs in solution under the excitation of light of various wave-lengths. In view of the meagre accurate data on the ultra-violet absorption, as well as, to find out whether there is any resemblance between the two sets of curves, as was reported by Grisebach and Mitra, it was thought desirable to make a systematic observation on the ultra-violet absorption of a large number of fluorescent dyestuffs in solutions.

EXPERIMENTAL ARRANGEMENTS

The absorption coefficients were determined by a calibrated rotating sector photometer (Adam Hilger) used in conjunction with a quartz spectrograph. The

source of light for the quantitative measurements has normally been a condensed tungsten-steel spark, about 4 mm. gap, the necessary potential being obtained from an X-ray induction coil with mercury interrupter in the primary. The results were in a few cases verified by the measurements of the absorption with a sensitive Moll thermopile and a galvanometer system.

A parallel beam of light from a point source of quartz mercury lamp was allowed to fall on a cell containing the dyestuff in solution through a suitable filter, which allowed only monochromatic radiation to pass. The intensities of the incident and transmitted light were measured with the help of a Moll thermopile and galvanometer. The absorption coefficients were measured from the well-known relation :—

$$I = I_0 e^{-ad},$$

where I and I_0 are the transmitted and incident intensity, respectively, of light, d , thickness of the cell containing the solution and a , the absorption coefficient.

The results of our observations in the case of both the experimental arrangements, thermoelectric and photographic, are given below for a comparative study. It will be evident that the agreement is fairly satisfactory.

TABLE I

Dyestuffs in alcoholic soln.	Absorption coefficient for λ 4358 Å	
	Thermoelectric	Photographic
Succ. fluorescein	.422	.40
Pinakryptol	.295	.30
Aniline orange	.248	.25
Pinaflavol	.447	.45

RESULTS

We have investigated the absorption of the following fluorescent dyestuffs in alcoholic and glycerine solutions. The figures within brackets indicate the concentrations.

1. Succinyl fluorescein	...	... (1.120000)
2. Succinyl eosin	...	... (1.70000)
3. Pinaflavol	...	... (1.200000)
4. Aniline orange	...	... (1.50000)
5. Acriflavine	...	... (1.50000)
6. Pinakryptol yellow	...	... (1.100000)
7. Pinakryptol green	...	... (1.125000)
8. Rose Bengal	...	... (1.100000)

Ultra-violet Absorption of the Dyestuffs in Solution

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All the above compounds were purified in the usual way. The results are shown graphically by the following curves (Figs. 1 to 8). As regards the resemblance between the two sets of curves, *viz.*, absorption and polarisation curves, as already reported in our introduction, we shall return to this point in another communication.

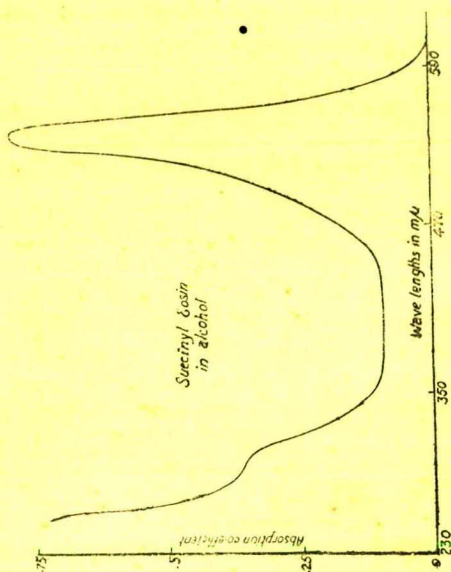


FIG. 2

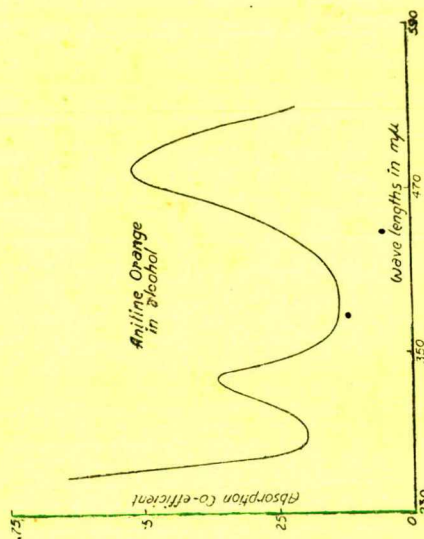


FIG. 4

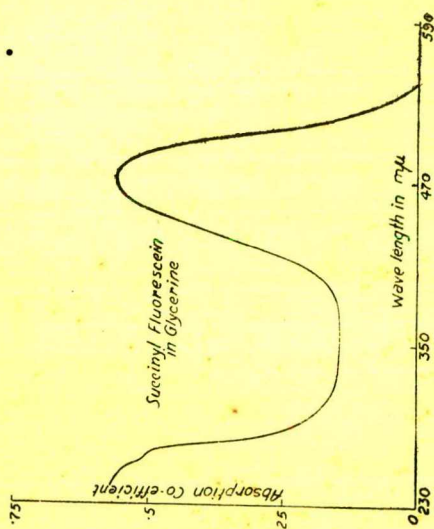


FIG. 1

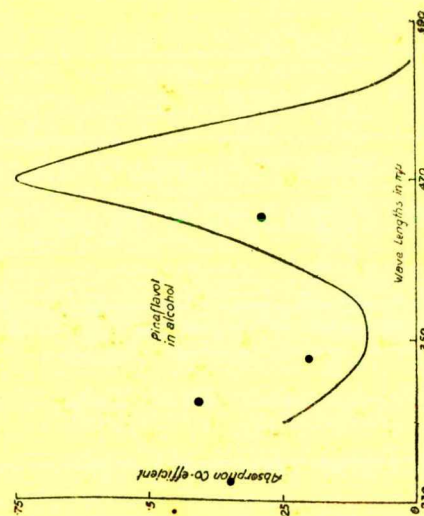


FIG. 3

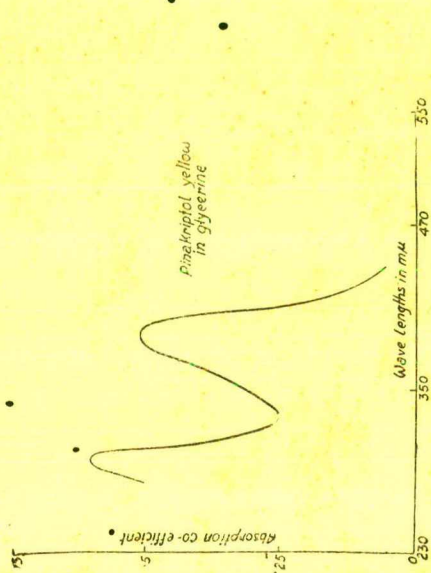


FIG. 6

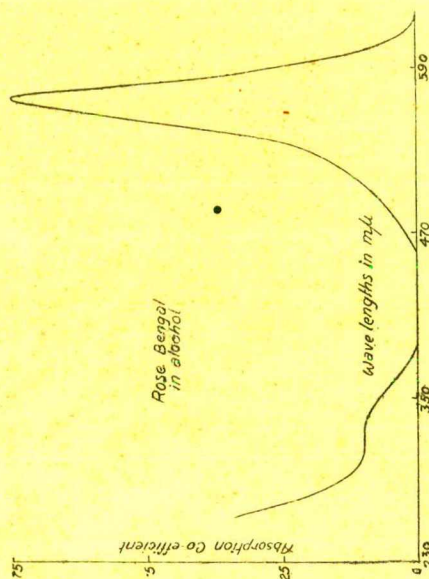


FIG. 8

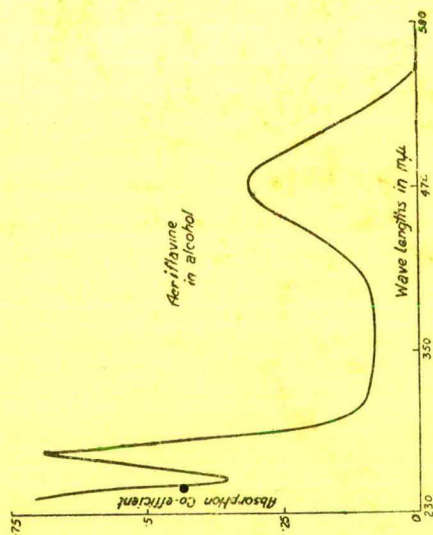


FIG. 5

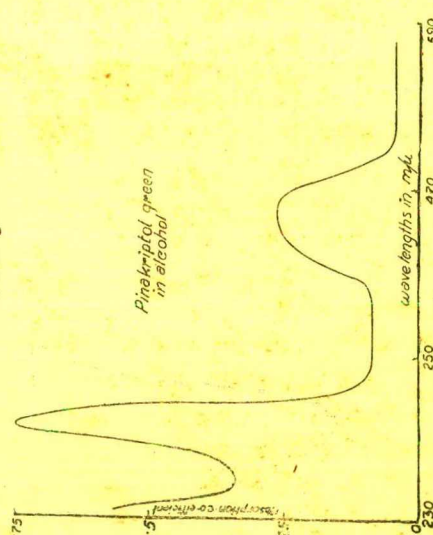


FIG. 7

INFLUENCE OF FOREIGN NEUTRAL SALTS ON THE ABSORPTION OF THE DYESTUFFS IN SOLUTION

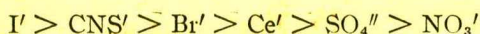
The quenching of the fluorescence of the dyestuffs in solution by foreign neutral salts is quite well known and has been investigated by a large number of workers. It appears that the majority of them are of the opinion that the phenomena of quenching are due to de-activating collisions of the second kind between the dyestuff molecules in the excited state and the negative ions of the added salts. The main argument in favour of the physical interpretation of the quenching effect is the increase of polarisation of the fluorescent radiation emitted by the dyestuffs in solutions, as was observed by Perrin,⁵ Franck,⁶ Mitra,⁷ and

others. But there may be an alternative explanation, *viz.*,—gradual “complex formation” due to the association of the molecules of the dyestuffs and those of the quencher with the gradual addition of the foreign substance—these complex molecules being non-fluorescent. These molecules, if any, will reveal their presence by a change (or by a new band) in the absorption spectrum of the dyestuff in presence of the quencher. So, unless one studies the influence of the foreign neutral salts on the absorption of the dyestuffs and demonstrates the absence of any such influence, the aforesaid alternative explanation, *viz.*,—gradual complex molecular formation, and consequent decrease in the number of emitting dyestuffs molecules, which is exhibited by a decrease in intensity of the fluorescent radiation, cannot be ruled out of the field.

The idea of complex molecular formation is not new. It is well known that as the concentration of the fluorescent substance is increased, the intensity of the fluorescent radiation also increases up to a maximum value, then the intensity falls down on further increase of the concentration of the fluorescent substance. That is, there is a definite concentration for a dyestuff for which the intensity of the fluorescent radiation is maximum. When the concentration is further increased, the resulting intensity of the fluorescent light dwindles down. In order to explain this concentration-quenching, Lewschin⁸ assumed the formation of complex molecules which are non-fluorescent unlike the mother molecules. In support of his assumption he showed that when the concentration of fluorescent dyestuffs is increased over that aforesaid maximum value, considerable alteration of the absorption spectrum of the dyestuff takes place.

One finds that Lampert,⁹ and Mitra¹⁰ measured the absorption co-efficient of a few dyestuffs in solution for both pure and after the addition of varying amounts of neutral salts. Besides these, no systematic investigations have been made on the subject so far. In view of the importance of the subject on the mechanism of quenching, we thought it prudent to investigate this point along with our absorption measurements.

It has already been mentioned that the intensity of the fluorescent radiation of the dyestuffs in solution suffers appreciable diminution when neutral salts are added to the solvent medium. The investigations of Perrin,¹¹ West, Jetty and Muller¹² indicate that the order of the extinguishing power of the different ions is as follows :—



which is practically the order of their deformability, that is, of the ease of displacement of an electron in the peripheral shell of the ion. This shows that iodide ions exert the greatest quenching influence on the fluorescing dyestuff molecules. In view of this, we have investigated at present the influence of KI on the absorption of a few dyestuffs in solution.

Our experimental procedure was as follows. A solution of the dyestuff, in alcohol of requisite concentration, was taken and its absorption at different wave-lengths was determined in the usual way by the rotating sector photometer.

Then to the same solution of the dyestuff, potassium iodide solution of known concentration was added drop by drop, till the fluorescence was quenched completely, as observed visually, the concentration, c of KI being determined from the number of drops added.

Then one cell of the photometer was filled up with the quenched dyestuff solution and the other cell with the KI solution of concentration c .

For the present, we have investigated the influence of iodide ions on succ. fluorescein, succ. eosin, acriflavine and pinakryptol yellow. The results are shown graphically by the accompanying curves (Figs. 9-11).

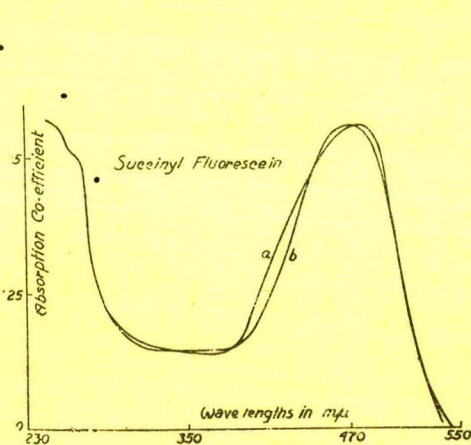


FIG. 9

Acriflavin
a—without KI
b—with KI

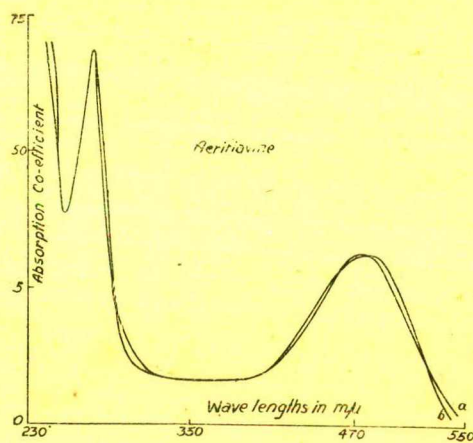


FIG. 10

Succ. fluorescein
a—without KI
b—with KI

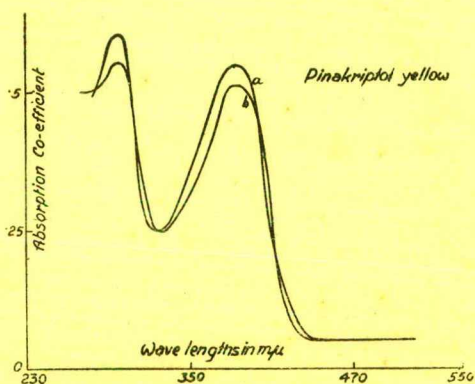


FIG. 11

Pina Kryptol yellow
a—without KI
b—with KI

Ultra-violet Absorption of the Dyestuffs in Solution 49

The graphs show that there is practically no change in the nature of the absorption curves on the addition of the foreign neutral salt. This shows that quenching of the fluorescent radiation on the addition of foreign salts takes place through collision of the second kind between the dyestuff molecules and the ions of the added salts.

In conclusion, it gives us great pleasure to thank Prof. S. N. Bose for his kind interest and Dr. S. M. Mitra for his kind guidance throughout the work.

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PART - 3.

ON A METHOD OF DETERMINING ELECTROLYTIC RESISTANCE.

ON A METHOD OF DETERMINING ELECTROLYTIC RESISTANCE.

The problem of the determination of electrolytic resistances has been attacked from time to time by different workers since Kohlrausch first devised a method. Most noteworthy are the works of Washburn, Grinnel Jones(1931),(1935),Shedlovsky(1930) and others. Washburn's contribution to the design of different forms of cells for substances of different resistances is invaluable. Grinnel Jones(1935) made an extensive study on the earthing of the circuit, the design of the bridge and the electrode loss at different frequencies and different degrees of platinisation using different metallic electrodes. Shedlovsky gave a very ingenious method of determining resistances with unplatinised electrodes, although he recommends slight platinisation for the sake of convenience and consistency. He gave a method of eliminating electrode effects with multiple-electrode cell.

The present paper shows an attempt at finding a satisfactory and convenient means of determining electrolytic resistances with unplatinised electrodes. It is to be noted that on account of certain inherent disadvantages it is preferable at least to some workers to avoid platinisation if possible, although it succeeds in making the effective electrode surface much larger than the effective cross-section of the line of flow of electric current through the solution and reduces the polarisation. It is now known from the works of Kohlrausch, Grinnel Jones, Wien(1936),(1902), Warburg(1901) and others that an electrolytic cell consists of (a) electrolytic resistance (b) polarisation capacitance(c) polarisation resistance. The polarisation capacitance is due to the reversible transformation of electrical energy into chemical energy and which is equivalent to an electrostatic condenser.

The polarisation resistance is according to Wien, due to the irreversible process at the electrode. Warburg suggested and developed the idea that diffusion is responsible for the irreversible process at the electrode. Perhaps much of the electrode loss is due to the employment of voltage higher than the decomposition voltage of the solution and, as the present paper will show, was not appreciable in the work of the author. The peak voltage used across the electrode was less than the decomposition voltage of the solution. The electrode resistance ΔR can therefore, be made to play insignificant part on the resistance of the solution. The polarisation capacitance can be compensated by introducing a capacitative reactance in an adjacent arm of the Wheatstone bridge.

The difficulties generally encountered as regards the measurement of conductivities of dyestuffs have already been referred to in our introduction. On account of these difficulties it is desirable to use bright platinum electrodes. The present paper deals with a method devised to measure electrolytic resistance using bright platinum electrodes. The conductivities of KCl at various concentrations have been redetermined. The agreement with the standard values is quite satisfactory. This method has, therefore, been employed in determining conductivities of dyestuffs.

**USE OF BRIGHT PLATINUM ELECTRODES FOR
MEASUREMENT OF ELECTROLYTIC
RESISTANCES**

By
KRISHNADAS CHOUDHURI

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CALCUTTA UNIVERSITY PRESS

USE OF BRIGHT PLATINUM ELECTRODES FOR MEASUREMENT OF ELECTROLYTIC RESISTANCES

BY KRISHNADAS CHOUDHURI

(Received for publication, Sept. 20, 1947)

ABSTRACT. On account of certain difficulties with platinised electrodes, it is desirable to use bright electrodes in measurements of electrolytic resistances. It has been shown that the Wheatstone's bridge method gives as satisfactory results with bright electrodes as with platinised electrodes by using a two-electrode cell and

- (1) an a. c. galvanometer of the wattmeter or of the dynamometer type through an amplifier,
- (2) a low impressed voltage,
- (3) a shunted capacitance in the R-arm and by making the ratio arms of equal resistance.

INTRODUCTION

After Kohlrausch introduced the use of alternating currents and electrodes coated with platinum black for the determination of electrolytic resistances, his method is almost invariably used for the purpose. The platinum black coating, although it effectively eliminates the disturbing effect of polarisation, has, however, certain inherent disadvantages, the notable among which are the following :—

- (1) it adsorbs the solute molecules and so it is necessary to stir the solution from time to time (in order to keep the strength of the solution between the electrodes constant) and to clean the cell carefully when changing the solution ;
- (2) it acts as a catalyst in the oxidation of certain substances, particularly dye-stuffs.

Attempts have, therefore, been made from time to time to avoid the coating altogether. Notable amongst the works in this line is that of Shedlovsky (1930), who recommended the use of multiple electrodes in the same cell. His final recommendation is, however, to platinise the electrodes slightly for the sake of consistency and constancy.

The present paper is an attempt in this direction using two-electrodes only.

DESIGN OF THE CELL

In designing the cell for strong electrolytes, the underlying idea is that the greater the ratio of the area of the electrodes to that of the cross-section of the current-carrying part of the solution, the less pronounced will be the effect of polarisation. For the solution of KCl, the form of the cell is that shown in Fig. 1. The area of each electrode is one sq. cm. whereas the

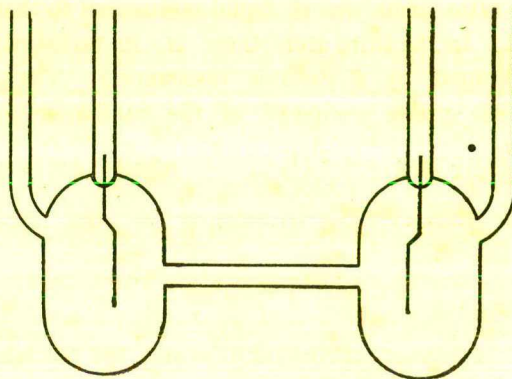


FIG. 1

area of the cross-section of the connecting tube is 0.07 sq. cm. The approximate resistance of normal KCl solution in this cell is 200 ohms. Since in the method employed the resistance of the diagonal arm containing the detecting instrument is practically ∞ , (i.e. $G = \infty$), this cell can be used up to a strength as low as N 500 (i.e. up to a resistance of about 10^5 ohms) with the same degree of accuracy.

ARRANGEMENT OF APPARATUS

The arrangement of apparatus is shown in Fig. 2. It is the usual Wheatstone's bridge arrangement in which an amplifier is used in the galvanometer or telephone arm. The detecting instrument is the vertical wattmeter devised by Mukherjee (1930, 1938). This instrument is composed

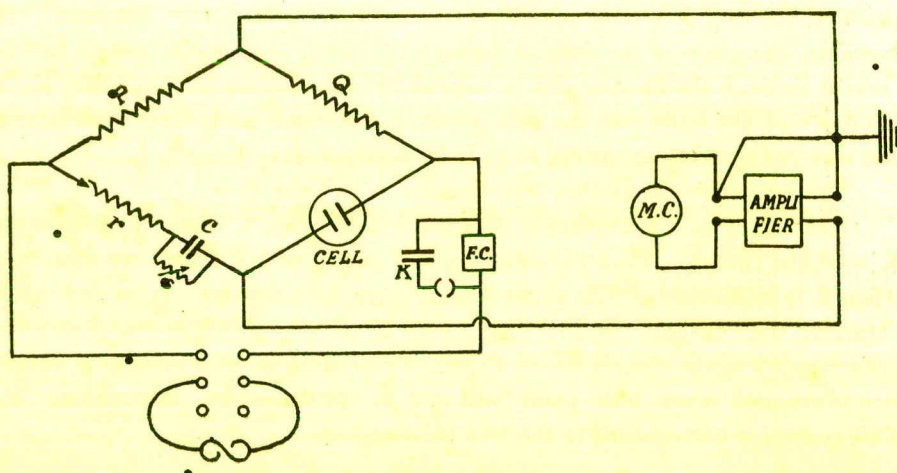


FIG. 2

of two systems of coils of which the fixed system produces the magnetic field and the moving system is deflected by the field. The former is put in

Bright Platinum Electrodes for Electrolytic Resistances 3

the battery arm of the bridge and the latter in the out-put side of the amplifier. The ratio arms are of equal resistances so that their inductances are also the same. In the third arm, there is, in series with a resistance r , a condenser shunted by a variable resistance s . The effective resistance and reactance of the system composed of the condenser and the shunt are respectively $\frac{s}{1+s^2c^2p^2}$ and $-\frac{s^2cp}{1+s^2c^2p^2}$, where $p=2\pi$ times frequency.

Therefore, when $V_c = V_D$, the resistance of the Ac-arm, namely,

$$r + \frac{s}{1+s^2c^2p^2} = R \quad \dots \quad \dots \quad \dots$$

is equal to the resistance of the solution and the reactance, $-\frac{s^2cp}{1+s^2c^2p^2}$,

balances the polarisation reactance of the solution as well as the residual inductive reactance of the Ac-arm.

METHOD OF FINDING THE BALANCE POINT

In detecting instruments of the wattmeter or dynamometer type, the deflection is given by

$$\delta = AI_f I_m \cos \psi$$

where I_f, I_m are the r.m.s. currents in the fixed coils and moving coils respectively and ψ , the phase-difference between them. The deflection is, therefore, zero when

$$(1) \quad I_f \text{ or } I_m = 0,$$

or
$$(2) \quad \cos \psi = 0 \text{ i.e., } \psi = \frac{\pi}{2}.$$

The balance corresponding to condition (1) is called the true balance. In practice, the null point corresponding to condition (2) is easily obtained. If, however, the phase of the current through the fixed coil with respect to the current through the moving coil is altered by introducing a condenser, K , in parallel with the fixed coil, the null point is disturbed and there is deflection one way or the other according as I_f is in advance of, or behind, I_m .

The procedure for finding true balance, is as follows:—

Keeping $s=0$, a null point is obtained by adjusting r , when the condenser K is off the circuit. Then the direction and extent of deflection are observed when K is introduced. The shunt is then given an arbitrary value and after obtaining the null-point by adjusting r with K off, the direction and extent of deflection are again observed with K on. Proceeding in this manner a condition is attained when null point will not be disturbed by introducing K . This condition corresponds to the true balance.

EARTHING

In working with alternating currents it is important to select the point which should be earthed. The question of earthing has been very elaborately

dealt with by Grinnel Jones (1935). In the present case, it has been found advisable to earth one end of the moving coil with a fairly thick wire and connect the other end to the output terminal through a tapping key—the earthed end being connected to the other output terminal which is joined to the negative terminals of the filaments of the valves. This way, it has been ensured that there should be no deflection of the moving coil, produced by the current in the fixed coil, unless the tapping key is pressed.

VOLTAGE CHOSEN

It has been found by Wien (1896, 1902) Warburg, (1899, 1901) Grinnel Jones (*loc. cit.*) that, within the cell containing the electrolyte, there occurs a loss of energy at the electrodes, as the result whereof the experimentally determined resistance of the solution is larger than the true resistance. Grinnel Jones' work has established that the extra resistance ΔR due to electrode loss does not vary with dilution in the same proportion as the true resistance. Assuming this electrode loss as due to employment of a voltage higher than the decomposition voltage of the solute and the solvent, the voltage chosen in the experiment under discussion was such that its peak value was fairly smaller than the decomposition voltage. The r.m.s. value of the voltage used was not more than 100 millivolts. The assumption appears to be justified by the fact that the cell constant, as determined with normal, $\frac{1}{10}$ normal, $\frac{1}{50}$ normal and $\frac{1}{100}$ normal solution of KCl, was constant as far as the accuracy in the values of the resistances used would lead to expect.

DETERMINATION OF C_p

A method for determining C_p has been described by Mukherjee (1938). In it, the moving coil of the wattmeter is first made non-inductive by Sumpner's compensation method and then from the nullpoint corresponding to $\psi = \frac{\pi}{2}$, the value of C_p is found with the aid of the formula

$$\frac{1}{C^2 p^2} = \frac{Q}{P} R \left(R + \frac{(P+Q)G}{P+Q+G} \right)$$

Fig. 3, shows the arrangement of apparatus.

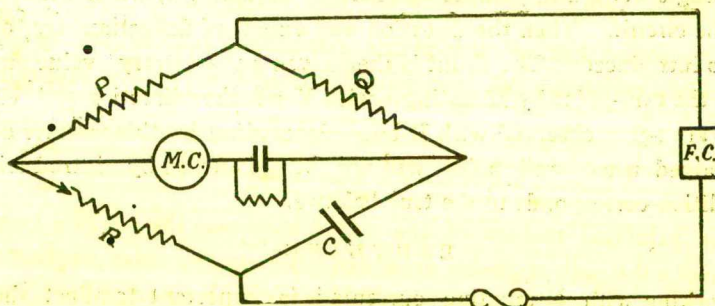


FIG. 3

Bright Platinum Electrodes for Electrolytic Resistances 5

EXPERIMENTAL RESULTS

In the actual experiment carried out in the laboratory the temperature was kept constant within $\frac{1}{500}$ th of a degree by means of a specially designed thermostat and measured with a platinum resistance thermometer. The amplifier was a simple resistance-capacity coupled one in which the anode resistances attached to the valves were much larger than the valve resistances—thus ensuring the straight-line character of the characteristic curves within a long range of grid voltages and eliminating the possibility of a feed-back effect. The output current from the amplifier was obtained through a $4\mu\text{f}$ condenser. The amplification was such as to give one ampere (output) current per volt (input).

It took the cell about 2 to 3 hours to come to a steady temperature. The resistance was measured and tested for constancy by taking readings every hour for 3 to 4 hours more. The following are the data and results obtained.

Solution used—KCl, Temperature— 31°C

Strength of Solute	Resistance	Specific Conductivity	Cell Constant	Equivalent Conductivity
N	205.54	.12460*	25.610	124.6
$\frac{\text{N}}{10}$	1765.29	.01450*	25.596	145.0
$\frac{\text{N}}{25}$	4232.8	.0060482†	...	151.2
$\frac{\text{N}}{50}$	8209.1	.003118*	25.596	155.9
$\frac{\text{N}}{75}$	12160	.0021053†	...	157.8
$\frac{\text{N}}{100}$	16052	.001595*	25.603	159.5

* From Landolt's tables. † Calculated from cell constants,
Mean cell constant—25.601.

By plotting the relation between $\frac{I}{\text{concentration}}$ and equivalent conductivity, it is found that all the points determined fall on the graph, so that the electrode resistance ΔR has an insignificant effect on the resistance of the solution.

CONCLUDING REMARKS

The principal feature of the experiment was the use of a galvanometer, which like a d.c. galvanometer gives deflection on two sides of the null-point. Such a galvanometer is more suitable for use with an amplifier than any other measuring instrument. For, even if there is a spurious current generated in

the amplifier due to a defect in its make up, that current would only pass through the moving system and not through the fixed system. On the otherhand, to produce a deflection of the moving system, it is necessary that both the fixed and the moving systems must be traversed by currents from the same source.

Another feature was the use of very low voltage between the electrodes.

ACKNOWLEDGMENTS

The author expresses his gratitude to Mr. H. Mukherjee. Lecturer in Physics of this University, for his guidance and help.

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DACCA UNIVERSITY.

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PART - 4.

ON THE MOLAR CONDUCTIVITY OF DYESTUFFS IN SOLUTION.

ON THE MOLAR CONDUCTIVITY OF DYESTUFFS IN SOLUTION.

It was pointed out by McBain(1913) that the equivalent conductivity of an electrolyte would be increased by the aggregation of ions of one kind to form ionic micelles and such aggregation was, therefore, put forward by him as the explanation of the remarkable increase of equivalent conductivity with increasing concentration observed in the aqueous solutions of soaps. Howell and Robinson(1936) have worked on the electrical conductivities of aqueous solutions of Sodium Dodecyl Sulphate and Sodium Hexadecyl Sulphate. They have found that the curve of the electrical conductivity against the square root of the concentration consists of three well defined sections. Over the first range the fall in conductivity is linear as for a simple electrolyte and is of the same order of magnitude. At the point where the first range is abruptly succeeded by the second it is shown that the mean free path of the anion is proportional to its rotational volume. Over the second range the fall in conductivity is extremely rapid. The anionic network postulated offers a satisfactory explanation and is in accordance with other properties observed over this range. At the point where the second range is succeeded by the third it is shown that the distance between the anions in the network is proportional to their length. In any homologous series the tendency to form micelle is proportional to the length of the anion. This is the point, therefore, at which the network falls into micelle formation.

Further work on this line was carried out by Robinson(1935) and his co-workers. Robinson and Moilliet determined the transport number as well as equivalent conductivities of some of the rigorously purified Dyestuffs.

Robinson(1935) has shown that Methylene Blue, which has been regarded as a dyestuff remaining in true solution, tends to form aggregates even at fairly dilute solution. Hartley, Collie and Samis (1936) have measured the equivalent conductivity and transport number of two salts with paraffin chain cations, containing 16 carbon atoms in the chain and have found evidence of the formation of ionic micelles.

We have carried out measurements of conductivity of dye-solutions at various concentrations in water and water-alcohol solvents to gain some insight as to the ionic state of dye molecules as well as to correlate the phenomena of absorption and quenching^{of} fluorescence.

EXPERIMENTAL.

The method described in the previous paper (1948) has been employed in determining conductivities of dyestuffs. With this method though the oxidising action of the platinised electrodes has been avoided, the polarisation effect cannot be removed altogether. The polarisation reactance of the solution as well as the residual inductive effect of the third arm can be balanced by using a shunted capacitance in the third arm and by making the ratio arms of equal resistance. Further, in order to reduce the electrolytic disturbance and polarisation effects to a minimum a source producing high audio frequency alternating current is generally employed. In our investigation an oscillator of the type shown in the figure was used.

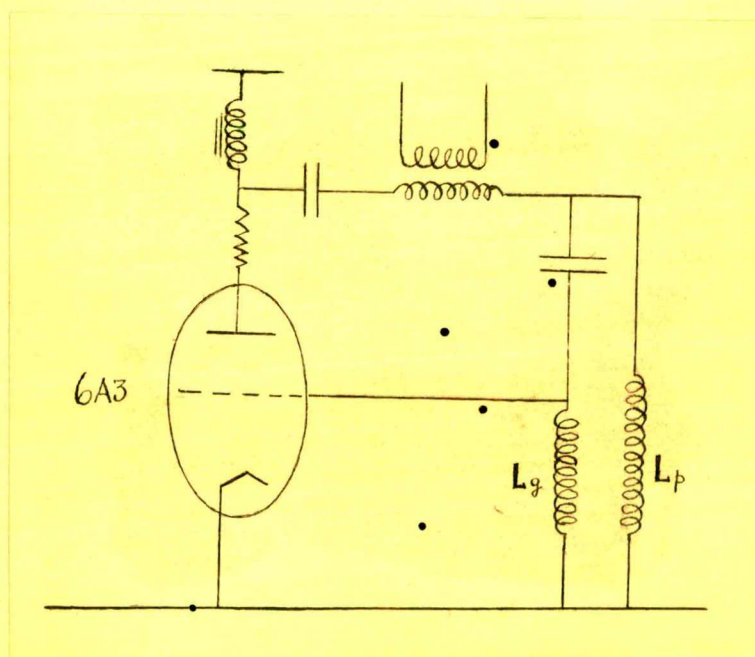


Fig.

The coils L_p and L_g are placed in such a way as to avoid mutual inductance between them and this arrangement gives a constant sinuous e.m.f. Moreover, the transformer from which the working current is derived, is placed outside the oscillating part of the circuit and therefore reactance of the working current does not alter the frequency of oscillation. The oscillator is shielded.

In the actual experiment the temperature as before, was kept constant within $\frac{1}{500}$ th of a degree and an amplifier was used to increase the sensitiveness of the bridge. The amplifier used is shown in the figure.

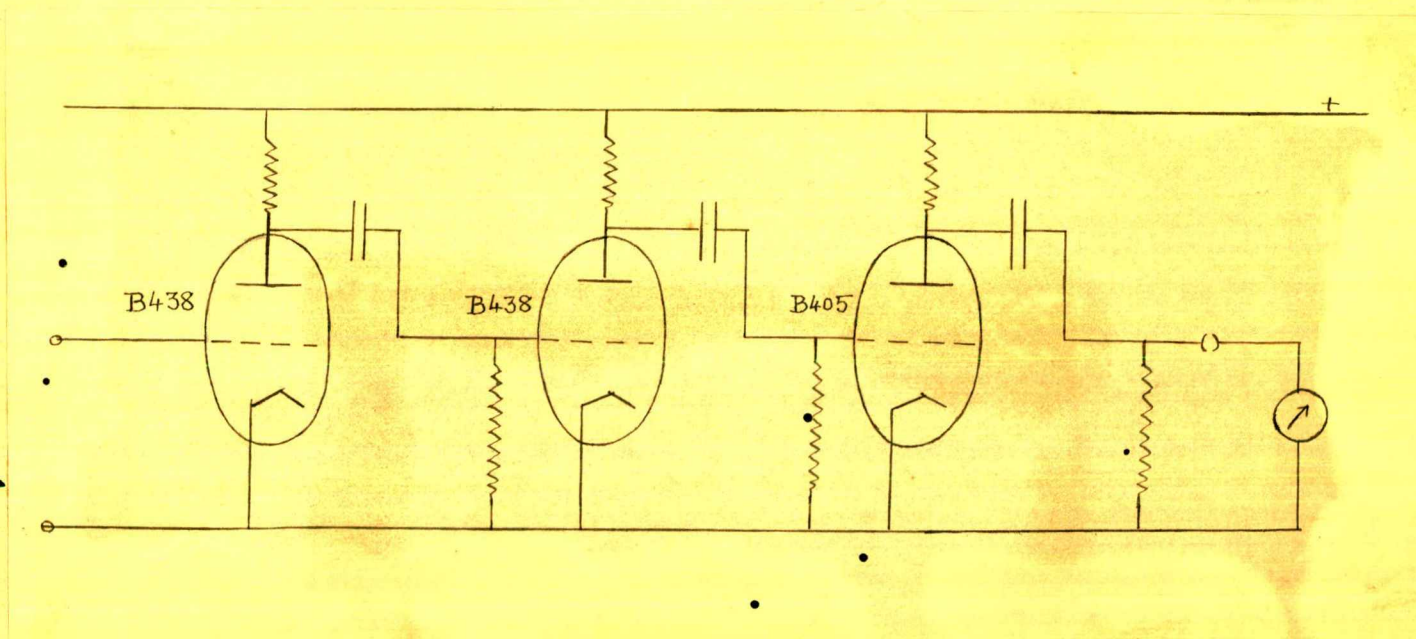


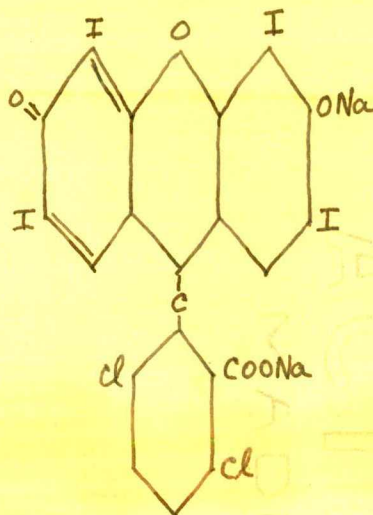
Fig.

RESULTS

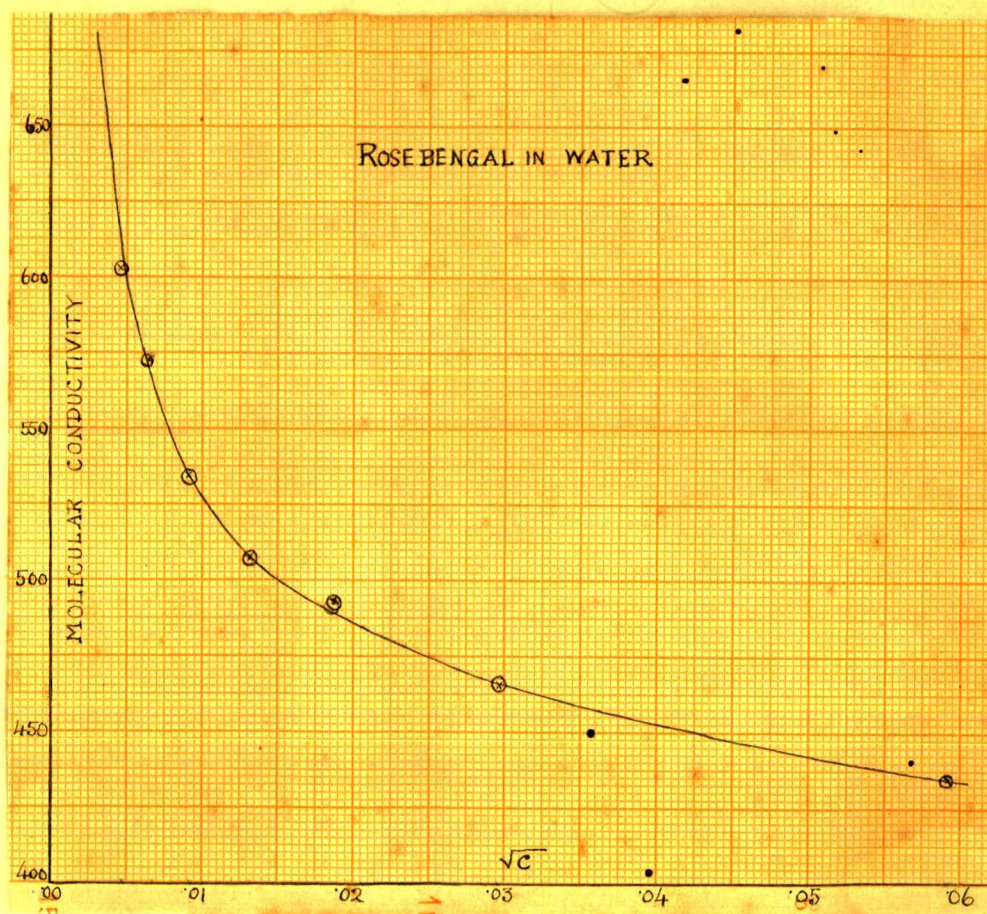
We have measured the conductivities of different dyestuffs in water and in alcoholic solution at different concentrations at constant temperature. The results of our measurements are given in the accompanying tables and graphs.

Table - 1 .

Rose Bengal in water.

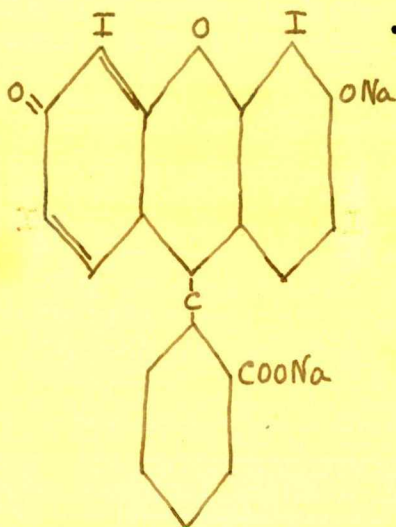


Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.003517	.05931	.001530	435.0
.0008792	.02965	.0004102	466.6
.0003517	.01875	.0001741	495.0
.0001758	.01326	.00008940	508.6
.0000879	.009375	.00004705	535.3
.0000439	.006626	.00002520	574.0
.0000219	.004680	.00001321	603.3

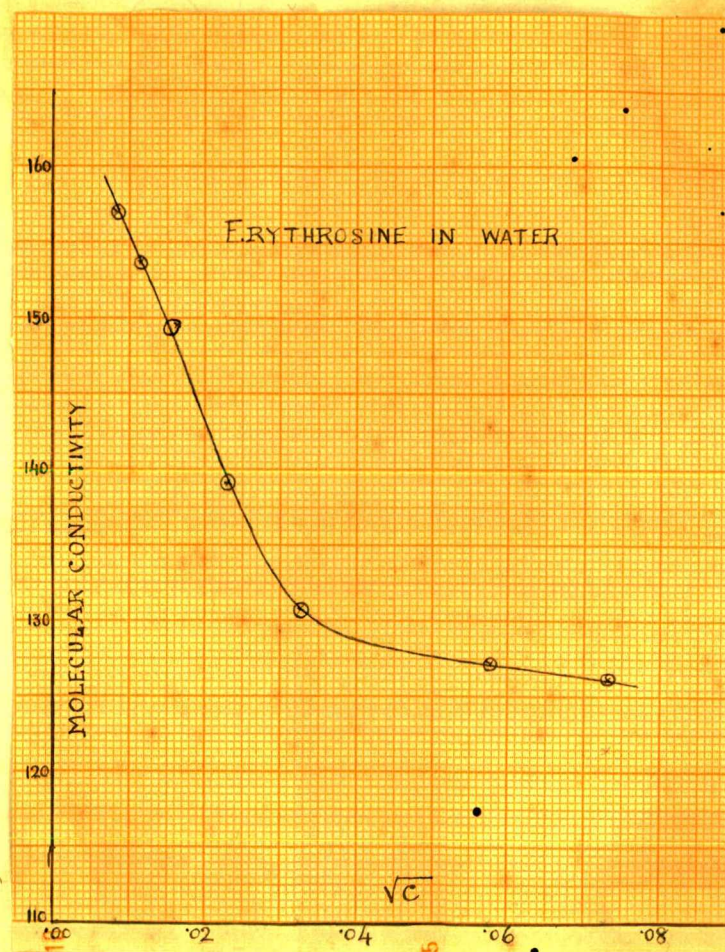


Dependence of molecular conductivity Rose Bengal in water on its concentration.

Erythrosine in water.



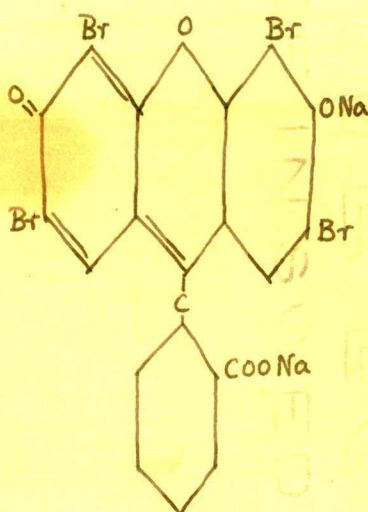
Molecular Concentration	c	$\sqrt{c}$	Sp. Conductivity	Molecular Conductivity
.005308		.07285	.0006710	126.4
.002654		.05752	.0003375	127.2
.001062		.03259	.0001389	130.8
.0005308		.02304	.00007389	139.2
.0002654		.01629	.00003970	149.6
.0001327		.01152	.00002040	153.7
.00006635		.008145	.00001042	157.0



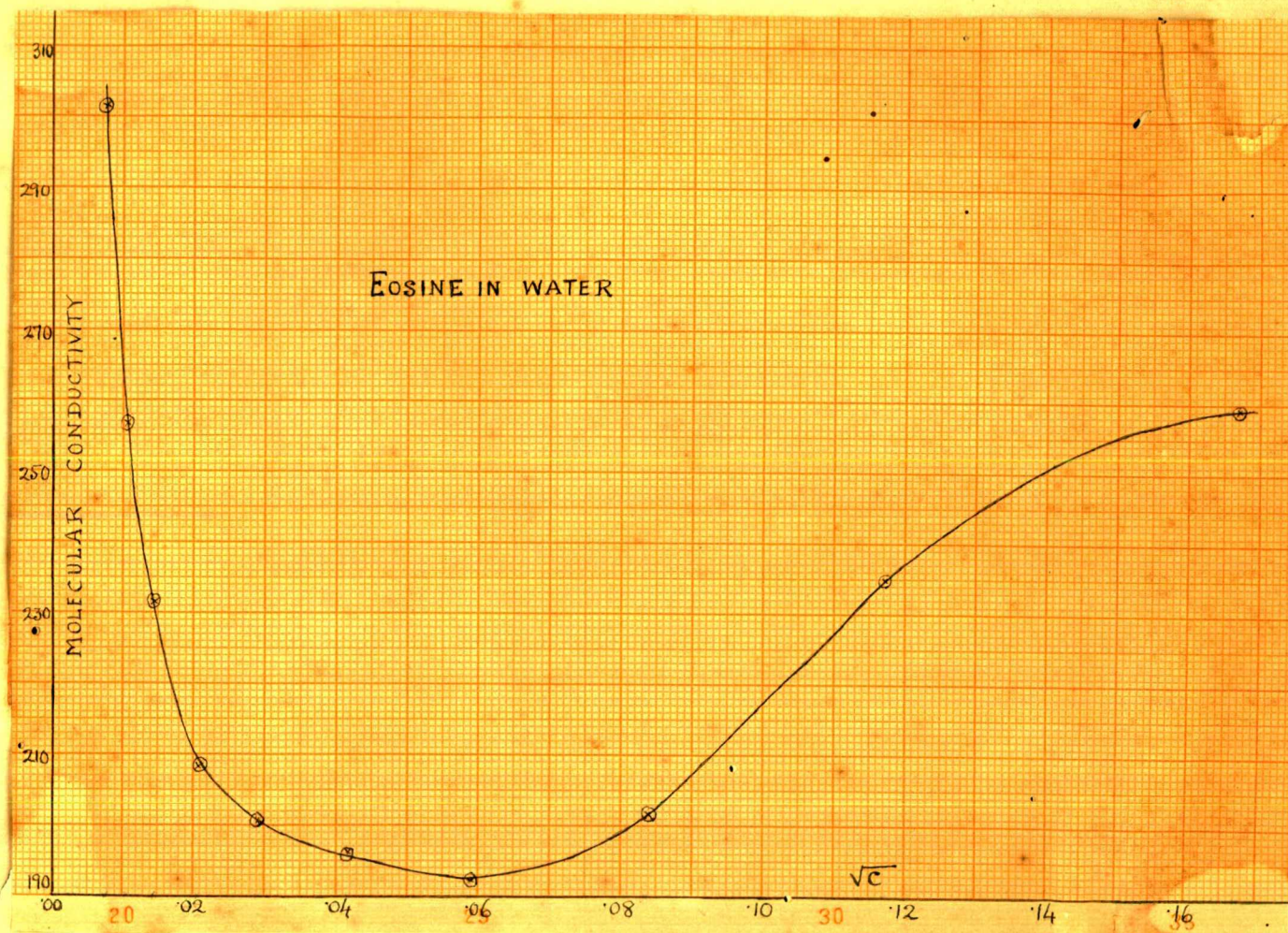
Dependence of molecular conductivity of Erythrosine on its concentration.

Table - 3.

Eosine in water



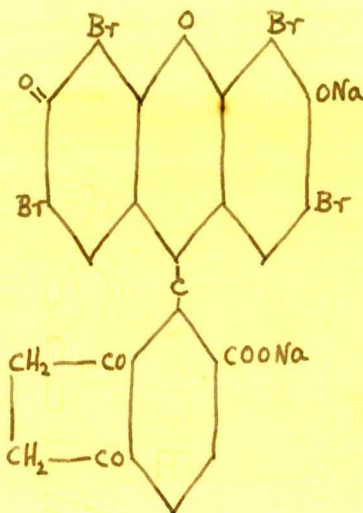
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.02792	.167	.007244	259.4
.01396	.117	.003286	235.0
.00698	.0835	.001442	201.6
.00349	.0590	.0006709	192.0
.001745	.0417	.0003432	196.3
.000872	.0290	.0001751	200.6
.000436	.0208	.00009107	208.7
.000218	.0147	.00004968	231.4
.000109	.0104	.00002800	256.7
.0000545	.0074	.00001646	301.8



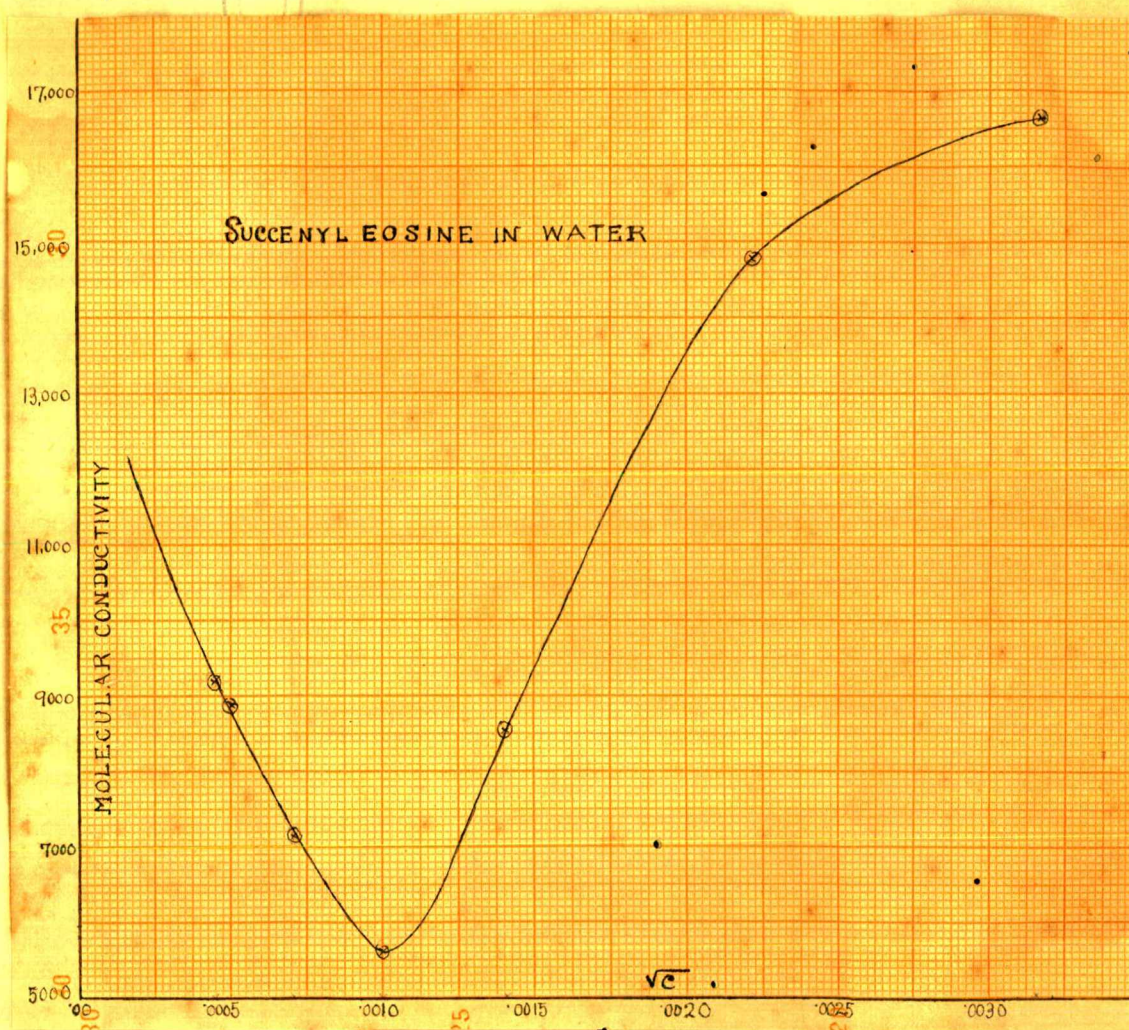
Dependence of molecular conductivity of Eosine in water on concentration.

Table - 4.

Succenyl Eosine in water.



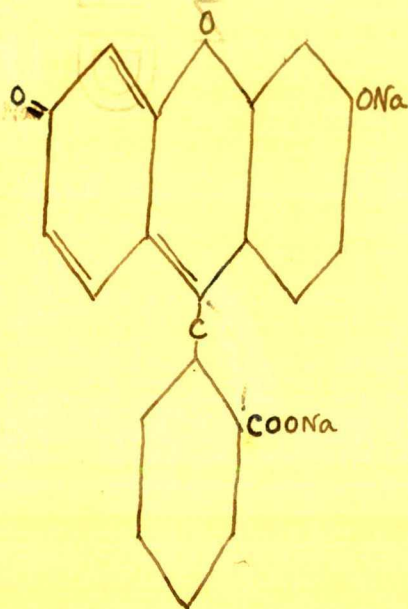
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.00002000	.004472	.0003492	17,460
.00001000	.003162	.0001667	16,670
.00000500	.002236	.00007353	14,706
.00000200	.001414	.00001707	8,535
.00000100	.001000	.00000561	5,610
.00000050	.0007072	.00000356	7,120
.00000025	.0005000	.00002227	8,908
.00000020	.0004472	.000001840	9,200



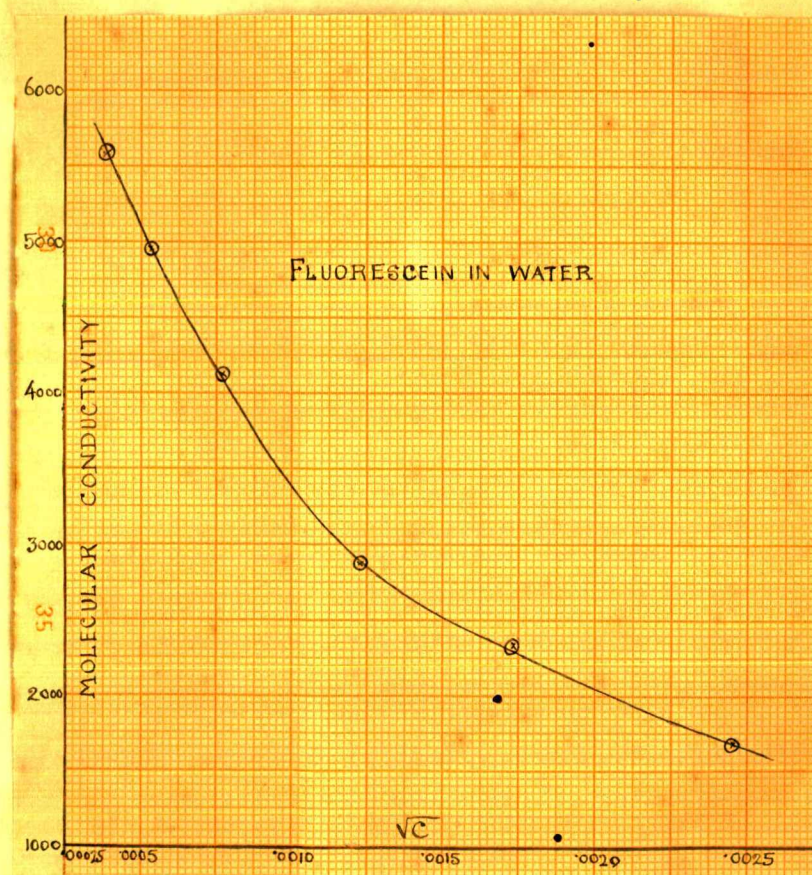
Dependence of molecular conductivity of Succenyl Eosine in water on its concentration.

Table - 5.

Fluorescein in water.



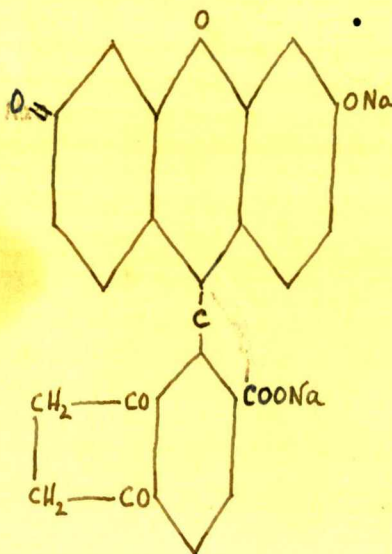
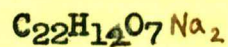
Molecular concentra- tion C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.000006024	.002455	.00001021	1695
.000003012	.001736	.000007085	2352
.000001506	.001227	.00000434	2882
.0000006025	.0007762	.00000249	4132
.0000003012	.0005488	.000001493	4958
.0000001506	.0003881	.000000840	5578



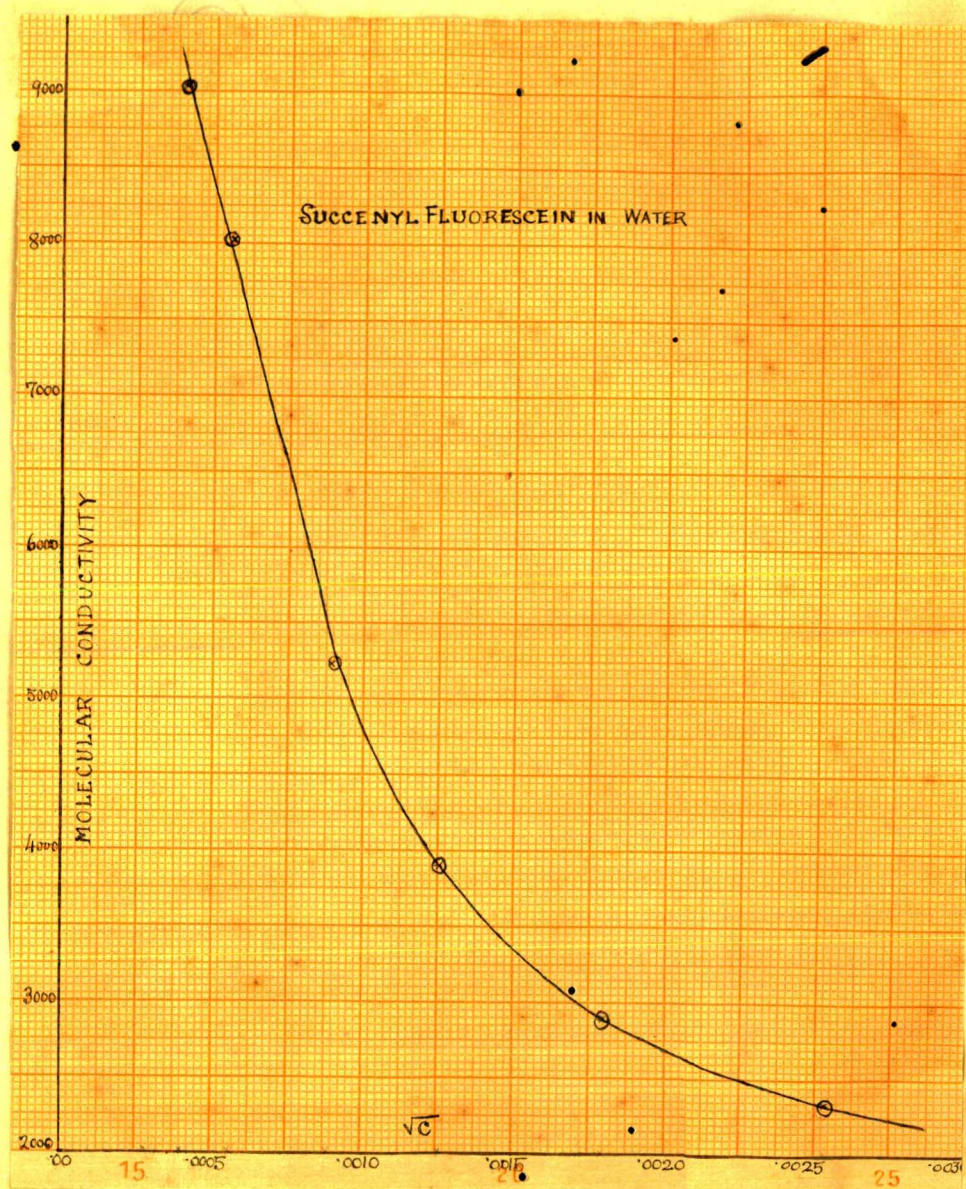
Dependence of molecular conductivity of Fluorescein in water on concentration.

Table - 6.

Succenyl Fluorescein in water.



Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.000006409	.002532	.00001501	2342
.000003204	.001790	.00000926	2891
.000001602	.001266	.00000625	3901
.000000801	.0008950	.00000418	5219
.0000003204	.0005660	.00000257	8023
.0000001602	.0004002	.000001448	9031
.0000000801	.0002830	.0000007762	9692



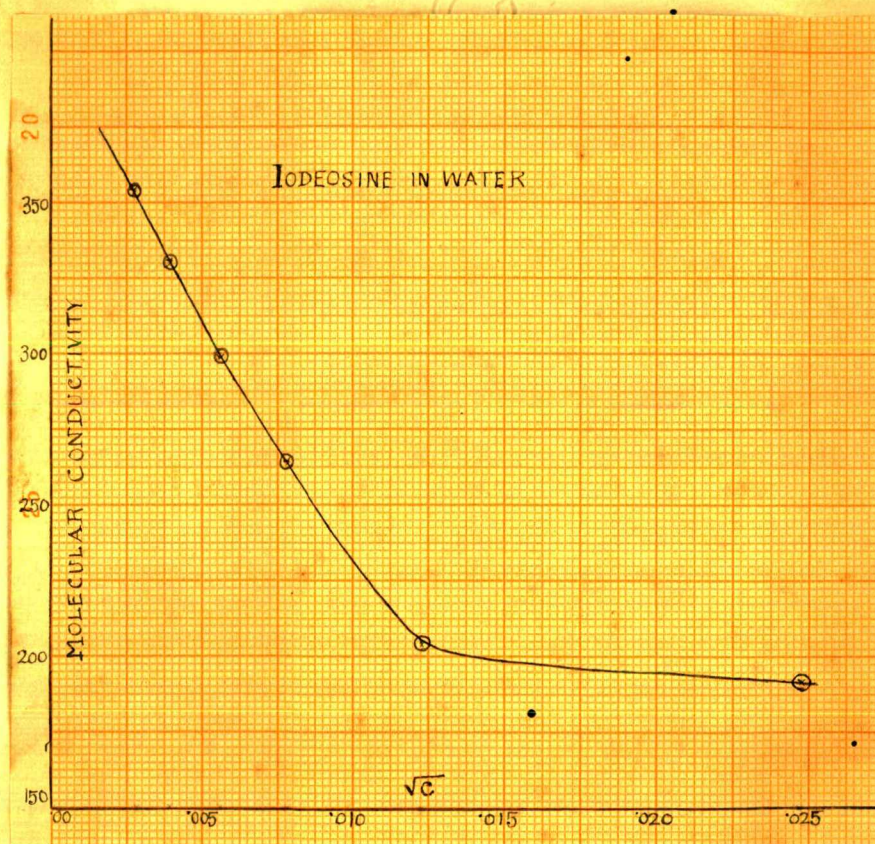
Dependence of molecular conductivity of Succenyl Fluorescein in water on concentration.

Table - 7.

Iod Eosine in water.



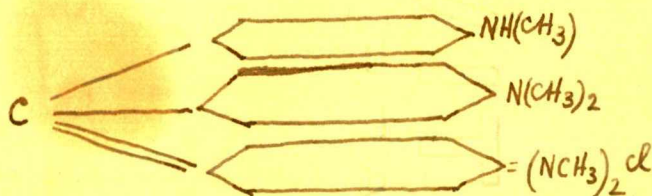
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.0006101	.02470	.0001171	192.0
.0001525	.01235	.00003111	204.0
.00006101	.007811	.00001615	264.7
.00003050	.005523	.00000914	299.6
.00001525	.003905	.00000505	331.1
.00000762	.002760	.00000270	354.3



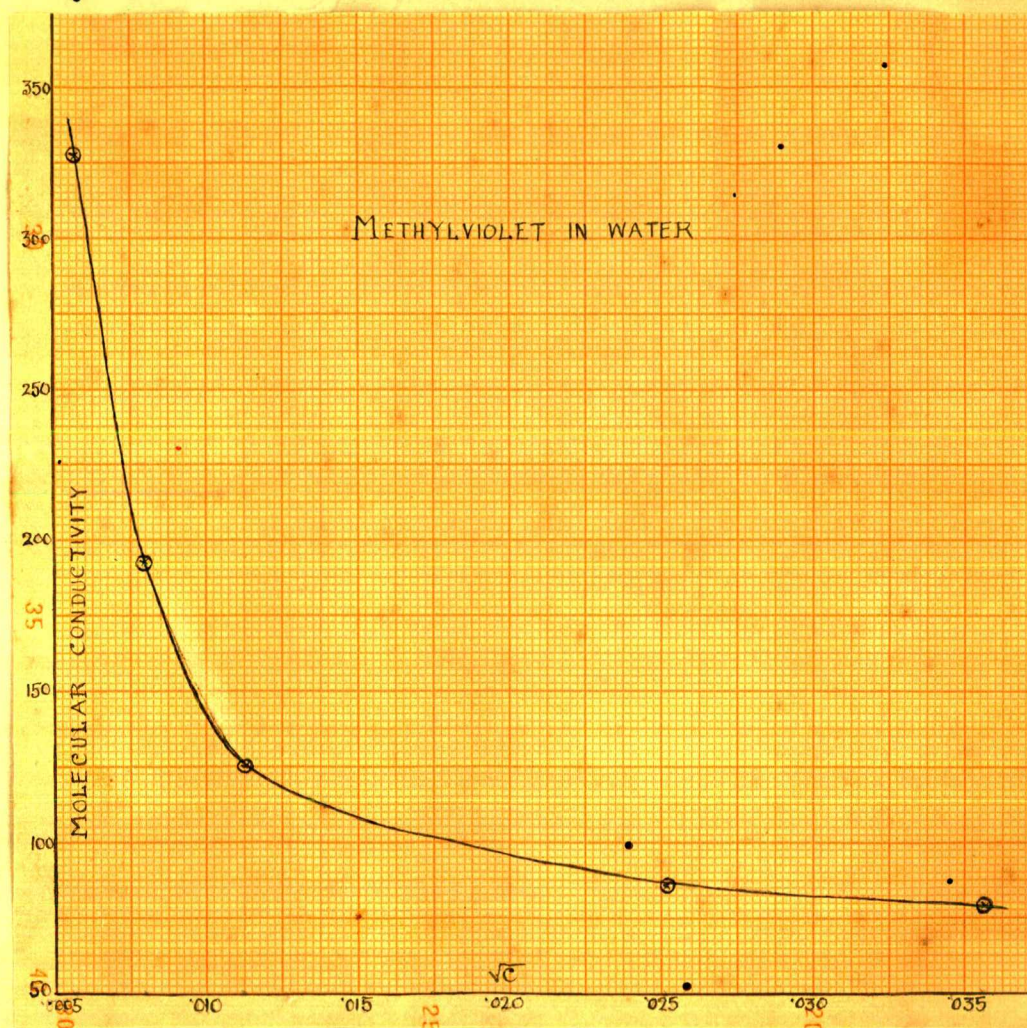
Dependence of molecular conductivity of Iod Eosine in water on concentration.

Table - 8.

Methyl Violet in water.



Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.001271		.0356	.0001021	80.35
.000635		.0252	.00005526	86.98
.0001271		.01127	.00001604	126.20
.0000635		.00790	.00001225	192.80
.00003175		.00563	.00001041	327.30



• Dependence of molecular conductivity of Methyl Violet in water on concentration.

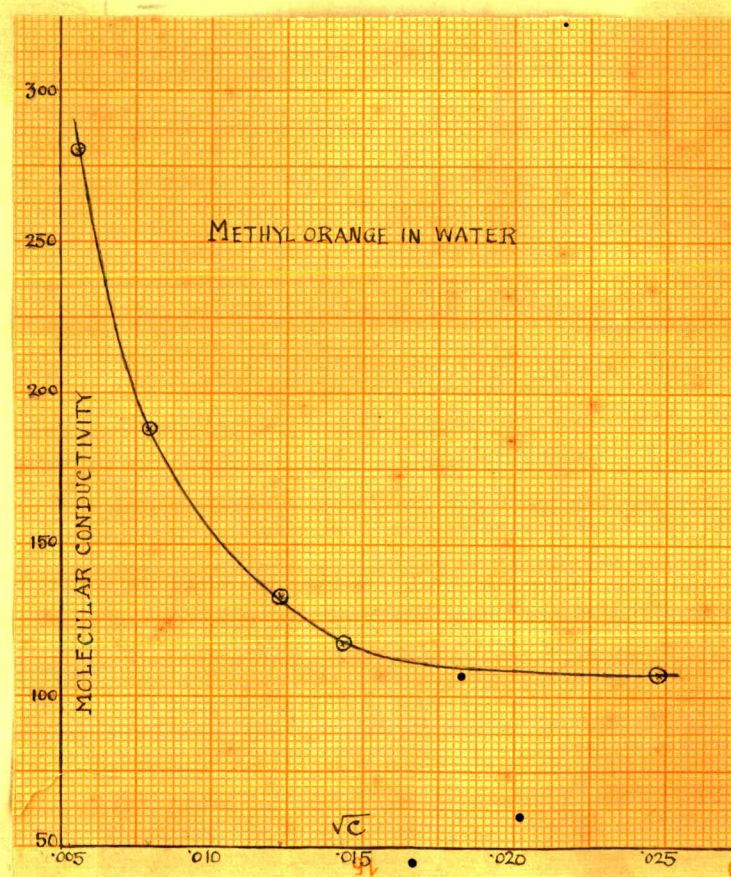
Table - 9.

Methyl Orange in water.

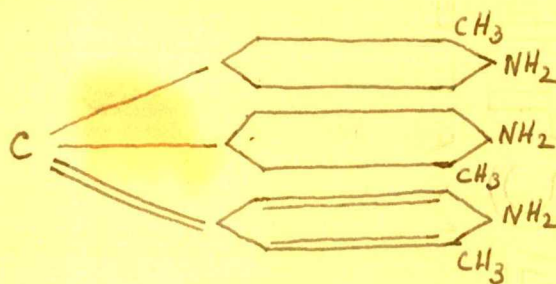


Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.0006116		.0247	.00006607	107.9
.0003058		.01435	.00003581	117.0
.0001529		.01237	.00002044	133.5
.00006116		.00790	.00001153	188.5
.00003058		.00553	.000008559	279.6

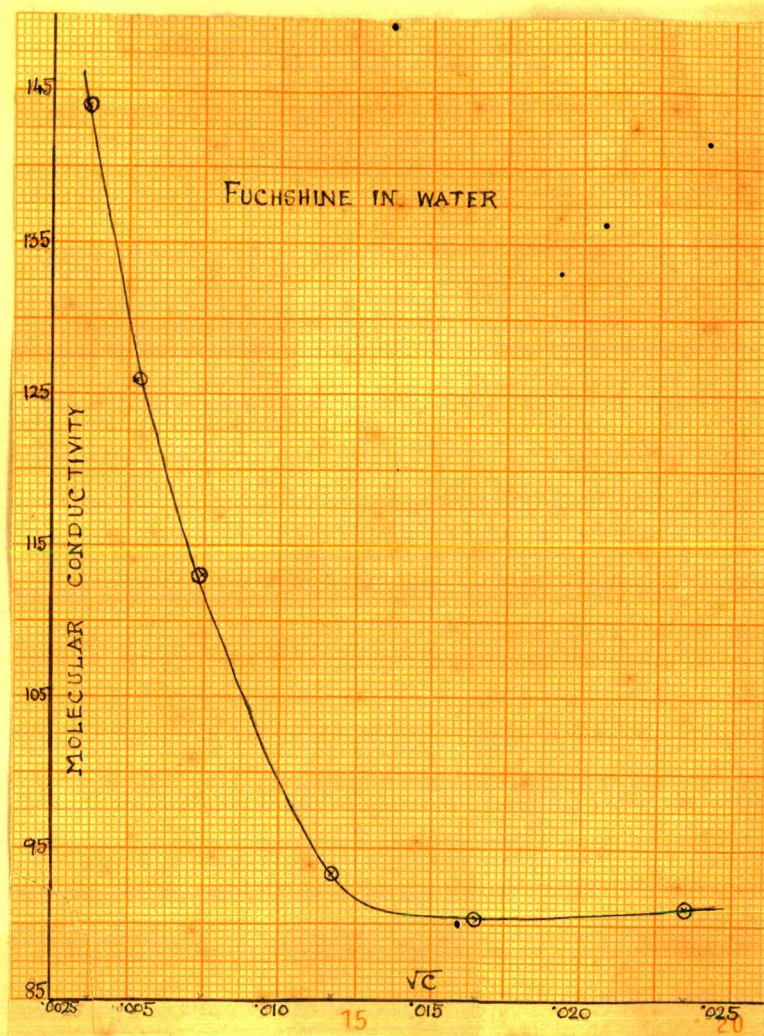
468986 .



Dependence of molecular conductivity of Methyl Orange on concentration.

Table - 10.Fuchshine in water.

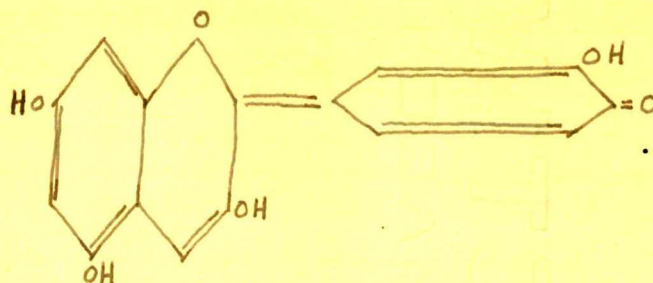
Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.0005471		.0234	.00004990	91.20
.0002735		.0165	.00002472	90.28
.0001367		.0117	.00001276	93.40
.0000547		.0074	.00000619	113.20
.00002735		.0052	.000003449	125.90
.00001367		.0037	.000001972	144.10



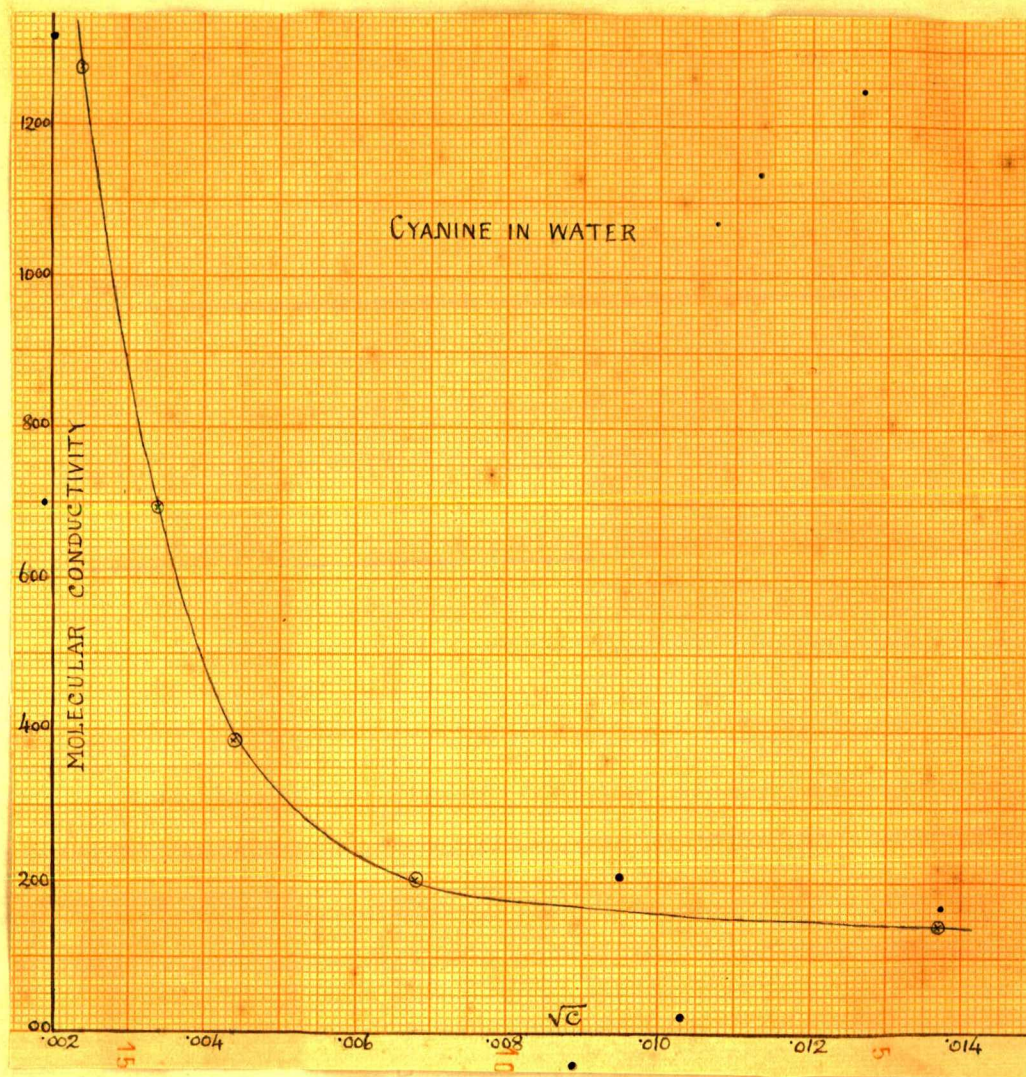
Dependence of molecular conductivity of Fuchshine in water on concentration.

Table - 11.

Cyanine in water.



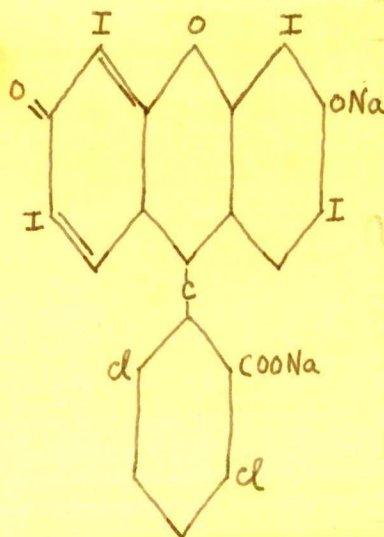
Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.0001859		.0137	.00002653	142.7
.0000465		.0068	.00001128	201.8
.00002325		.0044	.000008680	386.7
.00001162		.0034	.000007773	693.7
.00000581		.0024	.000007031	1277.0



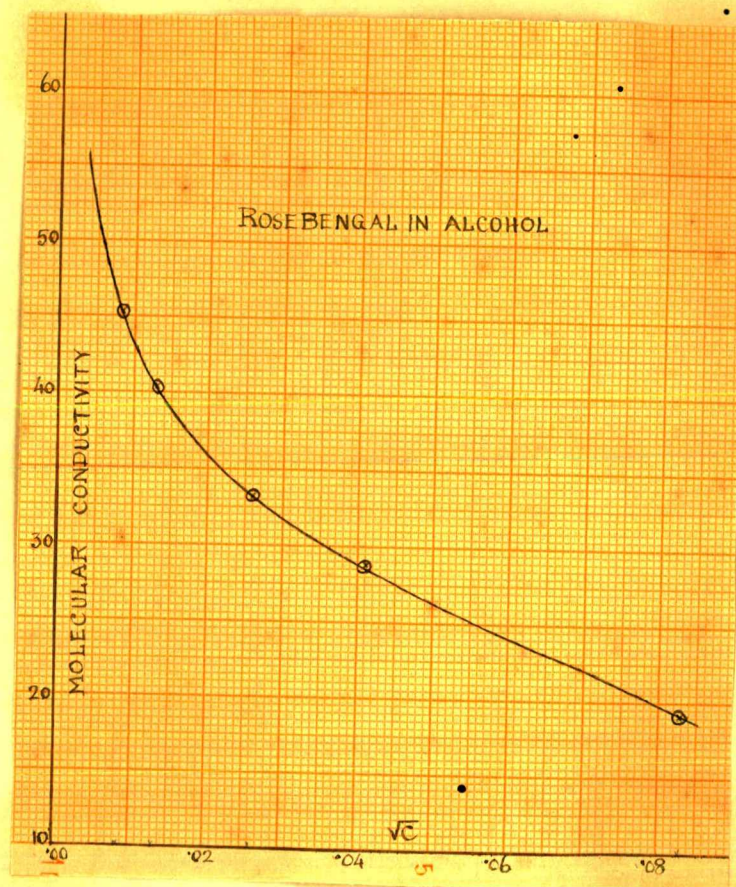
Dependence of molecular conductivity of Cyanine in water on
Concentration.

Table - 12.

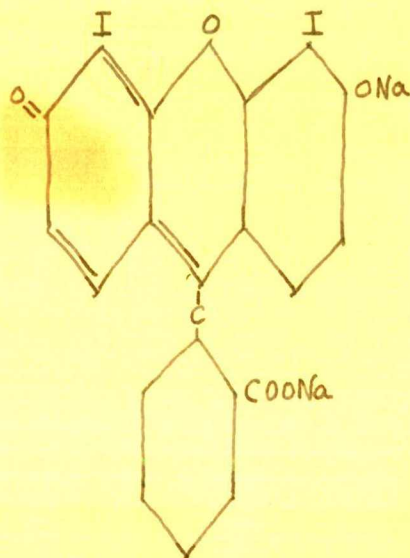
Rose Bengal in Alcohol.



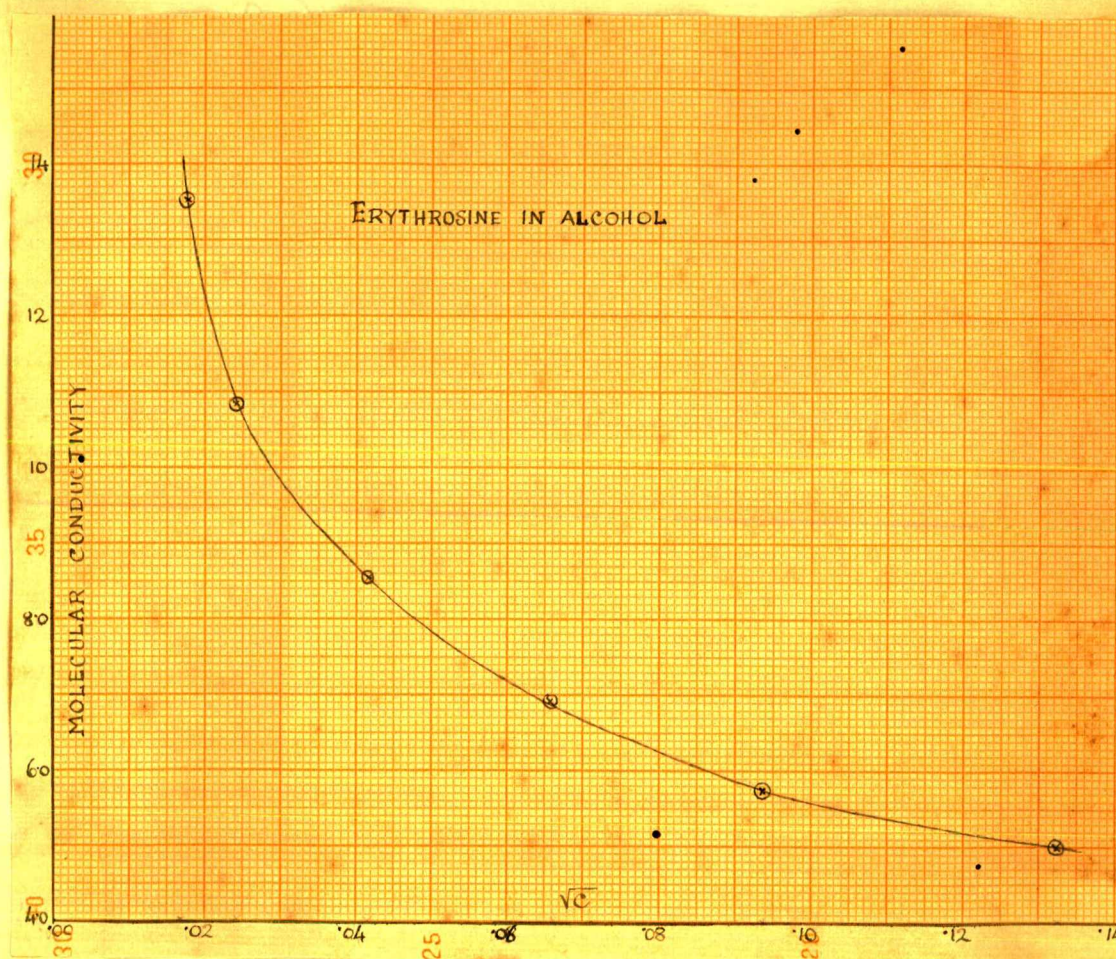
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.006855	.08279	.0001307	19.05
.001714	.04140	.0004942	28.83
.0006855	.02618	.00002274	33.16
.0001714	.01310	.00000695	40.55
.0006855	.008279	.000003112	45.38



. Dependence of molecular conductivity of Rose Bengal in Alcohol on concentration.

Table - 13Erythrosine in Alcohol.

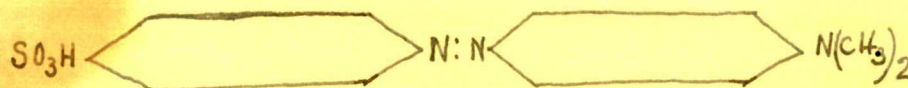
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.01752	.1324	.00008843	5.048
.008760	.09359	.00005048	5.762
.004380	.06618	.00003027	6.910
.001752	.04185	.00001499	8.557
.000584	.02417	.00000633	10.84
.000292	.01709	.00000395	13.53



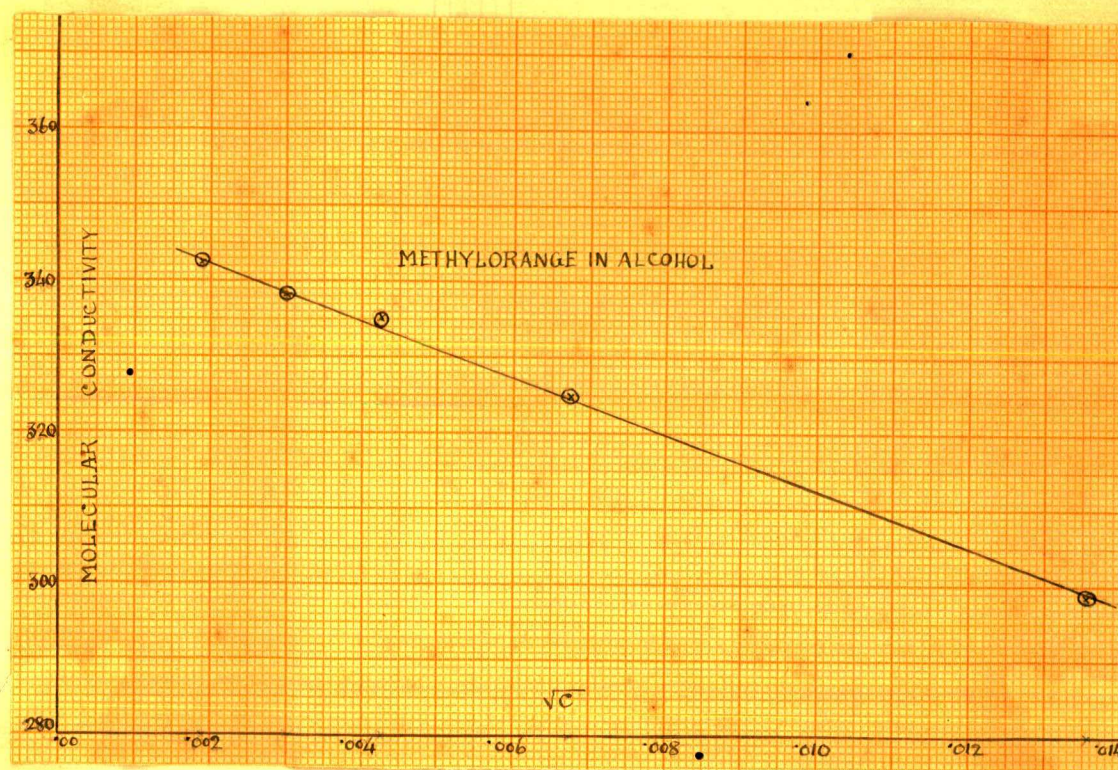
Dependence of molecular conductivity of Erythrosine in Alcohol on concentration.

Table - 14.

Methyl Orange in Alcohol.



Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.0001835	.01355	.00005475	298.4
.00004587	.006773	.00001490	324.8
.00001835	.004284	.000006150	335.2
.00000917	.003028	.000003100	338.1
.00000367	.001916	.000001258	342.7



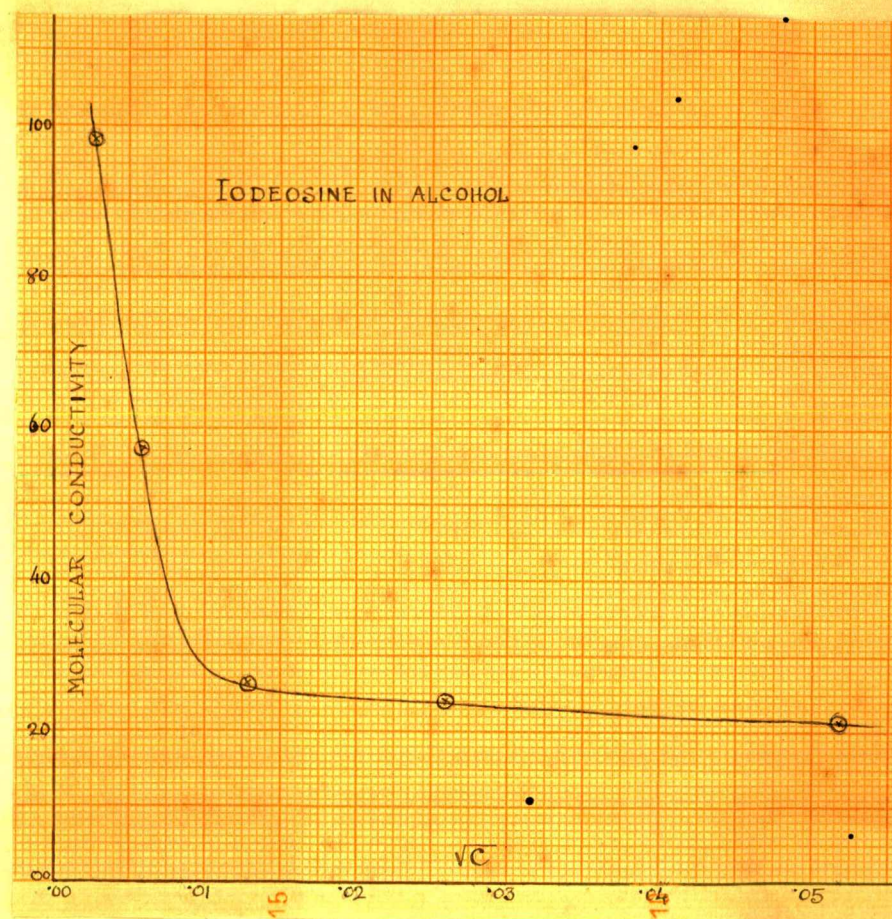
Dependence of molecular conductivity of Methyl Orange in Alcohol on concentration.

Table - 15.

Iod Eosine in Alcohol..



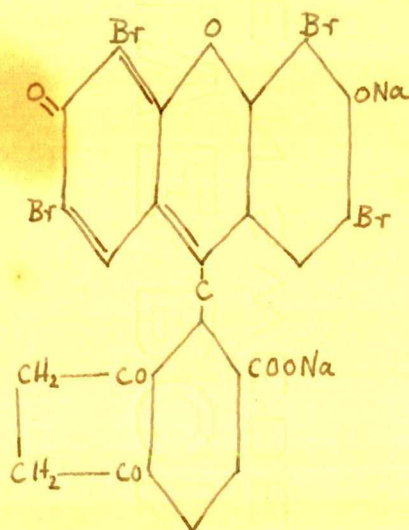
Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.002692		.05189	.00005795	21.53
.000673		.02594	.00001619	24.06
.0001682		.01297	.00000444	26.40
.00003364		.005800	.000001920	57.09
.00000672		.002594	.000000661	98.35



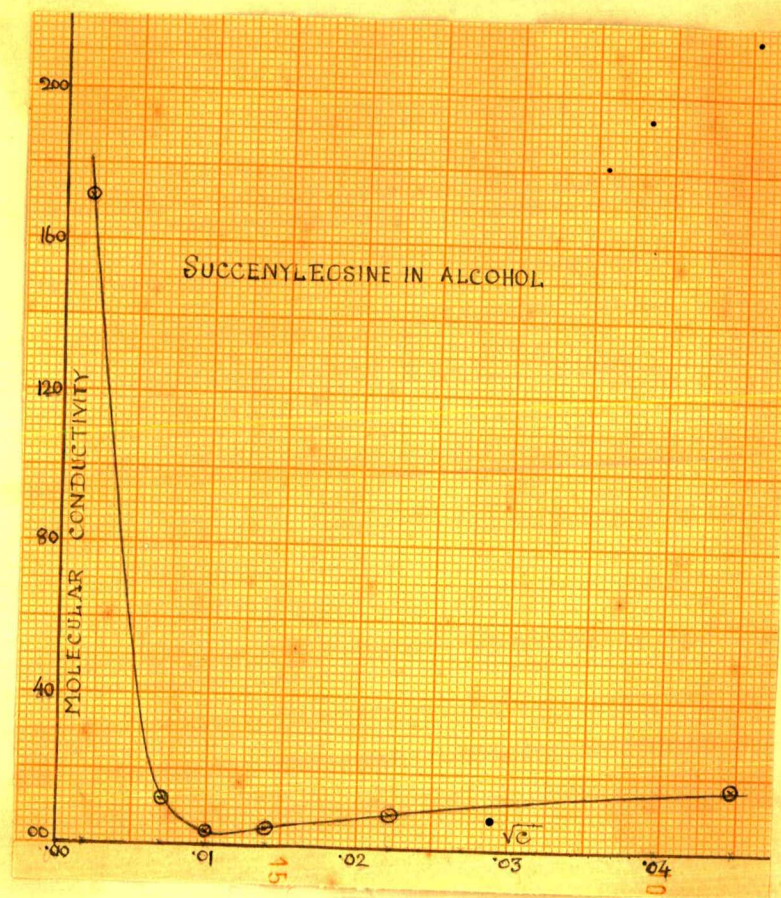
Dependence of molecular conductivity of Iod Eosine in Alcohol on
concentration.

Table - 16.

Succenyl Eosine in Alcohol.



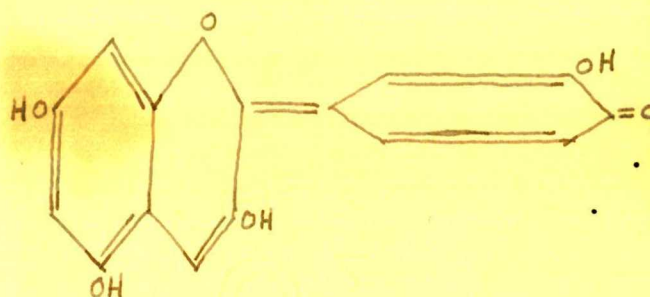
Molecular Concentration C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.002000	.04472	.00003438	17.19
.000500	.02236	.00000457	9.139
.0002000	.01414	.000000912	4.560
.0001000	.010000	.0000004035	4.035
.0000500	.007071	.000000594	11.88
.0000025	.001581	.000000429	171.6



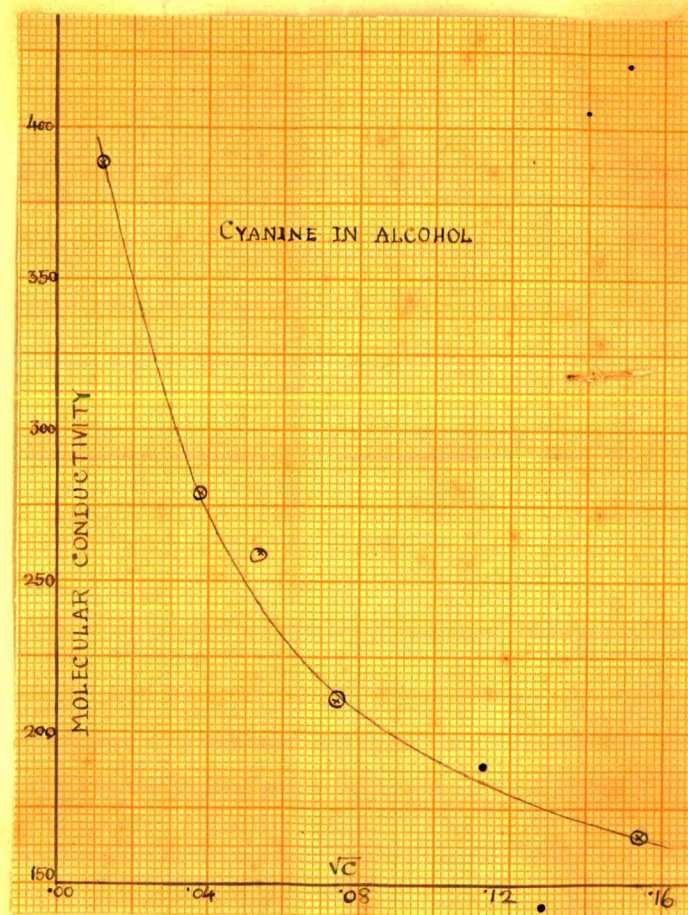
Dependence of molecular conductivity of Succenyl Eosine in Alcohol on concentration.

Table - 17.

Cyanine in Alcohol.



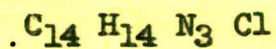
Molecular Concentration, C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.02324	.152	.0003845	165.5
.00581	.076	.0001236	211.7
.002905	.054	.00007532	259.2
.001452	.038	.00004055	278.9
.000242	.016	.000009406	388.6



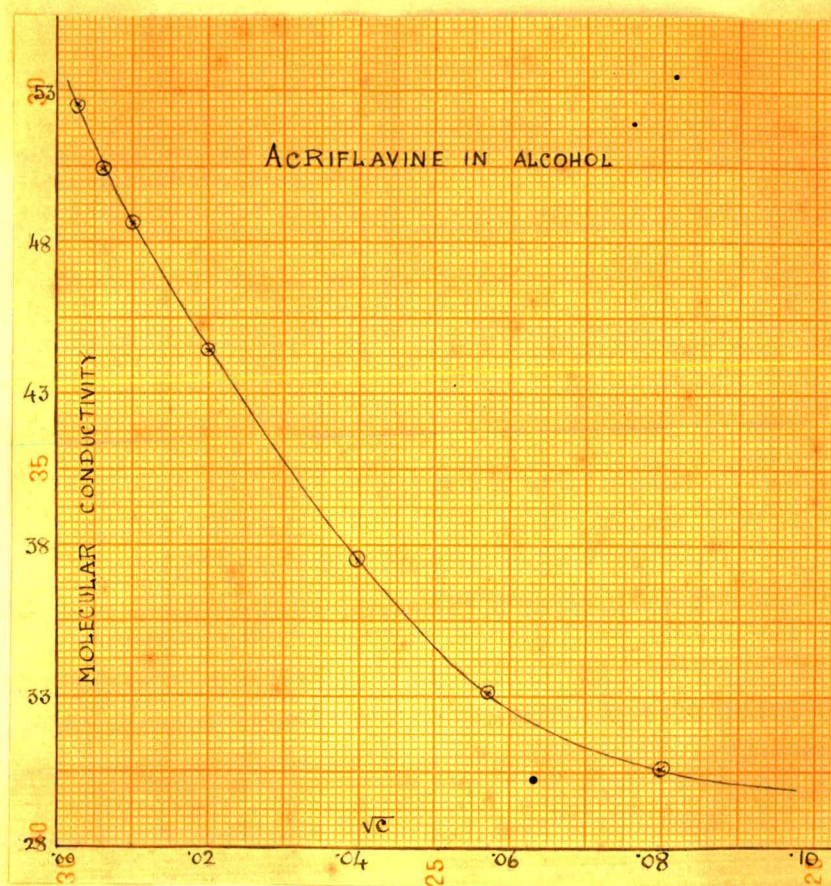
Dependence of molecular conductivity of Cyanine in Alcohol on concentration.

Table - 18.

Acriflavine in Alcohol.



Molecular Concentration	C	$\sqrt{C}$	Sp. Conductivity	Molecular Conductivity
.006560		.08099	.0002010	30.65
.003280		.0572	.0001086	33.10
.00164		.0405	.00006149	37.5
.00041		.0202	.00001821	44.4
.000102		.0101	.000004967	48.7
.000034		.00583	.000001714	50.4
.0000085		.00292	.0000004471	52.6



Dependence of molecular conductivity of Acriflavine in Alcohol on concentration.

It appears from the graphs that the molecular Conductivities of dyestuffs in aqueous solution do not have linear relations with square roots of concentration. The molecular conductivities when plotted against square root of concentration give curves in most of the cases similar to those of Dodecyl Sulphate and Hexadecyl Sulphate as found by Howell and Robinson. The curves are in fact identical with the second and third region of the curves found by them. This clearly shows the formation of ionic micelles at the point where the second range is succeeded by the third. Moilliet, Collie, Robinson and Hartley (1935) have worked on this line and according to them conductivity measurements alone may not give in all cases direct evidence of the formation of ionic micelles. The measurement of transport number together with the conductivity measurements however furnishes conclusive evidence of the formation of ionic micelles. In our present case, however, the shape of the curves furnishes enough proof of the formation of ionic micelles. In most of the cases the fall in conductivity is extremely rapid and is followed by a region where the conductivity either rises to maximum in certain cases or remains practically constant. At the point where the second range is succeeded by the third the net work falls into micelle formation.

In the case of alcoholic solution also there is no perfect linear relationship between the molecular conductivity and square root of concentration and the conductivity-concentration curves are similar to those for aqueous solution. Only in the case of Methyl Orange in Alcohol the electrical conductivity falls as a linear function of the square root of concentration and it is evident that Methyl Orange in Alcohol is present wholly as simple ions. The difference in the

behaviour of dyestuffs in these two solvents may be due to different degree of aggregation of ions. It has been shown by Mitra that quenching co-efficients of dyestuffs in alcoholic solution are distinctly less than in aqueous solution which also supplies evidence as to the low association in alcoholic solution.

At the point where the second range is succeeded by the third the network falls into ionic micelles. It is interesting to note that this critical concentration at which the network falls into ionic micelles fairly coincides (as found by Sen Goopta- thesis, Dacca, 1938 and others) with the concentration after which rapid quenching of fluorescence begins. It therefore, supports the view that quenching of fluorescence is due to the formation of ionic micelles.

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PART - 5.

ON THE AVERAGE LIFE -PERIOD OF FLUORESCING DYESTUFFS.

ON THE AVERAGE LIFE-PERIOD OF FLUORESCING DYE STUFFS.

The mean life of the fluorescing molecules in the excited state has a direct bearing on quenching. Wawilow(1929)(1931), Sevensni Koff (1935), Mitra(1939) and others have determined the average life-period of the fluorescing molecules from measurements on polarisation. For an increase in concentration of the dyestuff either the effective value of T will remain unaltered or probably due to increase in the number of collisions, the mean period of duration of the molecules in the excited state will be diminished. This on the basis of Perrin's (1929) theory will amount to an increase in the value of polarisation. The measurement of polarisation and the average life-period calculated thereof, therefore, furnish evidence as to the cause of quenching. Our measurements have, therefore, been extended to the determination of the polarisation of fluorescence of dyestuffs at various concentrations.

The experimental arrangement is fully discussed in a subsidiary paper(1944) entitled ' On the polarised fluorescence - dyestuffs in solution. Measurements were made on the polarisation of fluorescence of the dyestuffs under investigation in glycerine-water mixtures, whose relative proportions and hence the viscosity could be varied over a wide range. T was calculated from the expression of Perrin viz.

$$\frac{1}{p} = \frac{1}{p_0} + \left[\frac{1}{p_0} - \frac{1}{3} \right] \cdot \frac{RQ}{V\eta} T$$

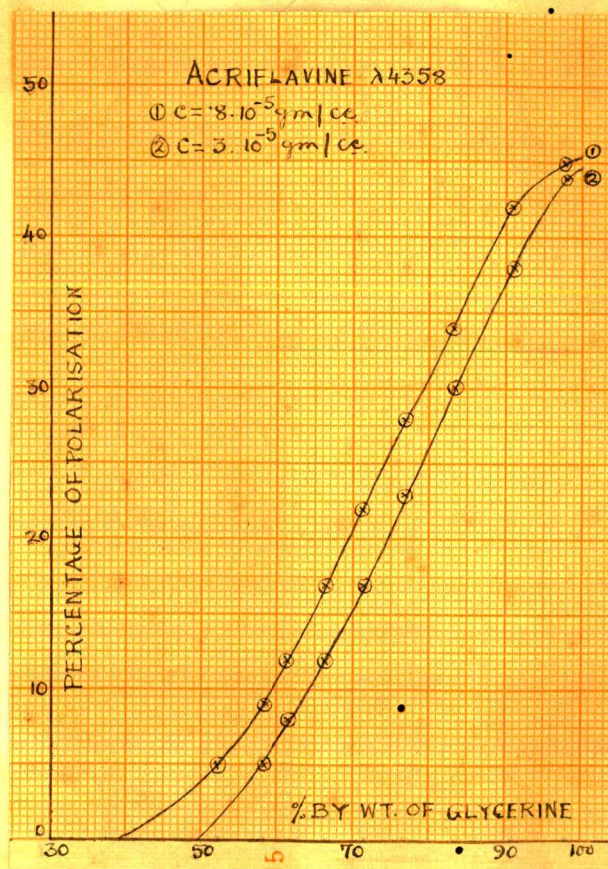
Where p is the degree of polarisation observed under the actual condition of the experiment and p_0 the value for the same molecules when they are not allowed to rotate from their initial orientations. R is the gas constant, V , the gramme-molecular volume, η the co-efficient of viscosity and θ the absolute temperature and T the mean duration of the fluorescing molecules in the excited state.

Table - 1.

Polarisation of Acriflavine in glycerine-water mixture

Exciting wave length - λ 4358 A

Percentage by wt. of glycerine.	Viscosity in poises.	Percentage of Polarisation.	
		$C=3.10^{-5}$ gm./c.c.	$C=8.10^{-5}$ gm./c.c.
98.0	4.56	41	45
90.9	1.65	38	42
83.3	0.611	30	34
76.9	0.367	23	28
71.4	0.185	17	22
66.6	0.127	12	17
62.5	0.097	8	12
58.5	0.070	5	9
51.2		almost zero	5



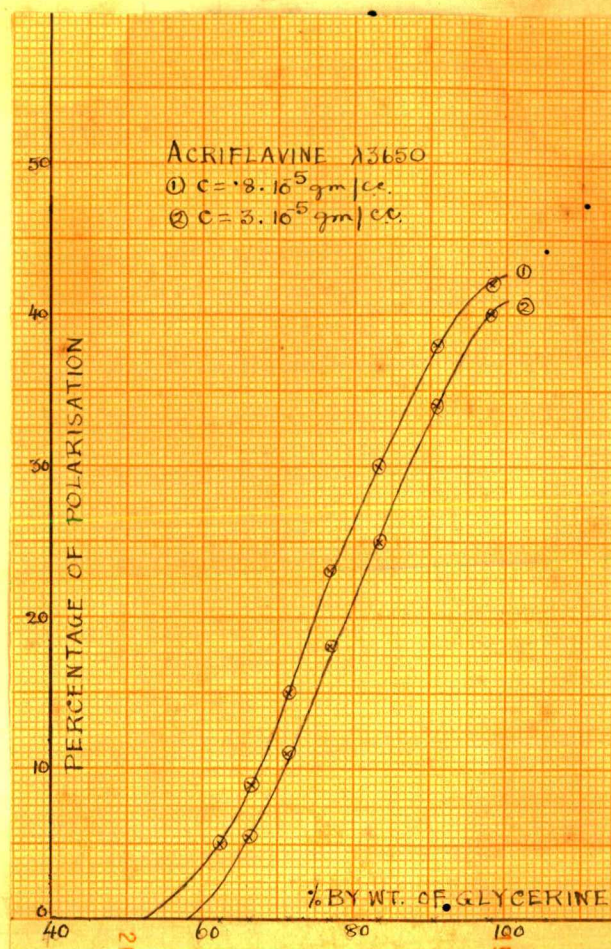
Percentage of polarisation of the fluorescence of Acriflavine in glycerine-water mixtures, excited by $\lambda 4358 \text{ A.}$

Table - 2.

Percentage of polarisation of Acriflavine in glycerine water

: mixture. Exciting wave length - λ 3650 A.

Percentage by wt. of glycerine	Viscosity in poises	Percentage of polarisation	
		C= $3 \cdot 10^{-5}$ gm./c.c.	C= $8 \cdot 10^{-5}$ gm./c.c
98.0	4.56	40	42
90.9	1.65	34	38
83.3	.611	25	30
76.9	.367	18	23
71.4	.187	11	15
66.6	.127	6	9
62.5	.097	—	5

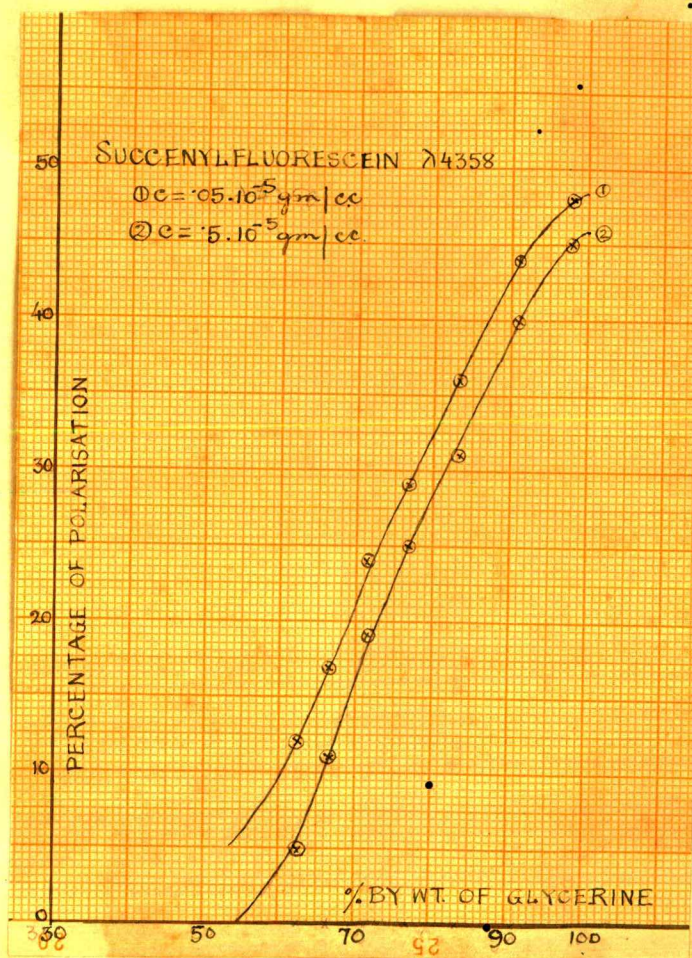


Percentage of polarisation of the fluorescence of Acriflavine in
 glycerine -water mixtures, excited by $\lambda 3650 \text{ A.}$

Table - 3.

Percentage of polarisation of Succenyl Fluorescein in glycerine-water mixtures. Exciting wave length λ 4358 Å.

Percentage by wt. of glycerine	Viscosity in poises.	Percentage of polarisation	
		$C = .05.10^{-5} \text{ gm./c.c.}$	$C = .5.10^{-5} \text{ gm./c.c.}$
98.	4.56	48	45
90.9	1.65	44	40
83.3	0.611	36	31
76.9	0.367	29	25
71.4	0.185	24	19
66.6	0.127	17	11
62.5	0.097	12	5

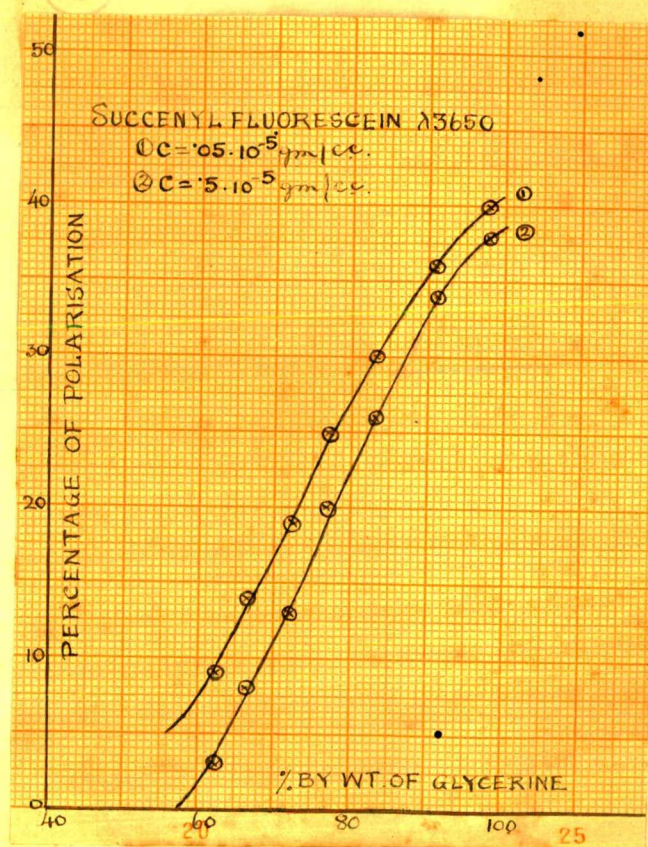


Percentage of polarisation of the fluorescence of Succenyl Fluorescein
~~in~~ in glycerine -water mixtures, excited by $\lambda 4358 \text{ A}$

Table - 4.

Percentage of polarisation of Succenyl Fluorescein in glycerine -
water mixture . Exciting wave length λ 3650 Å.

Percentage by wt. of glycerine.	Viscosity in poises.	Percentage of polarisation.	
		$C = .05.10^{-5}$ gm./c.c	$C = .5.10^{-5}$ gm./cc
98.0	4.56	40	38
90.9	1.65	36	34
83.3	0.611	30	26
76.9	0.367	25	20
71.4	0.185	19	13
66.6	0.127	14	8
62.5	0.097	9	3



- Percentage of polarisation of the fluorescence of Succenyl Fluorescein in glycerine water mixtures excited by $\lambda 3650 \text{ A.}$

It will be seen from the accompanying tables and graphs that in all cases the degree of polarisation tends at high viscosity to reach asymptotically the maximum limiting value p_0 , whereas at low viscosity the polarisation tends towards zero value. The limiting value depends not only on the nature of the dyestuffs but also on the wave length of exciting radiation.

The mean life of the fluorescing molecules in the excited states has been calculated, the following tables give the result of our calculation. It is evident from the nature of the expression for T that for values of p very near p_0 , as also very near zero, the calculated value of T cannot be reliable. Hence T has been calculated only for the values of $p > .10 < .45$

Table - 5.

Average life T of Acriflavine in glycerine water mixture.

Viscosity in poises.	Excitation by $\lambda 4358$		Excitation by $\lambda 3650$	
	$C=3.10^{-5}$ gm./c.c.	$C=.8.10^{-5}$ gm/c.c.	$C=3.10^{-5}$ gm/c.c	$C=.8.10^{-5}$ gm/c.c
1.65	12.10^{-9} Sec	$7.5.10^{-9}$ Sec		
0.611	11.10^{-9} "	$6.9.10^{-9}$ "	10.10^{-9} Sec	6.10^{-9} Sec
0.367	13.10^{-9} "	$7.1.10^{-9}$ "	11.10^{-9} "	$7.0.10^{-9}$ "
0.185	12.10^{-9} "	$7.4.10^{-9}$ "	12.10^{-9} "	$7.7.10^{-9}$ "

Table - 6.

Average life T of Succenyl Fluorescein in glycerine water mixture.

Viscosity in poises.	Excitation by $\lambda 4358$				Excitation by $\lambda 3650$			
	$C = .5.10^{-5}$ gm/c.c		$C = .05.10^{-5}$ gm/c.c		$C = .5.10^{-5}$ gm/c.c		$C = .05.10^{-5}$ gm/c.c	
.1.65	10.6.10 ⁻⁹	Sec.	6.0.10 ⁻⁹	Sec	9.7.10 ⁻⁹	Sec.	6.8.10 ⁻⁹	Sec.
.611	9.7.10 ⁻⁹	"	6.1.10 ⁻⁹	"	9.4.10 ⁻⁹	"	6.1.10 ⁻⁹	"
.367	9.7.10 ⁻⁹	"	6.8.10 ⁻⁹	"	10.1.10 ⁻⁹	"	6.2.10 ⁻⁹	"
.185	10.10 ⁻⁹	"	5.2.10 ⁻⁹	"	10.3.10 ⁻⁹	"	5.6.10 ⁻⁹	"

It is evident from the tables that within the limits of experimental errors the values of T are practically independent of the viscosity (provided it is low), though the values are widely different for the different concentrations of the dyestuffs. Moreover, the values of the average life are independent of the exciting wavelength.

Table - 7.

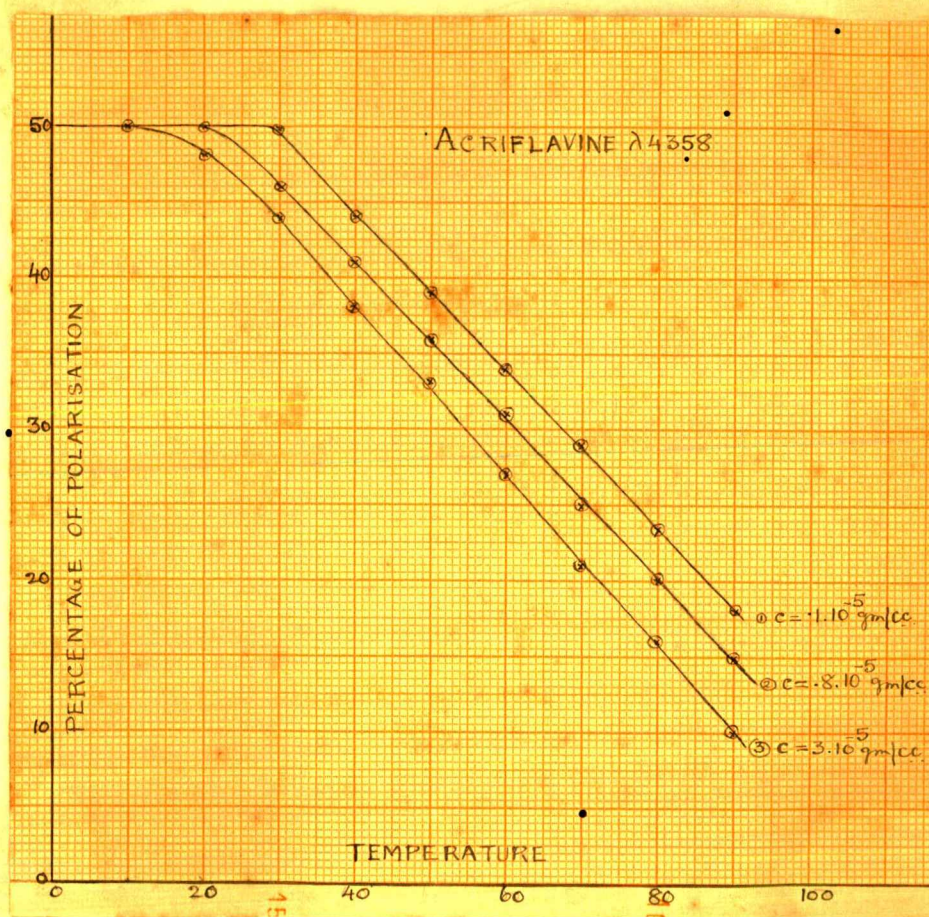
Influence of temperature on the polarisation of fluorescence of
Acriflavine in glycerine excited by λ 4358 .

Temperature in °C	Percentage of Polarisation.		
	$C=3.10^{-5}$ gm/c.c	$C=.8.10^{-5}$ gm/c.c.	$C=.1.10^{-5}$ gm/c.c.
10	50	50	50
20	48	50	50
30	44	46	50
40	38	41	44
50	33	36	39
60	27	31	34
70	21	25	29
80	16	20	23
90	10	15	18

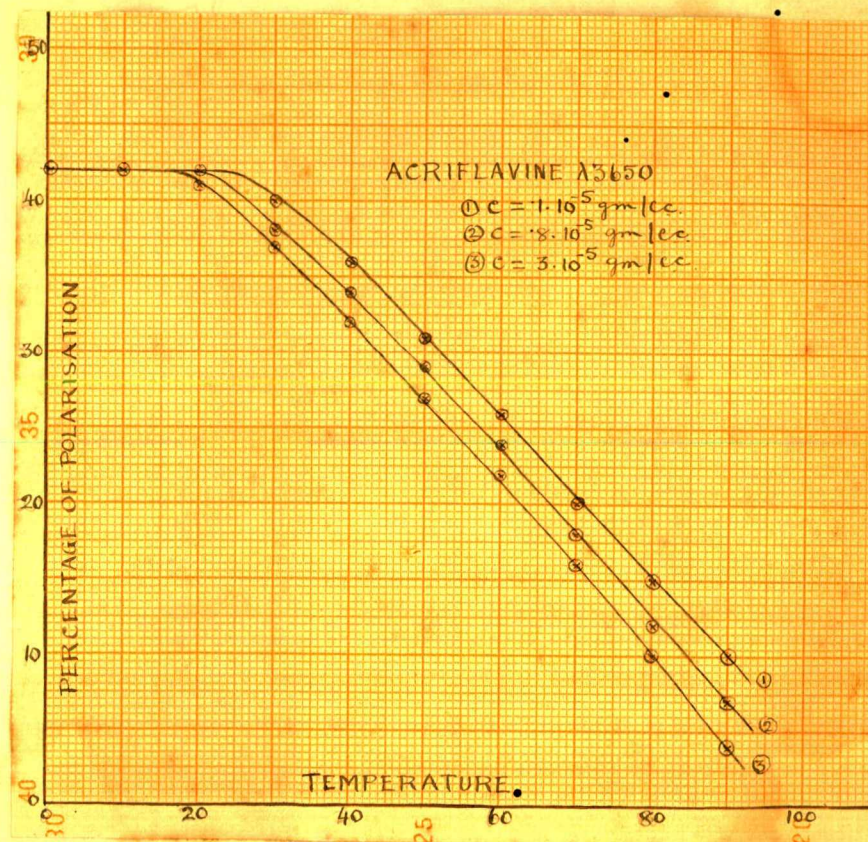
Table - 8.

Influence of temperature on the polarisation of fluorescence of
Acriflavine in glycerine excited by $\lambda 3650$.

Temperature in °C	Percentage of Polarisation.		
	C= 3.10^{-5} gm/c.c.	C= $.8.10^{-5}$ gm/c.c.	C= $.1.10^{-5}$ gm/c.c
0	42	42	42
10	42	42	42
20	41	42	42
30	37	38	40
40	32	34	36
50	27	29	31
60	22	24	26
70	16	18	20
80	10	12	15
90	4	7	10



Influence of temperature on the polarisation of fluorescence of
Acriflavine in glycerine excited by $\lambda 4358$.



Influence of temperature on the polarisation of fluorescence of
 Acriflavine in glycerine, excited by $\lambda 3650$.

The general nature of the curves is the same as that representing the variation of p with the viscosity. At low temperatures p tends to reach asymptotically the limiting value p_0 as for large viscosities, while at higher temperature p tends to vanish. On calculating the value of T on the basis of Perrin's theory we get the following results:-

Table - 9.

Influence of temperature on the Average life of the Acriflavine molecules in the excited state. Exciting wavelength $\lambda 3650 \text{ A.}$

Temperature in $^{\circ}\text{C}$	Average life of the molecules.					
	$C=3.10^{-5}$ gm/c.c		$C=.8.10^{-5}$ gm/c.c		$C=.1.10^{-5}$ gm/c.c	
30	13.10^{-9}	Sec.	8.10^{-9}	Sec.	—	
40	13.10^{-9}	"	9.10^{-9}	"	6.10^{-9}	Sec.
50	11.10^{-9}	"	8.10^{-9}	"	6.10^{-9}	"
60	13.10^{-9}	"	9.10^{-9}	"	7.10^{-9}	"

Table - 10.

Influence of temperature on the Average life of the Acriflavine molecules in the excited state. Exciting wavelength λ 3650 A.

Temperature in °C	Average life of the molecules.					
	C=3.10 ⁻⁵ gm/c.c.		C=.8.10 ⁻⁵ gm/c.c.		C=.1.10 ⁻⁵ gm/c.c	
30	13.10 ⁻⁹	Sec	10.10 ⁻⁹	Sec	-	
40	13.10 ⁻⁹	"	10.10 ⁻⁹	Sec	7.10 ⁻⁹	Sec.
50	11.10 ⁻⁹	"	9.10 ⁻⁹	"	7.10 ⁻⁹	Sec.
60	13.10 ⁻⁹	"	10.10 ⁻⁹	"	7.10 ⁻⁹	Sec.

These results reveal that though the value shows a very striking dependence on the concentration of the dyestuff, it is practically independent of the temperature within the ranges of concentrations we have studied. This shows that only effects of raising temperature are through increased thermal agitation, and the consequent larger value of expectation of the Brownian rotation of the dyestuff molecules per second and through diminished viscosity.

It has already been shown that the average life period is practically independent of temperature, viscosity and wavelength but is widely different for different concentrations. The following tables show the dependence of T on concentration.

Table - 11.

Variation of T with the concentration of Succ. Fluorescein in
glycerine at 30°C

Con. 10^{-5} gm/c.c.	$T \cdot 10^9$ Sec.
.05	6
.5	10
1	13
5	18
10	40

Table - 12.

Variation of T with Concentration of Acriflavine in glycerine
at 30°C .

Conc. 10^{-5} gm/c.c	$T \cdot 10^9$ Sec
.1	6.5
.8	9
3.0	13
6.0	17
12.0	45

It will be seen from the tables that T increases with concentration of the fluorescing molecules. This result is least expected as we should naturally expect that when we increase the concentration of the fluorescent dyestuffs, either the effective value of T remains unaltered or probably due to increase in the number of collisions, the excited molecules will have a tendency to dissipate their energy in the form of kinetic energy of translation of the molecules. This would be equivalent to diminishing the mean period of duration of the molecules in the excited state. Our results show the opposite effect. Since T is practically independent of temperature, viscosity and wavelength, the reason for this abnormal behaviour of T with concentration is to be sought in the loss of intensity due to micelle formation.

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ON THE POLARISED FLUORESCENCE OF DYE-STUFFS OF SOLUTION

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ON THE POLARISED FLUORESCENCE—PART
DYESTUFFS IN SOLUTION

By KRISHNADAS CHOUDHURI

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ABSTRACT. The variation of the polarisation of fluorescence of the dyestuffs with the wavelengths of the exciting radiation has been investigated in detail. It is found that the polarisation decreases with the increase in wavelength of the exciting radiation, reaches a negative value and then increases again. The negative value occurs at wavelengths of the exciting radiation characteristic for the molecules of the dyestuff. A comparison of the polarisation curves and the absorption curves of the fluorescent dyestuffs has also been made.

The variation of the polarisation of fluorescence of the dyestuffs with the change of (1) the viscosity of the solution, (2) the temperature of the solution and (3) the concentration of the dyestuff has been investigated experimentally. It has been observed that the degree of polarisation tends to vanish asymptotically at low viscosities or at high temperatures or at high concentrations of the dyestuffs, while the polarisation tends to attain asymptotically a certain maximum value at very high viscosities or low temperatures or at very low concentration of the dyestuff. For a particular solvent this maximum value is dependent on (1) the nature of the dyestuff, (2) the wavelength of the exciting radiation. Besides the investigations mentioned above the average life of the dyestuff molecules in the excited state has also been calculated. The results have been discussed on the basis of Perrin's theory.

INTRODUCTION

The phenomenon of fluorescence of the dyestuffs in solution is quite well known and a lot of experimental investigations has been made during recent years. But the results obtained by the various workers are highly contradictory and the discrepancy is so much wild and wide that they can be considered only as giving the order of the magnitude. This is true of all the dominion of fluorescence, including the phenomena of polarisation of the fluorescent radiation emitted by the dyestuffs in solution.

In view of the contradictory nature of the results obtained by the various workers a systematic measurement was undertaken on the polarisation of fluorescence of a few dyestuffs in solution and its exact dependence on the wavelengths of the exciting radiations, on the temperatures, concentration of the dyestuff in solution and the viscosities of the solvent. For our measurements we have selected a set of dyestuffs which has not been systematically investigated as yet. The present report gives the results of our measurement. The results in the case of the inorganic compounds will be given in a subsequent report.

EXPERIMENTAL ARRANGEMENT

The experimental arrangement adopted in our present investigation is as follows :—Light from a mercury arc, automatic zinc or cadmium arcs, rendered monochromatic with the help of a monochromator or suitable colour filters was focused by a lens on a fused quartz cell containing the fluorescent solution. In order to eliminate the uncertain polarisation introduced by the monochromator a polarising prism of Glan type was introduced between the cell and the lens. Thus the fluorescent light was excited by plane polarised monochromatic radiation. The

partial polarisation of the transverse fluorescent light was measured in the usual way with a double image prism and a nicol (Cornu method). Measurements were also made with a Savart plate and an analyser coupled with a pile of glass plates.

As regards the notation adopted by us, the measurements refer to the fluorescent radiation normal to the plane containing the direction of vibration and the direction of propagation of the incident light. The fluorescent light, as already alluded to, is partially polarised, its vibration along with direction of propagation I_2 being usually less intense than that of vibration I_1 perpendicular to the above direction, the percentage of polarisation is given by the relation

$$P = \frac{I_1 - I_2}{I_1 + I_2} \cdot 100 = p_{100}; \text{ when } I_2 > I_1, P \text{ is negative.}$$

DEPENDENCE OF POLARISATION OF THE FLUORESCENCE ON THE EXCITING WAVELENGTHS

The fact that the polarisation of the fluorescent radiations emitted by the dyestuffs in viscous solution depends markedly on the wavelength of the exciting radiation was first observed by Frohlick (1925) and nearly a systematic study was first attempted by Wawilow (1929, 1931) who measured the polarisation of a few dyestuffs (Fluorescein, Eosin, Rhodamine) in glycerine solution, when excited by five different wavelengths. The experimental arrangement used by him was to use the light from the monochromator (which was illuminated by a mercury arc) to excite the fluorescence, and measure the polarisation by the Cornu method. Wawilow assumed that the light issuing out of the monochromator, which was used for the excitation of the fluorescence is perfectly unpolarised: but it can readily be seen (as was observed by Krishnan and Sirker, 1931) if a measurement be made that the light issuing out of the monochromator is in general considerably polarised,—the actual degree of polarisation differing for different wavelengths. This may be explained as arising out of the selective refraction of the two principal vibrations at the refracting faces of the prism, coupled with a rotation of the plane of polarisation on passing through the quartz parts of the monochromator. On the face of this, the results obtained by Wawilow cease to be of much significance. Later on, Mitra (1939), Jablonski (1934) and Griseback (1936) carried out a systematic investigation on the point.

The results of our measurements of the polarisation of fluorescence excited by different wavelengths are given in the following tables. These tables conclusively show that the polarisation generally decreases to a minimum value as the wavelengths of the exciting radiations decrease and then increases on the further decrease of the wavelengths. This minimum value is negative (*i.e.*, $I_2 > I_1$) and is reached when the exciting light is *near about* $\lambda_{3131} \text{ \AA}$.

Jablonski observed that in the cases of Rose Bengal and other colouring matters in glycerine solutions, the polarisation of the fluorescent radiation progressively decreased with the decrease in wavelengths of the exciting radiation—under the ultraviolet excitation, the polarisation practically vanishes. We are unable to agree with his observation even in the case of Rose Bengal. It seems that Jablonski measured the polarisation of the fluorescent light only for a very few exciting radiations of widely spaced wavelengths and was consequently misled to the wrong conclusions.

It may be mentioned in passing that Griseback observed in the case of eosin that the polarisation attains the maximum negative value at two wavelengths of the exciting radiation instead of at one ($312 \text{ m}\mu$), which was observed by Wawilow and Mitra. But in all the different dyestuffs that have been investigated, we did not observe any such thing.

TABLE I

Percentage of polarisation of fluorescence of a few dyestuffs in glycerine solution

Temperature : -28°C
Concentration : c gm/c.c.

Wavelengths in $m\mu$	Succ. Fluorescein $c = 5 \cdot 10^{-5}$	Pinakriptol yellow $c = 25 \cdot 10^{-5}$	Acriflavin $c = 8 \cdot 10^{-5}$
546	...	36	...
535	...	40	...
517	...	42	...
509	...	43	...
436	45	41	45
405	45	...	44
365	41	38	40
320	0	...	...
313	-10	20	-7
298	-9	-8	...
278	6	0	...
265	20	...	...
254	31	12	36

TABLE I—contd.

Percentage of Polarisation of a few dyestuffs in glycerine solution

Wavelengths in $m\mu$	Pinafavol $c = 05 \cdot 10^{-5}$	Rose Bengal $c = 5 \cdot 10^{-5}$	Succ. Eosin $c = 4 \cdot 10^{-5}$	Erythrosin $c = 4 \cdot 10^{-5}$
546	46	42	39	50
535	...	...	43	50
509	...	...	...	49
436	36	38	45	45
405	...	...	...	41
365	26	27	27	24
326	...	...	-8	8
313	14	-9	-9	-10
298	-8	...	-7	-5
278	-8	...	...	...
254	20	37	36	35

POLARISED FLUORESCENCE IN OTHER SOLVENTS

We have also measured the polarisation of the fluorescent radiation emitted by these dyestuffs in other solvents. The solvents used were castor oil, collodion-ether mixture, sugar solution, etc. The Tables and curves show beyond doubt that the value of "P" is different for different solvents, the general nature of the graphs practically remains the same as in glycerine.

TABLE II

Percentage of Polarisation of Fluorescence in Castor oil

Concentration : c gm/c.c.
Temperature : -28°C

Wavelength in $m\mu$	Succ. Fluorescein $c = 5 \cdot 10^{-5}$	Succ. Eosin $c = 4 \cdot 10^{-5}$	Acriflavin $c = 8 \cdot 10^{-5}$	Pinafavol $c = 05 \cdot 10^{-5}$
546	...	35	...	42
436	42	40	42	32
365	38	25	35	24
326	0	-10	...	...
313	-12	-12	-8	10
278	5	...	...	9
254	25	30	32	20

TABLE II

Percentage of Polarisation of Fluorescence in collodion-ether mixture

Concentration : c gm/c.c.
Temperature : -28°C

Wavelength in $m\mu$	Succ. Fluorescein $c = 5 \cdot 10^{-5}$	Succ. Eosin $c = 4 \cdot 10^{-5}$	Acriflavin $c = 8 \cdot 10^{-5}$	Pinafavol $c = 05 \cdot 10^{-5}$
546	...	40	...	45
436	45	43	42	38
365	40	29	40	25
326	0	-5	...	...
313	-12	-12	-8	12
278	...	...	...	-6
254	20	30	33	21

TABLE III

Percentage of Polarisation of Fluorescence in sugar solution

Concentration of the compounds : c gm/c.c.
Temperature : -28°C

Wavelength in $m\mu$	Succ. Fluorescein $c = 5 \cdot 10^{-5}$	Succ. Eosin $c = 4 \cdot 10^{-5}$	Acriflavin $c = 8 \cdot 10^{-5}$	Pinafavol $c = 05 \cdot 10^{-5}$
546	...	42	...	41
436	43	40	41	36
405	41	...	...	...
365	35	25	36	26
326	0	-8	...	...
313	-10	-10	-9	8
278	6	...	...	-7
254	21	27	30	23

ULTRAVIOLET ABSORPTION OF THE DYESTUFF AND THE NEGATIVE POLARISATION

The observations of Griseback and Mitra reveal the resemblance of the absorption and the polarisation curves of the fluorescent dyestuffs. Griseback found in the case of fluorescein, eosin and rhodamine B that the maximum negative value for the polarisation was obtained when the dyestuff is excited by radiation of wavelength which corresponds to the junction of the two absorption bands in the ultraviolet. On the other hand Mitra observed the same in the case of fluorescein alone but not in the case of eosin or rhodamine B.

However, as the ultraviolet absorption data are now at our disposal (Chowdhury and Bose, 1943) we can gauge how far contentions of the aforesaid workers are true. In the accompanying graphs are drawn the absorption coefficient curves as well as the polarisation curves superimposed on the same graph :—

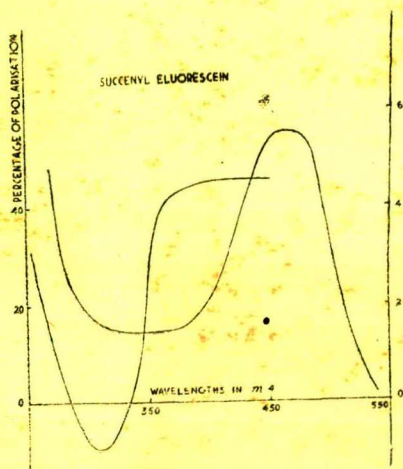


FIG. 1

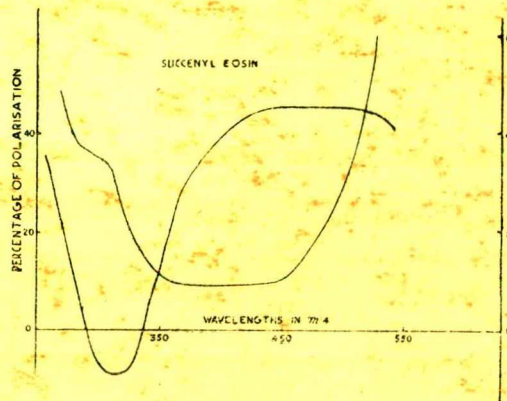


FIG. 2

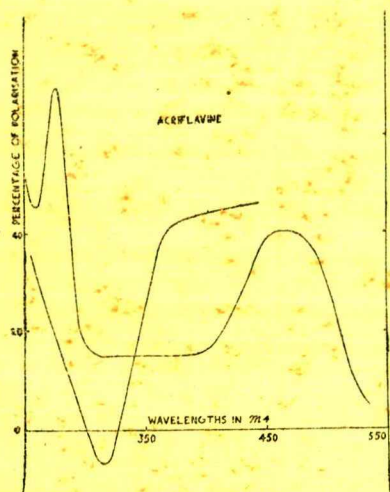


FIG. 3

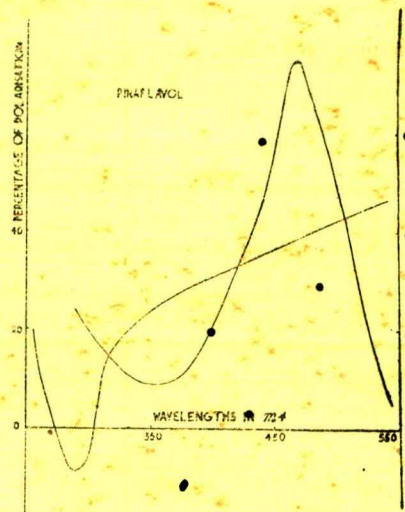


FIG. 4

Fig. 1, 2, 3, 4 show absorption and polarisation curves of Succ. Fluorescein, Succ. Eosin, Pinaflavol, and Acriflavin.

INFLUENCE OF THE VISCOSITY OF THE SOLUTION OF THE POLARISATION

We have already alluded to the fact that the polarisation of the fluorescence depends on the viscosity of the fluorescing solution. This has been experimentally demonstrated by the investigations of Pringsheim (1924), Perrin (1929), Wawilow (1922), Mitra (1938, 1939) and others.

It is first Perrin who gave a satisfactory theory of the dependence of the polarisation on the viscosity of the fluorescing solution, and deduced on the basis of the theory of Brownian rotation of the molecules an expression for the above dependence. The principle of his theory is as follows:—Assuming that the molecules are rigidly fixed in space, if an incident polarised light excites fluorescence in the medium, the polarisation of the fluorescent radiations will have a certain value p_0 which is characteristic of the substance. If, on the other hand, as in actual experiments, the molecules are rotating, the mean square of the angle of rotation per second can be calculated in terms of the viscosity of the solution and its temperature from Einstein's theory of Brownian motion; hence the "expectation" of rotation for a time τ can be calculated, where τ is the mean duration of the molecules in the excited state. The smaller this angle of rotation, the more closely would the actually observed value of the polarisation p approach the ideal value p_0 . Thus for very large viscosity p should reach asymptotically the limiting value p_0 , while at low viscosities the polarisation ought to reach again asymptotically zero value.

TABLE IV

Polarisation of Acriflavin in glycerine-water mixtures. Exciting wavelength:— λ 4358 Å

Percentage by wt. of glycerine	Viscosity in poises	Percentage of Polarisation	
		$c=3.10^{-5}$ gm/c.c.	$c=.80.10^{-5}$ gm/c.c.
98	4.56	44	45
90.9	1.65	38	42
83.3	.611	30	34
76.9	.367	23	28
71.4	.185	17	22
66.6	.127	12	17
62.5	.097	8	12
58.5	.070	5	9
51.2		almost zero	5

TABLE V

Percentage of Polarisation of Acriflavin in glycerine-water mixtures. Exciting wavelength:— λ 3650 Å

Percentage by wt. of glycerine	Viscosity in poises	Percentage of Polarisation	
		$c=3.10^{-5}$ gm/c.c.	$c=.80.10^{-5}$ gm/c.c.
98	4.56	40	42
90.9	1.65	34	38
83.3	.611	25	30
76.9	.367	18	23
71.4	.187	11	15
66.6	.127	6	9
62.5	.97	—	5

We shall quote here only the final expression obtained by Perrin, viz.,

$$\frac{1}{p} = \frac{1}{p_0} + \left[\frac{1}{p_0} - \frac{1}{3} \right] \frac{R\theta}{V\eta} \tau.$$

where p is the degree of polarisation observed under the actual condition of the experiment and p_0 the value for the same molecules when they are not allowed to rotate from their initial

orientations. R is the gas constant, V , the gram-molecular volume, η the co-efficient of viscosity and θ the absolute temperature and τ is the mean duration of the fluorescing molecules in the excited state.

TABLE VI

Percentage of Polarisation of Erythrosine in glycerine-water mixtures.

Exciting wavelength:—
 λ 4358 Å
Concentration:—
 2.10^{-5} gm/c.c.

Percentage by wt. of glycerine.	Viscosity in poises.	Percentage of Polarisation.
98	4.56	35
90.9	1.65	27
83.3	.611	20
76.9	.367	14
71.4	.185	9
66.5	.127	5

TABLE VII

Percentage of Polarisation of Rose Bengal in glycerine-water mixtures.

Exciting wavelength:—
 λ 4358 Å
Concentration:—
 $1.2.10^{-5}$ gm/c.c.

Percentage by wt. of glycerine.	Viscosity in poises	Percentage of Polarisation.
98	4.56	35
90.9	1.65	26
83.3	.611	18
76.9	.367	13
71.4	.185	7
66.5	.127	3

TABLE VIII

Percentage of Polarisation of Succ. Fluorescein in glycerine-water mixtures.

Exciting wavelength;—
 λ 4358 Å

Percentage by wt. of glycerine.	Viscosity in poises.	Percentage of Polarisation	
		$c = .05.10^{-5}$ gm/c.c.	$c = .5.10^{-5}$ gm/c.c.
98	4.56	48	45
90.9	1.65	44	40
83.3	.611	36	31
76.9	.367	29	25
71.4	.185	24	19
66.6	.127	17	11
62.5	.097	12	5

TABLE IX

Percentage of Polarisation of Succ. Fluorescein in glycerine-water mixtures.

Exciting wavelength:—
 λ 3650 Å.

Percentage by wt. of glycerine.	Viscosity in poises.	Percentage of Polarisation	
		$c = .05.10^{-5}$ gm/c.c.	$c = .5.10^{-5}$ gm/c.c.
98	4.56	40	38
90.9	1.65	36	34
83.3	.611	30	26
76.9	.367	25	20
71.4	.185	19	13
66.6	.127	14	8
62.5	.097	9	3

TABLE X

Percentage of Polarisation of Pinaflavol in glycerine-water mixtures.

Exciting wavelength:— λ 4358 Å.
Concentration:— $.05.10^{-5}$ gm/c.c.

Percentage by wt. of glycerine.	Viscosity in poises	Percentage of Polarisation.
98	4.56	38
90.9	1.65	32
83.3	.611	24
76.9	.367	18
71.4	.185	12
62.5	.097	4
58.3	.070	Zero

TABLE XI

Percentage of Polarisation of Pinakriptol yellow in glycerine-water mixtures.

Exciting wavelength:—
 λ 4358 Å. Concentration:— $.25.10^{-5}$ gm/c.c.

Percentage by wt. of glycerine.	Viscosity in poises	Percentage of Polarisation
98	4.56	38
90.9	1.65	27
83.3	.611	17
76.9	.367	12
66.6	.127	5
58.8	.070	0

In order to be able to have some information regarding this duration of the molecules in the excited states or the average life of the fluorescing molecules, as they are sometimes called, measurements were made on the polarisation of the fluorescence of the dyestuffs under investigation in glycerine-water mixtures, whose relative proportions and hence the viscosity could be varied over a wide range. The concentration of the dyestuffs per c.c. of the solution was kept constant in all the cases, so also the temperature of the solution.

The values of the viscosity were calculated from the extensive measurements as given by Shelly (1932) on viscosity at different temperatures and various concentrations by graphical interpolation.

The results of our measurements are shown in the accompanying tables. It will be observed that in all cases the degree of polarisation tends at high viscosity to reach asymptotically the maximum limiting value p_0 , whereas at low viscosity the polarisation tends towards zero value. This limiting value does not only depends on the nature of the dyestuff but also on the wavelength of the exciting radiation.

The mean life of the fluorescing molecules in the excited states τ has also been calculated, the following gives the results of our calculation. It is evident from the nature of the expression for τ that for values of p very near p_0 , as also very near zero, the calculated value of τ cannot be reliable. Hence τ has been calculated only for the values of $p > .10 < .45$.

TABLE XII

Average life τ of Acriflavin in glycerine water mixture.

Viscosity in poises	Excitation by λ 4358		Excitation by λ 3650	
	$c = 3.10^{-5}$ gm/c.c.	$c = .8.10^{-5}$ gm/c.c.	$c = 3.10^{-5}$ gm/c.c.	$c = .8.10^{-5}$ gm/c.c.
1.65	$1.2.10^{-8}$ Sec.	$7.5.10^{-9}$ Sec.		
.611	$1.1.10^{-8}$ Sec.	$6.9.10^{-9}$ Sec.	$1.0.10^{-8}$ Sec.	$6.0.10^{-9}$ Sec.
.367	$1.3.10^{-8}$ Sec.	$7.1.10^{-9}$ Sec.	$1.1.10^{-8}$ Sec.	$7.0.10^{-9}$ Sec.
.185	$1.2.10^{-8}$ Sec.	$7.4.10^{-9}$ Sec.	$1.2.10^{-8}$ Sec.	$7.7.10^{-9}$ Sec.

TABLE XIII

Average life τ of Sacc. Fluorescein in glycerine water mixture.

Viscosity in poises	Excitation by λ 4358		Excitation by λ 3650	
	$c = .5.10^{-5}$ gm/c.c.	$c = .05.10^{-5}$ gm/c.c.	$c = .5.10^{-5}$ gm/c.c.	$c = .05.10^{-5}$ gm/c.c.
1.65	$10.6.10^{-9}$ Sec.	$6.0.10^{-9}$ Sec.	$9.7.10^{-9}$ Sec.	$6.8.10^{-9}$ Sec.
.611	$9.7.10^{-9}$ Sec.	$6.1.10^{-9}$ Sec.	$9.4.10^{-9}$ Sec.	$6.1.10^{-9}$ Sec.
.367	$9.7.10^{-9}$ Sec.	$6.8.10^{-9}$ Sec.	$10.1.10^{-9}$ Sec.	$6.2.10^{-9}$ Sec.
.185	10.10^{-9} Sec.	$5.2.10^{-9}$ Sec.	$10.3.10^{-9}$ Sec.	$5.6.10^{-9}$ Sec.

TABLE XIV

"Average life" of Pinaflavol in glycerine-water mixtures.

Exciting wavelengths = λ 4358 Å.			Concentration = $.05.10^{-5}$ gm/c.c.		
Viscosity in poises =	4.56	1.65	.116	.673	.518
$\frac{(3-p_0) \cdot R\theta}{V} \cdot \tau$	1.44	1.54	1.37	1.46	1.38

It is evident from the tables that within the limits of the experimental errors the values of τ is practically independent of the viscosity (provided it is low), though the values are widely different for the different concentrations of the dyestuffs. Moreover, the values of the average life are independent of the exciting wavelengths.

We have already reported the phenomena of quenching of fluorescence by foreign neutral salts. We can consider this act of quenching as something like a quantum mechanical resonance, if we look at it in the light of collision process of the second kind. If now on undergoing different excitations with different wavelengths, the excited molecules had different probabilities of quenching, some dependence of the quenching on the wavelength of exciting light should be observed. But experimentally it was shown by Wawilow (1929) Sveshnikow

(1935) and Mitra (1938), that there is no dependence of the quenching action on the exciting wavelengths. Their conclusions show that the excited molecules have all the same energy level during the excited state. Thus our conclusions arrived at from the polarisation measurements are in agreement with those of the aforesaid investigators.

INFLUENCE OF TEMPERATURE ON THE POLARISATION OF THE FLUORESCENT RADIATIONS

As regards the influence of temperature on the polarisation of fluorescence Pringsheim and Perrin observed that with increase of temperature, the polarisation gradually dwindles down, finally vanishing to zero. Mitra, over and above this observed that with the decrease of temperature, the polarisation asymptotically tends towards the maximum value "*p*."

We have also measured the polarisation of the dye-stuffs under investigation in glycerine solution at various temperatures of the solvent. The results of our measurements are given below.

We can readily understand that the influence of temperature on the polarisation will be two-fold; directly owing to the greater thermal agitations at higher temperatures the "expectations" of rotation of the molecules after excitation from their initial positions will be greater and hence the value of the polarisation will correspondingly be smaller. It also affects indirectly by changing the viscosity of the solution. Both the effects work in the same direction; *viz.*, to diminish the polarisation at higher temperatures. Both these effects have been taken into consideration in the already alluded Perrin's theory. If now these are the only effects of temperature, the average life calculated on the basis of the aforesaid theory ought to be independent of the temperatures. Such an independence was shown by Mitra to be experimentally true only in the case of dilute solution of the dyestuff; but in the case of concentrated solutions the life-time of the molecules gradually falls down with the increase of temperature, showing thereby that there are other effects of temperature besides the two already mentioned.

Experimentally the value of the polarisation was measured for the temperatures from 0° to about 90°C.

The results of our measurements are given in the following Tables:—

TABLE XV

Influence of temperature on the polarisation of fluorescence of Acriflavin in glycerine excited by λ 4358

Temperature in °C	Percentage of Polarisation		
	$c = 3.10^{-5}$ gm/c.c.	$c = 8.10^{-5}$ gm/c.c.	$c = 1.10^{-5}$ gm/c.c.
10	50	50	50
20	48	50	50
30	44	46	50
40	38	41	44
50	33	36	39
60	27	31	34
70	21	25	29
80	16	20	23
90	10	15	18

TABLE XVI

Influence of temperature on the polarisation of fluorescence of Acriflavin in glycerine excited by λ 3650

Temperature in °C	Percentage of Polarisation		
	$c = 3.10^{-5}$ gm/c.c.	$c = 8.10^{-7}$ gm/c.c.	$c = 1.10^{-5}$ gm/c.c.
0	42	42	42
10	42	42	42
20	41	42	42
30	37	38	40
40	32	34	36
50	27	29	31
60	22	24	26
70	16	18	20
80	10	12	15
90	4	7	10

TABLE XVII

Influence of temperature on the polarisation of fluorescence of Pinaflavol and Rose Bengal in glycerine excited by $\lambda 4358$

Concentration: 1×10^{-5} gm./c.c.

Temperature in °C	Percentage of Polarisation	
	Pinaflavol	Rose Bengal
0	42	45
10	42	44
20	42	41
30	41	35
40	36	29
50	28	22
60	22	15
70	15	8
80	8	—
90	—	—

TABLE XVIII

Influence of temperature on the polarisation of fluorescence of Pinakripta in glycerine

Concentration— 1.19×10^{-5} gm./c.c.

Temperature in °C	Percentage of Polarisation excited by λ	
	4358	3650
0	45	42
10	45	42
20	41	36
30	36	32
40	30	25
50	24	18
60	16	12
70	10	6
80	5	—

TABLE XIX

Influence of temperature on the polarisation of fluorescence of Succ. Eosin in glycerine

Concentration = 2.10×10^{-5} gm./cc.

Temperature in °C	Percentage of Polarisation excited by λ	
	4358	3650
0	45	42
8	45	42
20	43	39
30	39	35
40	35	28
50	29	23
60	24	17
70	19	11
80	13	6

The general nature of the curves is the same as that representing the variation of p with the viscosity. At low temperatures p tends to reach asymptotically the limiting value p_0 as for large viscosities, while at high temperatures p tends to vanish. On calculating the value of τ on the basis of the Perrin's theory we get the following results:—

TABLE XX

Influence of temperature on the average life of the Acriflavin molecules in the excited state.
Exciting wavelength — $\lambda 4358$

Temperature in °C	Average life of the molecules		
	$c = 3.19 \times 10^{-5}$ gm./c.c.	$c = 8.10 \times 10^{-5}$ gm./c.c.	$c = 1.10 \times 10^{-5}$ gm./c.c.
30	13.10^{-9} sec.	8.10^{-9} sec.	—
40	13.10^{-9} „	9.10^{-9} „	6.10^{-9} sec.
50	11.10^{-9} „	8.10^{-9} „	6.10^{-9} „
60	13.10^{-9} „	9.10^{-9} „	7.10^{-9} „

TABLE XXI

Influence of temperature on the average life of the Acriflavin molecules in the excited state,
Exciting wavelength — $\lambda 3650$

Temperature in °C	Average life of the molecules		
	$c = 3.10 \times 10^{-5}$ gm./c.c.	$c = 8.16 \times 10^{-5}$ gm./c.c.	$c = 1.10 \times 10^{-5}$ gm./c.c.
30	13.10^{-9} sec.	10.10^{-9} sec.	—
40	13.10^{-9} „	10.10^{-9} „	7.10^{-9} sec.
50	11.10^{-9} „	9.10^{-9} „	7.10^{-9} „
60	13.10^{-9} „	10.10^{-9} „	7.10^{-9} „

These results reveal that though the value shows a very striking dependence on the concentration of the dyestuff, it is practically independent of the temperature within the ranges of concentrations we have studied. This shows conclusively that only effects of raising the temperature are through increased thermal agitation and the consequent larger value of expectation of the Brownian rotation of the dyestuff molecule per second and through diminished viscosity.

DEPENDENCE OF THE POLARISATION ON THE CONCENTRATION OF THE DYESTUFF IN SOLUTION

We have also seen from the foregoing tables that the polarisation of fluorescence exhibits a conspicuous change with the change of the concentration of the fluorescing dyestuffs.

The dependence was first experimentally shown by Pringsheim, who observed that as the concentration is increased the polarisation decreases. This observation was afterwards confirmed by Gaviola, Wawilow and others. Mitra carried out a detailed investigation and found that with the increase of concentration polarisation tends to vanish while at very small concentration it tends to reach asymptotically the same limiting value as is reached at large viscosities and low temperatures.

Our data also reveal that with the increase of concentration the values of the polarisation tend to vanish; while at very small dilutions, it tends to reach asymptotically the same limiting value as is reached at large viscosities or low temperatures.

ON THE MAXIMUM VALUE OF THE POLARISATION OF THE FLUORESCENCE OF THE DYESTUFFS

It has already been referred that the limiting value of the polarisation is its value when the molecules after excitation are not allowed to rotate from their initial orientations, which is evidently the value of the polarisation when the viscosity is very large or temperatures very low. The following table exhibits the values of this limiting polarisation for the various dyestuffs in glycerine solution when excited by radiation of various wavelengths as were obtained in our present investigation.

TABLE XXII

Dyestuffs in glycerine	Excitation wavelength in Å	Maximum limiting value of polarisation
Acridflavin	4358	.50
	3650	.42
Pinakriptol	4358	.45
	3650	.42
Succ. Eosin	4358	.45
	3650	.42
Rose Bengal	4358	.45
Pinaflavol	4358	.42

In conclusion, it gives me great pleasure to thank Prof. S. N. Bose for his kind interest in the work. Thanks are also due to Dr. S. M. Mitra for his kind help and guidance.

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PART - 6.

INFLUENCE OF POTASSIUM IODIDE ON THE CONDUCTIVITY OF
DYESTUFFS IN SOLUTION.

INFLUENCE OF POTASSIUM IODIDE ON THE CONDUCTIVITY OF
DYESTUFFS IN SOLUTION.



We have already referred to the quenching of fluorescence of dyestuffs in solution by foreign neutral salts. The quenching depends markedly on the concentration of the foreign substance and on the temperature of the solution and is independent of the exciting wavelength. The quenching is generally explained as due to deactivating collisions of the second kind between the dyestuff molecules in the excited state and the negative ions of the added salt. But quenching due to complex formation cannot be ruled out altogether as in certain cases higher temperature increases the intensity of fluorescent radiation. In our measurements on absorption (1943) of dyestuffs with or without foreign neutral salts, it has been found that there was no change in the nature of absorption curves. This showed that quenching took place through collision of the second kind. In order to investigate further into the subject we have extended our measurements to the determination of the influence of foreign molecules or ions on the conductivity of the fluorescent compounds in solution. The results of our measurements are shown in the accompanying tables.

Table - 1.

Succenyl Eosine with KI.

Sp. Conductivity of KI added K ₁	Sp. conductivity of Succ. Eosin taken: K ₂	Sp. Conductivity of the solution of KI added & Succ. Eosine taken.	K ₁ + K ₂
.001832	.0003490	.002178	.002181
.003545	.0003434	.003884	.003888
.006742	.0003354	.007074	.007077
.01256	.0003206	.01287	.01288
.02259	.0002940	.02283	.02288
.03094	.0002712	.03124	.03121
.03788	.0002523	.03816	.03813

Table - 2.

Erythrosine with KI.

Sp. conductivity of KI added K ₁	Sp. conductivity of Erythrosine taken K ₂	Sp. conductivity of the solution of KI added & Erythrosine taken.	K ₁ + K ₂
.001832	.0006439	.002469	.002475
.003545	.0006387	.004173	.004183
.006742	.0006207	.007364	.009362
.01256	.0005951	.01311	.01315
.02259	.0005513	.02318	.02314
.03094	.0005136	.03140	.03145
.03788	.0004809	.03828	.03836

Succenyl Fluorescein with KI.

Sp. conductivity of KI added K_1	Sp. conductivity of Succ. Fluorescein taken K_2	Sp. conductivity of the solution of KI added & Succ. Fluorescein taken.	$K_1 + K_2$
.001832	.00001501	.001851	.001847
.003545	.00001485	.003562	.003559
.006742	.0000140	.006753	.006756
.01256	.0000140	.01256	.01257
.02259	.0000130	.02262	.02260
.03094	.000013	.03094	.03095
.03788	.000013	.03787	.03789

Table - 4.

Fluorescein with KI.

Sp. conductivity of KI added K_1	Sp. conductivity of fluorescein taken K_2	Sp. conductivity of the solution of KI added & Fluorescein taken.	$K_1 + K_2$
.001832	.00001021	.001839	.001842
.003545	.000010	.003550	.003555
.006742	.000010	.006754	.006752
.01256	.000009	.01254	.01257
.02259	.000009	.02259	.02260
.03094	.000009	.03098	.03095
.03788	.000009	.03788	.03789

Rose Bengal with KI.

Sp. conductivity of KI added K_1	Sp. conductivity of Rose Bengal taken K_2	Sp. conductivity of the solution of KI added & Rose Bengal taken.	$K_1 + K_2$
.001832	.001530	.003369	.003362
.003545	.001506	.005048	.005051
.006742	.001475	.008213	.008217
.01256	.001414	.01395	.01397
.02259	.001307	.02385	.02389
.03094	.001215	.03217	.03215
.03788	.001137	.03903	.03901

It will be seen from the tables that the conductivity of the solution is very nearly equal to the sum of the individual conductivities of the dyes and KI in solution. This shows that no new molecules are formed due to the gradual addition of KI and that collision of the second kind is the major cause of quenching by foreign neutral salts. Our results are in agreement with those of Lewschin(1927) and others who have found that in the case of halides the quenching is always external.

Polarised Fluorescence of dyestuffs in solution
with foreign neutral salts.

Wawilow(1929), Pringsheim(1924), Mitra(1939) and others have worked on the polarised fluorescence of dyestuffs in solution. Mitra carried out a systematic investigation on this subject and it has now

been definitely known that fluorescent radiations emitted by the dyestuffs in solution are polarised and this polarisation depends among others on the following facts- the viscosity and the temperature of the solution, the concentration of the dyestuff and the wavelength of the exciting radiations. Perrin (1931) has derived a formula on the basis of Brownian motion and the results of the various workers agree well at least for the medium concentrations. It has already been mentioned that the addition of small quantities of a foreign substance to a fluorescent solution causes a quenching of its fluorescent radiation. It has now been revealed from the works of Mitra and others that the polarisation of the fluorescent radiation increases with the addition of foreign neutral salts with a simultaneous decrease in the intensity of fluorescent radiation. The increase of polarisation with increase in concentration of KI is to be expected from Perrin's theory. The collision of the second kind between the molecules of the excited dyestuff and those of the neutral salt causes a decrease in the average life period of the excited molecules, since the molecules would not have sufficient time to rotate far from its original orientation where it was excited, and thus the polarisation will approximate closer to its upper limiting value. Therefore, this increase in polarisation further lends support to the theory of the collision of the second kind for the decrease in intensity of the fluorescent radiation.

We have investigated the effect of addition of KI to Succenyl Fluorescein and Acriflavine on the polarised fluorescence of these dyestuffs. The method employed was the usual Cornu method. In some cases the measurements of the polarisation were made by a Savart plate in the usual way.

The results of our measurements are given in the following tables.

Table -6.

Succenyl Fluorescein in water.

Concentration of KI in 10^{-3} gm./c.c.	0	5	10	15	20	25	30
Percentage of polarisation 'p' for 4358	0	1.5	3.5	5.5	8	10	13
Percentage of polarisation 'p' for 3650	0	1	3	5	6.5	8.5	11

Table - 7.

Acriflavine in water.

Concentration of KI in 10 gm./ c.c.	0	2.5	5	10	15	20	25	30
' p ' for 4358	0	1	-	4	6	8.5	11	14
' p ' for 3650	0	-	1	3	5.5	7.5	-	12

It will be seen from the tables that the polarisation as expected increases with increase in concentration of KI for both wavelengths of excitation.

CONCLUSION.

The conductivity of dyestuffs with and without KI has been determined. It has been found that the conductivity of the solution is practically equal to the sum of the conductivities of the dyestuffs and KI at various concentrations. This then suggests that quenching of fluorescence of the molecules with the addition of foreign salts is due to deactivating collision of the second kind. This view gets further support from the observations of polarised fluorescence of dyestuffs with foreign salts.

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PART - 7.

CONCLUDING REMARKS.

CONCLUDING REMARKS.

The absorption measurements of dyestuffs with foreign neutral salts reveal that quenching is due to the collision of the second kind between the excited molecules of the dyestuff and the ions of the added salts. This view gets further support from observations on conductivity and polarised fluorescence of dyestuffs with foreign neutral salts.

As regards the quenching of fluorescence of dyestuffs with increase in concentration, it is to be noted that the conductivity concentration curves reveal the formation of ionic micelles. It was pointed out earlier that the critical concentration at which the network falls into micelle formation fairly agrees with the concentration after which rapid quenching of fluorescence begins. These complex clusters are, therefore, non-fluorescent and their formation reduces the number of fluorescent molecules and consequently the intensity is diminished. This is really not a true case of quenching as quenching is always accompanied with a diminution of the average life period. The measurements on polarisation reveal that the average life-period though practically independent of temperature, viscosity and wavelength increases with concentration of the dyestuff. This increase of life-period with concentration is a direct consequence of the formation of non-fluorescent complex molecules. Since the formation of ionic micelles reduces the number of fluorescent molecules to a great extent, this amounts to an increase in the average life-period. The loss of intensity is, therefore, due to the formation of ionic micelles.

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