PHYSICO-CHEMICAL STUDIES
ON THE
COAGULATION & SOL-GEL TRANSFORMATION
OF
HYDROPHOBIC SOLS IN PRESENCE OF DYES

Thesis submitted for the award of the
Degree of Doctor of Philosophy
in Chemistry

By
IQBAL AHMAD KHAN

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE (INDIA)
February, 1966

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CERTIFICATE

Certified that the thesis entitled " PHYSICO-CHEMICAL STUDIES ON THE COAGULATION AND SOL-GEL TRANSFORMATION OF HYDROPHOBIC SOLS IN PRESENCE OF DYES" which is being submitted by Mr. Iqbal Ahmad Khan for the award of the degree of Doctor of philosophy in Chemistry of the University of Roorkee, is a record of his own work under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is further to certify that he has worked for a period of two years and three months from October 5, 1963 to January 4, 1966 at this university and also for six months (April 25, 1963 to October 4, 1963) in Aligarh University to prepare this thesis.

Wahid U. Malik.

Dr. Wahid U. Malik
Ph.D., D.Sc., F.R.I.C.
(London), F.N.A.Sc.
Prof. and Head of the
Chemistry Department
University of Roorkee
Roorkee (India)

Roorkee

Date: Feb.1, 1966

ACKNOWLEDGEMENT

I gratefully acknowledge my indebtedness to my teacher Professor Wahid U. Malik, D.Sc., Ph.D., F.N.A.Sc., F.R.I.C. (London), Head of the chemistry department, university of Roorkee, under whose guidance this work was carried out.

Iqbal Ahmad Khan

CONTENTS

GENERAL INTRODUCTION

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1. Slow and rapid coagulation:

The last part of the nineteenth and the beginning of the twentieth century witnessed many new developments in the realm of colloid science, which gradually paved the way for more comprehensive and critical studies in the years to follow. The striking observations of Schulze (1), Linder and Picton (2), Hardy (3), Zsigmondy (4), Perrin (5), Burton (6) and others on the influence of small amounts of electrolytes on the stability of inorganic colloids and the existence of electrokinetic potentials in these colloidal systems awakened the interest of a number of eminent workers to study the problem of the stability of colloids in a quantitative way. Not considering for the present the behaviour of the lyophilic and biocolloids, which considerably differ from the lyophobic colloids interms of electrokinetic properties (7) and stability (8) (attributed mainly to solvation), the quantitative aspect of the investigations may be divided under the following subheads: (I) Kinetics of Coagulation, (II) the nature of the electrical double layer and the sol stability interms of potential energy curves, and (III) application of conductometric and potentiometric titrations in the study of the constitution of sols.

I. Kinetics of Coagulation:

Inspite of the several modifications made from time to time in the Smoluchowski's equation and the theoritical interpretations putforward to fit in the results on slow coagulation, this equation would always remain a living testimony to the marvellous imagination of Smoluchowski (9) and the great practical ingeneunity of Zsigmondy (10).

Zsigmondy (loc. cit) during the course of his studies on the action of electrolyte on gold sols distinguished two types of coagulation (as observed from the change in colour of the gold sol from red to violet), viz; slow and rapid ones. In the case of rapid coagulation the velocity is independent of the concentration, valency and nature of the coagulating ion while in the region of slow coagulation the behaviour is entirely different since the particles are not completely discharged and a residual charge always persists in particles undergoing agglomeration.

A short resume of Smoluchowski's fundamental studies on the velocity of rapid coagulation is worth considering.

Theoritical equation for the velocity of rapid coagulation have been worked out by Smoluchowski on the basis of Zsigmondy's assumptions. Smoluchowski considers that coagulation depends on the probability of collision between the particles and on the probability of their adhesion when collision does takes place; the second assumption is that due to collision duplets, triplets and quadriplets etc. would be formed by the collision of two singlets, one singlet and one duplet, one singlet and one triplet; the third assumption made by him is that he considers a sphere of attraction to surround each particle and postulates that collision occurs only when the centre of the sphere surrounding one particle enters the sphere of attraction of another particle. The minimum value for the radius of the sphere of attraction is thus twice the radius of the particles, for in such case the particles just touch when the centre of one enters the sphere of attraction of the other. Now as every collision between two colloidal particles leads to their adhesion, an estimate of the number of collisions in unit time gives atonce the rate of coagulation. The diffusion equation for a problem of spherical symmetry is $D \cdot \frac{\partial^2(rc)}{\partial r^2} = \frac{\partial(rc)}{\partial t}$ ....(i) where D is the diffusion constant and c the concentration (number of particles in unit volume) at time t and distance r from the centre of symmetry. The solution $c = c_o \cdot (1 - \frac{R}{r})$, (where R and c_o are constants) of the above equation is such that at all times c = o on the surface of sphere of radius R, and $c = c_o$ at large enough distances, r, from the centre. This solution can be obtained as shown below:

The solution of the equation (i) is done by the method of separation of variables i.e. c = R(r)T(t) which means that concentration of the colloidal particle at any time is a function of radius and time t, such that R(r) is a function of r alone and T(t) is a function of t alone that is R(r) and T(t) are independent variables.

$$\therefore \frac{\partial(rc)}{\partial t} = \frac{\partial}{\partial t}\left[r\,R(r)\,T(t) \right]$$

$$= r\,R(r)\,\frac{\partial}{\partial t}T(t)$$

$$= r\,R(r)\,\frac{d}{dt}T(t)$$

Now $D\frac{\partial^2(rc)}{\partial r^2} = D\frac{\partial^2}{\partial r^2}\Big[r\,R(r)\,T(t)\Big]$

$$= DT(t)\frac{\partial^2}{\partial r^2}\Big[r\,R(r)\Big]$$

$$= DT(t)\frac{d^2}{dr^2}\Big[r\,R(r)\Big]$$

$$= DT(t)\frac{d}{dr}\Big[\frac{d}{dr}\,r\,R(r)\Big]$$

$$= DT(t)\frac{d}{dr}\Big[r\cdot\frac{d}{dr}R(r) + R(r)\Big]$$

$$= DT(t)\Big[r\,\frac{d^2R(r)}{dr^2} + 2\,\frac{d}{dr}R(r)\Big]$$

Substituting these values in (i) we get

$$DT(t)\Big[r\cdot\frac{d^2R(r)}{dr^2} + 2\,\frac{d}{dr}R(r)\Big] = r\,R(r)\cdot\frac{d}{dt}T(t)$$

dividing both sides by $rR(r)\cdot T(t)$ we get

$$D\,\frac{1}{r\,R(r)}\Big[r\cdot\frac{d^2R(r)}{dr^2} + 2\,\frac{d}{dr}R(r)\Big] = \frac{1}{T(t)}\cdot\frac{d}{dt}T(t)$$

$$D\,\frac{1}{r\,R(r)}\Big[r\cdot\frac{d^2R(r)}{dr^2} + 2\,\frac{d}{dr}R(r)\Big] = \frac{1}{T(t)}\cdot\frac{d}{dt}T(t) = \alpha, \quad \text{...(ii)}$$ where

α is a constant

$\therefore \frac{1}{T(t)}\frac{d}{dt}T(t) = \alpha$ or $\frac{d\,T(t)}{T(t)} = \alpha\,dt$. Integrating it we get

$T(t) = e^{\alpha t}.\,e^{c}$

$\therefore T(t) = A\,e^{\alpha t}$

The possibilities for α are (i) α is real and (ii) α is imaginary. Now considering the case when α is real (positive or negative) which shows that concentration at any point should go on increasing or decreasing, which is impossible. Now considering the second case when α is imaginary, we get $T(t) = A\,\mathrm{Sin}\beta t + A'\mathrm{Cos}\beta t$, this equation represents periodicity since the concentration of duplets, triplets etc. are not formed periodically but continuously. Any imaginary value of α is, therefore, not possible.

The only choice is now to put $\alpha = 0$, then we get $\hat{T}(t) = A$. Now considering R.H.S. of equation (ii), we have

$$\frac{1}{R(r)}\frac{d^2R(r)}{dr^2} + \frac{2}{rR(r)}\frac{dR(r)}{dr} = 0,$$ multiplying by $rR(r)$ we get,

$$r\frac{d^2R(r)}{dr^2} + \frac{2\,dR(r)}{dr} = 0$$

or $$\frac{d}{dr}\left[r\frac{dR(r)}{dr} + R(r)\right] = 0$$

or $$R(r) + r\frac{dR(r)}{dr} = G,$$ where G is constant

$$\therefore \frac{dR(r)}{G-R(r)} = \frac{dr}{r},$$ putting $G-R(r) = Z$ and integrating it we get

$$-\int\frac{dZ}{Z} = \int\frac{dr}{r}$$

$$-\ln Z = \ln r + \ln\frac{D}{D'}$$ putting $\frac{D}{D'} = E$

we get $\ln Z^{-1} = \ln rE$ or $Z = \frac{1}{rE}$, let $\frac{1}{E} = \eta$

$$\therefore Z = \frac{\eta}{r} \text{ or } G-R(r) = \frac{\eta}{r} \qquad \text{..............(iii)}$$

where G and η are arbitary constants of a mathematical problem and have to be determined from the chemistry of the process.

Taking Smoluchowski's assumptions according to which $c = 0$ at distance $(r) = R$ and $c = c_0$ at large enough distances. On substituting these boundary conditions we get $c = c_0 \cdot (1 - \frac{R}{r})$. This equation represents the equilibrium concentration distribution around a small, perfectly absorbing sphere of radius R drawn in the bulk of colloidal solution of average concentration c_0. The amount of colloidal material absorbed by the sphere in unit time is $4\pi R^2 D\cdot\left(\frac{\partial c}{\partial r}\right)_{r=R} = 4\pi RDc_o$ ....(iv)

If the sphere, R, be now identified with the (average) sphere of attraction of a particle in the solution, a correction must be applied for the motion of the particles. Smoluchowski showed that the correction for the Brownian motion of the absorbing sphere of attraction is equivalent to replacing D, in the (iv) equation by 2D. The number of collisions on a colloidal particle in unit time is thus $8\pi RDc_o$ and the number of collisions in unit time per unit volume is $4\pi RDc_o^2$. At t = o, when the coagulation may be supposed to be started, let c_o identical particles in unit volume are present. After a time t there will be concentrations c_1, c_2, c_3 ....c_m ....of the particles formed by the adhesion of 1, 2,3,...m.... of the original particles. Considering first the single particle, they experience among themselves $4\pi RDc_1^2$ collisions in unit time, and are being reduced in number at the rate $8\pi RDc_1^2$ per sec. They also make $8\pi RD\,(\Sigma c-c_1)\cdot c_1$ collisions in unit time with particles of other sizes, and thus total loss of single particles in unit time per unit volume is

$$-\frac{dc_1}{dt} = 8\pi RD(\Sigma c-c_1)\cdot c_1 + 8\pi RDc_1^2 \text{ ......(v)}$$

The double particles are increasing at a rate $4\pi RDc_1^2$ in unit time and decreasing at a rate $8\pi RDc_2\Sigma c$ per sec.,

$$\therefore \frac{dc_2}{dt} = 8\pi RD\left[\frac{c_1^2}{2} - c_2\Sigma c\right] \text{ ....(vi)}$$

The triple particles are increasing at a rate $8\pi RDc_1c_2$ per sec and decreasing at a rate $8\pi RDc_3\Sigma c$,

$\therefore \frac{dc_3}{dt} = 8\pi RD\left[c_1\, c_2 - c_3\Sigma c\right]$ ....(vii) and so on.

The solution of these differential equations is

$c_m = \frac{c_o(4\pi RDc_ot)^{m-1}}{(1+4\pi RDc_ot)^{m+1}}$, where c_m represents the concentration of colloidal particles after time t (following the addition of an electrolyte to the colloid), c_o represents the total number of particles initially present per unit volume. The most general form of Smoluchowski's equation $c_m = \frac{c_o}{1+t/T}$ for rapid coagulation has been verified repeatedly by Zsigmondy (11), Westgren and Reistotter (12), Garner and Lewis (13), Muller (14) developed a mathematical application of the Smoluchowski theory to polydisperse systems in the region of rapid coagulation. Weigner and Tuorilla (15) confirmed this application.

Smoluchowski also gave an equation for slow coagulation by introducing ϵ in the above equation as $c_m = \frac{c_o}{1+\frac{t}{T}\epsilon}$ where c_m represents the number of particles after time t (following the addition of electrolyte to the colloid), c_o represents the total number of particles initially present and T is the specific coagulation time.

It is almost impossible to deal with the available data on slow coagulation, constantly accumulating after Smoluchowski pioneering work, in this short space. It will, however, be worthwhile to describe some of the major developments.

Freundlich (16) on the basis of his studies on the variation in viscosity with time on the addition of electrolytes was of the view that the process of slow coagulation was an autocatalytic one and that the kinetics of the process may be expressed as $K = \frac{1}{t(1+b)} \log \frac{1+bx}{1-x}$, where x is the relative increase in coagulation at time t, b is a constant and K is the coagulation velocity constant. As expected his equation was that of the second order since the rate of coagulation depended entirely on the electrolyte concentration.

A noteworthy advancement to solve the complexities of slow coagulation was putforward by Bhattacharya (17). His empirical equation, $c = a + \frac{m.\frac{1}{t}}{n+1/t}$, where c is the concentration of the electrolyte, t is the time of coagulation, a, m and n are constants for a particular sol fitted in very satisfactorily in his own experimental data on various lyophobic sols and those of the other workers (18). On plotting the time of coagulation against '1/c-a' straight lines were obtained from which they could infer that the relation between the concentration of the electrolyte and time for the same stage of coagulation could be well expressed by the new equation irrespective of the method employed. This equation has recently been tested by Malik and co-workers (19) and also by Ghosh (20) for metal oxide sol.

Almost simultaneously with Bhattacharya's equation on slow coagulation a new relationship showing theoritical dependence of the rate of flocculation on the concentration of the electrolyte was putforward by Reerink (21). According to Ghosh (22) Bhattacharya equation can be deduced from Reerink's equation in the following manner.

Reerink has derived an equation connecting the stability ratio W of a colloid with the concentration and valency of an added electrolyte as $W=2\int_{2}^{\infty}\frac{ds}{s^2}$. An approximation evaluation of the integral leads to the expression $W=\frac{1}{2K_a}e^{Vm/KT}$, where K_a represents the ratio of the particle radius a, to the thickness $\frac{1}{k}$ of the double layer, V_m the maximum value of the energy of interaction in the curve plotted with $e^{V/KT}$ as the ordinate and s as the abscissa. From known expressions, worked out by Verwey and Overbeek for the energy of repulsion V_R and the energy of attraction V_A, an evaluation of V_m was made and this leads to the equation $\log W = -(\alpha+\frac{1}{2})\log c_z^2 - (2\alpha+\frac{1}{2})\log\frac{4.9\times10^4 z^2 A}{\gamma^2} - (\alpha+\frac{1}{2})$ $\log\frac{8\pi e^2 N\times10^{-6}}{DKT} - \log 2a$ .... (viii)

where $\alpha = \frac{0.85\times10^{-6} a\gamma^2}{kTz^2}$ and $\gamma = \frac{\exp\left(\frac{Ze\psi_0}{2kT}\right)-1}{\exp\left(\frac{Ze\psi_0}{2kT}\right)+1}$

z represents valency, A, the Vander Waals attraction constant, e, the electronic charge, N the Avogadro Number, D the dielectric constant, k=R/N, T the temperature and ψ_0, the surface potential of the colloidal particles. For a given colloid and electrolyte assuming all the terms excepting c, as constant, equation (viii) can be expressed as follows:

$\log W = -(\alpha+\frac{1}{2})\log c - \log K$..........(ix)

Where K stands for all the constant terms. Therefore, a plot of log W against log c will give a straight line. This relationship was confirmed by Reerink from his own data on silver iodide sol and those of others on a few colloids.

Since Reerink's equation has got a theoritical basis, it is worthwhile considering if Bhattacharya's equation can be deduced from it.

The above equation (ix) can be expressed as $W=1/K.c^{\beta}$ where $\beta=(\alpha+\frac{1}{2})\gamma$; writing $c=a_1+(c-a_1)$, where a_1 is a constant and less than c, we have $W=\frac{1}{k\left[a_1+(c-a_1)\right]^{\beta}}$

or $W=\frac{1}{k\,a_1^{\beta}\left[1+\left(\frac{c-a_1}{a_1}\right)\right]^{\beta}}$

or $W=\frac{1}{k\,a_1^{\beta}\left[1+\frac{\beta(c-a_1)}{a_1}\right]}$, since terms involving higher powers of $\left(\frac{c-a_1}{a_1}\right)$ can be neglected by adjusting the values of c in such a way that $\frac{\beta(c-a_1)}{a_1}$ is always a fraction.

$$W=\frac{1}{k\,a_1^{\beta}a_1^{-1}\left[a_1+\beta c-\beta a_1\right]} \qquad \text{or}$$

$$W=\frac{1}{k\,a_1^{\beta-1}\left[a_1(1-\beta)+\beta c\right]} \qquad \text{or}$$

$$W=\frac{1}{k\,a_1^{\beta-1}.\beta\left[\frac{a_1(1-\beta)}{\beta}+c\right]}, \text{ putting } -a=\frac{a_1}{\beta}(1-\beta)=\text{a constant}$$

$$W=\frac{1}{k\,a_1^{\beta-1}.\beta(c-a)} \qquad \text{..........(x)}$$

Now W=t/T where t is the time required for coagulation when the concentration of the added electrolyte is c, and T is the time required at a sufficiently high concentration of an electrolyte when the velocity of coagulation is the most rapid and constant. According to the Smoluchowski's equation for rapid coagulation $T=1/8\pi D_a n_o$. As the stability ratio W can not be less than unity, therefore we can write $W=\frac{t+T}{T}$, so that even if t be put equal to zero, W cannot be less than unity, using this expression for W, equation (x) can be written as $t/T + 1 = \frac{1}{k\ a_1^{\beta-1} \cdot \beta(c-a)}$

or $\frac{n}{m}\, t + \frac{1}{m} = \frac{1}{c-a}$ where $ka_1^{\beta-1} \cdot \beta = 1/m$ and $1/T = n$

This equation is identical in form with that of Bhattachárya et.al (loc.cit).

Another equation worthmentioning is that of Ghosh (23) who starting from Smoluchowski's equation on slow coagulation derived an equation $\frac{\Sigma n}{n_o} = \frac{1+\alpha t}{1+\beta t}$. Ultramicroscopic counting of particles of several selenium sols at different intervals of time, after the addition of electrolytes was used to verify the above equation and for the subsequent evaluation of α and β. Malik and Ali(24,25) derived the following two equations purely on kinetic energy considerations.

Of the different factors, viz., deformation of the electrical double layer, dehydration, collision of almost uncharged particles etc., influencing the coagulation of colloidal solution, one factor, which appears to be of some significance to us, has not been considered by the different authors till now. It deals with the kinetic energy of the particles possessing residual charge. It appears quite probable that this energy may be quite sufficient to overcome the repelling action of charged particles thereby bringing about coalescence. Based on this assumption we have attempted to derive an equation which interestingly enough has taken the same form as the Smoluchowski's equation for slow coagulation.

Suppose only particles having an average critical energy ε are responsible for effective collision, when ε has got many degrees of freedom, then the probability P of the molecules having the average energy ε is given by (26).

$$P = \frac{e^{-\varepsilon/KT} . (\varepsilon/KT)^{s/2-1}}{\underline{|s/2-1}}$$ where s is the degree of freedom,

If n_o is the number of molecules then $1/KT=3n_o/\nu E$

$$P= \frac{e^{-3\varepsilon n_o/\nu E} . (3\varepsilon n_o/\nu E)^{s/2-1}}{\underline{|s/2-1}}$$

Let Σn be the total number of molecules

$$P= \frac{e^{-3\varepsilon \Sigma n/\nu E} . (3\varepsilon\Sigma n/\nu E)^{s/2-1}}{\underline{|s/2-1}}$$

Putting $3\varepsilon/\nu E=K$ and $(s/2-1) = B$ then $P= \frac{e^{-K\Sigma n} K^{B} \Sigma n^{B}}{\underline{|B}}$

or $P= A\ e^{-K\Sigma n} . \Sigma n^{B}$ where $A= K^{B}/\underline{|B}$

For a single particle the number of collision is $8\pi RD(\Sigma n-n_1)$ where n_1 is the number of n doublets.

Since in our case only the particles having an excess average energy ε are responsible for collision and the probability for this is given by $A\ e^{-K\Sigma n} . \Sigma n^{B}$. Hence total number of particles having the excess energy will be $\Sigma n\ A\ e^{-K\Sigma n} . \Sigma n^{B}$.

Therefore the number of collision in Unit time will be

$8\pi RD(\Sigma n\ A\Sigma n^{B}\ e^{-KN} - n_1)\ n_1 = 8\pi RD(A\Sigma n^{\nu}\ e^{-K\Sigma n} - n_1)n_1$

where $\nu = 1 + B$

Since $K<1$ the number of collision will be positive.

Thus $dn_1/dt = -8\pi RD\ n_1^2 - 8\pi RD\ (A\Sigma n^{\nu}\ e^{-K\Sigma n} - n_1)n_1$

or $dn_1/dt = -8\pi RD\ A\Sigma n^{\nu}\ n_1\ e^{-K\Sigma n}$

the doublets will decrease at the rate of $8\pi RD\ A\Sigma n^{\nu} . n_2\ e^{-K\Sigma n}$

$dn_2/dt = 8\pi RD(n_1^2/2 - n_2\ A\Sigma n^{\nu}\ e^{-K\Sigma n})$

Similarly the triplets will decrease at the rate of

$8\pi RD\ A\Sigma n^{\nu}\ n_3\ e^{-K\Sigma n}$

$$dn_3/dt = 8\pi RD\,(n_1.n_2 - A\,n_3\Sigma n^{\gamma}\,e^{-K\Sigma n})$$

The solution of the differential equations is

$$nm = \frac{n_o(4\pi RD n_o t)^{m-1}}{(1+4\pi RDA\,n_o^{\gamma}\,e^{-Kn_o}t)^{m+1}}$$

On further calculations

$$\Sigma n^{\gamma}\;e^{-K\Sigma n} = \frac{n_o^{\gamma}\cdot e^{-Kn_o}}{(1+4\pi R\,D\,A\,n_o^{\gamma}\;e^{-Kn_o}\,t)}$$

$$\text{or}\quad \Sigma n^{\gamma}\;e^{-K\Sigma n} = \frac{n_o^{\gamma}}{(1/e^{-Kn_o} + 4\pi R\,D\,A\,n_o^{\gamma}\,t)}$$

$$\text{or}\quad \Sigma n^{\gamma}\;/e^{K\Sigma n} = \frac{n_o^{\gamma}}{(e^{Kn_o} + 4\pi R\,D\,A\,n_o^{\gamma}\,t)}$$

$$\text{or}\quad \Sigma n^{\gamma}\;/1+K\Sigma n = \frac{n_o^{\gamma}}{(1+K\,n_o + 4\pi R\,D\,A\,n_o^{\gamma}\,t)}$$

Since $1/\gamma < 1$

$$\frac{\Sigma n}{(1+K\Sigma n)^{1/\gamma}} = \frac{n_o}{(1+Kn_o + 4\pi RDA\,n_o^{\gamma}\,t)^{1/\gamma}}$$

putting $1/\gamma = b$ and expanding and neglecting higher powers being small.

$$\frac{\Sigma n}{1+Kb\Sigma n} = \frac{n_o}{(1+bKn_o + b4\pi RDA\,n_o^{1/b}t)}$$

put $b4\pi RDA\,n_o^{1/b}\,t = C$

$$\frac{\Sigma n}{1+\,Kb\Sigma n} = \frac{n_o}{(1+\,bKn_o + Ct)}$$

$$\text{or}\quad \frac{1+Kb\Sigma n}{\Sigma n} = \frac{1+bKn_o + Ct}{n_o}$$

$$\text{or}\quad \frac{1}{\Sigma n} = \frac{1}{n_o} + \frac{Ct}{n_o}$$

$$\text{or}\quad \Sigma n = \frac{n_o}{1 + Ct}$$

The second equation derived purely on kinetic energy considerations by Malik etal (25) is

$$\frac{\Sigma n}{\Sigma n_o} = \frac{1+\alpha t}{1+\beta t}$$

II. The nature of the electrical double layer and sol stability interms of potential energy curves:

That the stability of a hydrophobic sol is related to its electrokinetic potential is a fairly well established fact now. Many eminent workers including Hardy (27), Gouy (28), Freundlich (29), Buzagh (30), Ivanitzkeye (31), Kruyt and Briggs (32), Pnnyscich (33) etc. have contributed to both the theoritical and the experimental aspects of the problem. However, this phenomenon which is usually ascribed to the diffused outer layer or a portion thereof has been subjected to criticism by McBain (34) and his school. According to them the mathematical treatment on which the calculation of zeta potential is derived assumes a continuous uniform electrification, whereas the charges upon surfaces and particles are spaced so far apart that they are practically independent of each other. In fact the charge distribution is so discontinuous that each charge would possess its independent ionic sphere. Also the charges on the given surface or particles are not all of the same sign. The electrokinetic potential has never been measured but is the linear movement in centimeters per sec per volt per centimeter multiplied by $\frac{4\pi\eta}{D}$, which would give a value of -102.6 mv for an ordinary chloride ion at infinite dilution as compared to +58.6 mv for the corresponding positive particle in $Fe(OH)_3$ sol. Another reason is that the conductivity observed for surfaces is too great to be accounted for by a diffused ionic atmosphere.

The conductivity produced by the electric double layer distinctly discriminates between sessile charges which are directly adsorbed on the surface. The conductivity in metallic sols results from impurities in the dispersion medium (35). In general, the conductivity of sols decreases with increasing purity of sol. In some cases the conductivity is even less than that of the dispersion medium. This may arise due to adsorption of residual electrolyte impurities by the particles.

The views of Verwey (36) and Dutch school of colloid chemists gave the most important contribution to a theory of the stability of hydrophobic sols. Hamaker (37) proposed a general theory of sol stability interms of potential curves which give the potential energy of two particles with respect to each other as a function of their mutual distance. He considered different types of potential curves, all of which consisted of an attractive potential due to London-Vander Waals forces between the particles, superimposed on a repulsive potential due to the introduction of the double layers surrounding the particles.

The view of Hamaker that a system of charged colloidal particles and oppositely charged counterions will show an attraction between the particles for certain distances was challenged by Langmuir (38), who argued that a system of charged colloidal particles and oppositely charged counter ions will show an attraction between the particles for certain distances, but was supported by Levine and Dube (39) and Corkill and Rosenhead (40), who said that attractive forces always predominate from the double layer interaction.

In the light of the conflicting view points, the theory of the interaction of double layers was reviewed in detail by Verway (36) in relation to sol stability. He concluded that the interaction must be associated with an increase of the free energy, leading to a repulsion between the particles. The repulsive potential, calculated from a consideration of the free energy for certain special cases, has been combined with the London-Vander Waals attractive potential calculated by Hamaker to obtain curves of potential against distance which agrees well with the experimental data including those on the effect of electrolyte concentration and valencies of the ions on coagulation.

Pacter (41) studied the effect of electrolytes on certain metal salt sols in the light of Verwey-Overbeek theory.

III. Application of conductometric and potentiometric titrations in the study of the constitution of sols:

When the precipitation of hydrophobic sols with electrolytes takes place, the precipitating ions enter into exchange adsorption with the counter ions in the outer diffuse portion of the double layer on the particles. For instance, in the precipitation of As_2S_3 sol, the precipitating cations are taken up in exchange with hydrogen ions; and in the case of Fe_2O_3 sol, anions are adsorbed in exchange with chloride ions. If the electrolyte is added stepwise, there is a stepwise exchange adsorption of the precipitating ion. At the same time, counter ions may be displaced from the attached (Stern) portion of the double layer. This simultaneous adsorption and counter ion displacement has been followed quantitatively with many hydrosols. The stepwise displacement of chloride from hydrous oxide sols was determined potentiometrically (42).

Conductivity changes during the addition of electrolytes to sol have been studied by a number of workers, but the problem still remains complex though some interesting conclusions have been arived at on the basis of their investigations. Smoluchowski (43) suggested a formula interconnecting the rate of cataphoresis of the particle and the conductivity.

$$k = \frac{n}{N} \cdot \frac{4\pi r \eta (r+\delta) u^2}{\delta}$$

where n is the number of particles per c.c., u is the cataphoretic velocity under the gradient of one-volt centimeter, N is the Avogadro number, η is the viscosity, δ is the thickness of the double layer, r is the radius of the particle, and k is the conductivity. According to the above formula k should increase with n and r, the quantities η, δ and u, being less variable in comparison to n and r as pointed out by Nordenson (44), but from the conductivity of the system containing the same amount of the substance in various degrees of dispersity, he found the conductivity to vary inversely as the squares of the radii of the particles. Von Hevesy (45) calculated k for values of r for gold micelle and showed that the conductivity due to micelle became negligibly small with increase of the radii of the particle. Similar observation for the conductivity of metallic sols were made by a number of other Workers (46) and they concluded that the small conductivity of metallic sols arose from the residual electrolyte, the conductivity k, due to the colloidal micelle being negligible. Mulfitano (47) observed the same behaviour for ferric oxide and arsenic penta sulphide sols. On the other hand, Duclaux (48) observed, contrary to the observations of Malfitano (loc.cit.), that ferric hydroxide and Prussion blue showed appreciable conductivity. Rabinovitch and Wassilier (49) titrated As_2S_3 sol conductometrically with barium chloride and found a discontinuity in the curve at a point by which they supposed that H^+ ions of the double layer were completely displaced by Ba^{++} ions of the electrolyte. Pennycuick (50) explained their results on the titration of platinum sol by acids, bases and salts on the assumption that counter ions were liberated from the double layer during titrations, thereby increasing the conductance of the sol, and that surface reaction of the added electrolyte with the colloidal micelles resulted in a decrease in the conductivity. He has also put forward the view that stabilizing ions may also be released due to the dissociation of the surface compounds.

Outstanding contribution on the stability of the sol by investigating the action of electrolyte on silver iodide sol has been made by Kruyt and coworkers (51). Their ideas on the different aspects of the problem, especially on exchange of counter ions and adsorption of added electrolyte on the surface have found experimental support by the observations of a number of workers. More recently work on similar lines was done by Pauli (52). Recently Malik and coworkers (53) studied the changes in the conductivity of copper ferrocyanide sol by gradual addition of electrolytes and the effect of ageing. They have suggested that by adding gradually increasing amounts of electrolyte to the sol the conductivity increases which is due to the replacement of the H^+ ions from the outer layer and the order of increase depends upon the valency of the precipitating ions, the lowering of conductivity in the intermediate stage after the addition of certain amount of the electrolyte may be due to several factors such as change in the intermiceller structure due to adsorption, surface reaction and interaction between the precipitating and peptizing ions. Increase in conductivity by keeping the sol and electrolyte overnight may be due to the joint effect of the release of the stabilizing ions along with the counter ions, and finally the slight increase in conductivity due to ageing of the sol is due to the release of the peptizing ions inconsequence of coalescence.

Potentiometric method was employed by several workers to estimate the concentration of exchanged chloride ions from the outer layer of the colloidal particles of ferric hydroxide sol (54). Weiser and Gray (55) estimated the concentration of H^+ ions released during coagulation by the same method. Malik and Beg (56) estimated the exchanged H^+(counter ions) replaced in exchange of the precipitating ions of various valencies of electrolytes added to copper ferrocyanide sol and found that the higher the valency of the precipitating ion, the greater is the displacement of the counter H^+ by exchange.

2. Sol-gel transformation:

The problem of sol-gel transformation has got a unique position in colloids. For the real understanding of the term 'gel' (the term given by Thomas Graham) much controversies exist. D.J. Llyoyd (57) began her survey on the problem of gel structure with words " the colloidal condition, the gel is one which is easier to recognise than to define". The term gel is assigned to the system characterized by the following points.

(i) They should be coherent colloid dispersed system of atleast two components, (ii) They should exhibit mechanical properties, characteristics of the solid state, (iii) both the dispersed component and dispersion medium extend themselves continuously throughout the whole system.

Von Nageli (58), focussing attention on natural objects like cell walls, starch grains and the like, postulated a discontinuous granular structure of very small crystalline particles, carrying round themselves concentric shells of tightly bound water. The birefringence of these objects would be due to the orientation of these crystallites termed micelles. The micellar theory in its essential features was supported by numerous authors like Zsigmondy (1911), Bachmann (1912), Arisz (1915), Bradford (1918) and others. This theory may be classified as the solid-liquid theory of gel structure. W. Ostwald (1909) put forward a liquid-liquid theory which has but historical interest.

The point of view generally accepted at the present moment is a similar form of the solid-liquid theory postulating that both the solid and the liquid components are continuous in themselves. Von Weimarn (1910) held similar ideas, entirely filling in with modern views. One of the earliest forms of this theory may be called fibrillar theory. The solid component is assumed to be of a more or less fibrillar nature and to form a continuous framework or meshwork throughout the system. This idea has been especially suggested by the study of gels formed by certain low molecular substances, which under other conditions can also crystallise from their solutions.

Extensive elucidating researches on gel formation from a number of inorganic substances have been carried out by Von Weimarn (59). He has given the equation $n = K \frac{P}{L}$ where L is the solubility, P the degree of supersaturation, K a factor involving viscosity, n the number of crystallisation centres (germs) generated. Crystallisation is largely governed by two factors, the number of crystallisation centres formed and the velocity of crystallisation. Generally speaking, the number of germs and the crystallisation velocity will be small in very dilute solutions and low degrees of supersaturation. Few, slowly growing, crystals will be formed, but in length of time the crystals may become larger and larger if a small degree of supersaturation is maintained. In concentrated solutions of highly soluble reactants, the degree of supersaturation P will be large, n will, hence, be at maxima and an enormous number of very small crystals will be formed.

The fibrillar theory was first suggested by Von Bemmelen (1898). In Butschi's honey comb idea (Wabenstruklur) a continuous structure of the solid component and a discontinuous dispersion of the fluid were assumed, the latter being enclosed in polygonal cells formed by the former.

The solid-liquid theory has attributed much use to discuss whether the solid component is crystalline, as Nageli has postulated, or not; if not, the problem is more or less irrelevant with respect to the general conception of the conditions of the gel, since all gels have not the same architecture. As early as 1914, Procter (60), while investigating the swelling of ~~gelation~~ gels, put forward the solid-solution theory. His theory was supported by Katz in 1918.

Valuable contributions regarding the clarification of gel structure and the terminology concerned were made by Frey-Wyssling (61). He proposed to conceive the classical Nageli terminology in a modified form, designating the typical gel structure consisting of two dispersed components each continuous in itself as micellar system in contrast to the common disperse system consisting of individual dispersed particles in dispersion medium.

In connection with the study of swelling phenomena and chemical reactions in crysto-crystalline macromoleoular systems, the term intramicellar and intermicellar processes were introduced by Katz. The former refers to processes occuring between crystallites and the latter to occurances inside them. According to Frey-Wyssling, intramicellar processes are those occuring inside the solid frame work structure and intermicellar ones those occuring in its interstices. Hardy (1899) has discriminated heat-reversible and heat non-reversible gels, according as the gel can be liquefied and solidified at will by a change in temperature.

A number of physical methods can be employed in studying sol-gel transformation. These are transition temperature, thermochemical effects, increase in intensity of light, volume changes, swelling, viscosity, mechanical agitation (thixotropy), electrical conductivity, and hydrogen ion concentration. A few of these methods pertaining to the present work, are given below.

VISCOSITY:

The most important practical applications of the science of lyophobic colloids are doubtless to be found in the domain of mechanical and rheological properties. The rheological properties are described by relations between stress and strain (elasticity) or between stress and rate of strain (flow). In the simplest cases these relations are a simple proportionality as in the viscosity of Newtonian liquids. The basis for consideration on the viscosity of suspension has been given by Einstein (62) who calculated the viscosity of a dilute suspension of rigid spherical particles. Making the assumptions of incompressibility of the system, no slip between the particles and the liquid, no turbulance, absence of inertia effects, and the flow of the liquid which may be described by macroscopic hydrodynamical equations also in the immediate neighbourhood of the particles, he derived the following equation for dilute suspensions. $\eta_s = \eta_o \cdot (1+2.5\phi)$, where η_s is the viscosity coefficient of the dispersed system and η_o that of the medium of dispersion, ϕ the total volume fraction occupied by the spherical particles The correctness of the expression $\eta_s = \eta_o(1+2.5\phi)$ has been tested with good results provided the conditions mentioned above, viz., rigid, spherical, uncharged particles, were satisfied.

Einstein's equation has been extended by Smoluchowski for the case where the dispersed particles are the carriers of an electrical double layer. The outermost layers extending into the liquid, which are carried along by moving liquid, experience a drag through the opposite charge on the particles, whereby an extra increase of the internal friction occurs (electroviscous effect). The modified Einstein's equation given by Smoluchowski (63)

$$\frac{\eta_s - \eta_o}{\eta_o} = K\phi\left[1 + \frac{1}{\lambda \eta_o r^2}\left(\frac{\zeta \epsilon}{2\pi}\right)^2\right]$$

in which λ is the specific conductivity and ϵ the dielectric constant of the system, r, the radius of the particles and ζ (zeta) the difference of potential in the double layer.

Von Smoluchowski published his equation without indicating the derivation. It was not until 1936 that Krasny-Ergen (64) gave the derivation resulting in an equation of the same form as above. More recently, Booth (65) reconsidered the whole equation and concluded that both Von Smoluchowski and Krasny-Ergen's results were too high and that the electroviscous effect, although existing, was much smaller than that predicted by the above equation. His equation is more complicated one. Similar type of equation has been published by Finkelshtein and Chursin (66). Experimental investigations on electroviscous effect have been mainly carried out on hydrophilic colloids. Apart from more or less incidental empirical relations, equation with a theoritical background have been published by Guth, Gold and Simha (67), Simha (68), De Bruyn (69),Saito (70) and by Vand (71).

It has been observed that the viscosity of the hydrophobic sols is more or less the same as that of the dispersion medium and the concentration of the sol generally does not change the viscosity to a great extent. A considerable amount of original work has been contributed by Dhar, Ghosh, Chakravarty and Coworkers (72) on the viscosity changes in a large number of these sols by the addition of small quantities of electrolytes and on the basis of their extensive work they concluded (i) other things being equal, the uncharged substance is more hydrated than the sol (ii) the greater the hydration of the substance the greater is the viscosity (iii) when a sol adsorbs an ion carrying the same charge as the sol, because of chemical affinity, the charge on the sol is increased which should result in the decrease of viscosity.

By comparing the behaviour of not less than thirty sols Dhar and Collaborators showed that the changes in viscosity of a sol on the addition of an electrolyte will certainly depend on the ratio of the adsorption of the positive and negative ions. If the sol absorbs more of the ions carrying opposite charge than the ions carrying the same charge, the charge on the sol will be decreased, more hydration will follow and consequently its viscosity will be increased and vice versa.

In recent years a number of workers namely Varadwani (73) Mata Prasad and Mehta (74), Mata Prasad and Modak (75), Mushram and Satya Prakash (76), Malik and Bhattacharya (77), Malik and Ali (78), Mushran and Agrawal (79) have studied the viscosity of hydrophobic colloidal solutions under different conditions i.e. during dialysis or during the transformation into jellies.

Jirgenson (80) has discussed the relation between the solvation and shape of colloidal particles as well as between solvation and viscosity. In his view, the solvation increases when a corpuscular particle is transformed into a rod like or thread like particle and consequently the viscosity also increases. If the threads are further broken down into smaller fragments, the viscosity decreases but a further increase in the chemical solvation is supposed to take place. Greenberg, Chang and Jamutouzki (81) studied viscosity changes while establishing the nature of polysilicic acid.

THIXOTROPY:

In loosely packed and ramifying aggregates, the apparent viscosity decreases on increasing the rate of shear due to the breakdown or distortion. Yet another extreme case may arise. The ramification may proceed to such an extent that the system begins to resemble an electrical solid, a sol becomes jelly. In these systems the structural viscosity depends upon the previous history and the treatment of the system and how long it had been kept undisturbed. When such a system is stirred, the structure is partly destroyed but slowly regains its original form on standing. Pterfi (82) gave to this phenomenon the name "thixotropy", which has been extensively studied by the famous German chemist like Freundlich (83). Practical applications include studies on clays, paints (84), quick sand and drilling units etc.

Quantitative treatment of the phenomenon of 'thixotropy' has been carried out by a number of workers. These studies also include inorganic gel forming systems, such as hydrous oxide sols. Employing falling sphere viscometer, C.F. Goodeve and G.W. Whitfield (85) showed that the apparent viscosity when plotted against the rate of shear gave a slope which can be numerical measure of the degree of thixotropy. E. Schalek and A. Szegwari (86) gave an empirical equation $\log \theta = A-BC$, where θ is the time of solidification, A and B are constants and C the concentration of the added electrolyte for the solidification of an iron oxide sol by the addition of sodium oxalate and sodium sulphate, thereby showing that thixotropic gelation is just like slow coagulation. This has also been confirmed by earlier workers (87-96) on the basis of potential energy curves. Malik and Singhal (97) studied the thixotropic behaviour of 'Alkali' bentonite suspension, bentonite shows a great tendency to undergo gelation.

Another interesting phenomenon closely related to the thixotropic behaviour of sol is that of 'rheopexy'. The latter term was introduced by Freundlich for systems which can be transformed quickly into gels by gently rolling the reaction vessel between hands.

ELECTRICAL CONDUCTIVITY:

This property can be employed as a quantitative measure for studying gelation, the effects are neither so marked nor so useful as viscosity measurements or other properties. Malik and Bhattacharya (98) studied the variation in conductivity during dialysis of concentrated suspensions of Prussian and Turnbull's blue. They observed that the conductivity changes during the period of dialysis, were either very small or practically constant, depending upon the specific concentration of the reactants mixed. It was found that in inorganic gel the electrical conductivity does not show any appreciable change at the gel formation stage inspite of tremendous changes in viscosity. "This proves that mobility of the ions is not restricted and, hence, the gels must contain an anastomising systems of capillary spaces filled with the unchanged solvent".

A number of workers Laing and Mc Bain (99), Dhar, Chakarvarty and Coworkers (100) have studied the conductivity changes during gelation for silicic acid, cerium hydroxide, thorium hydroxide and other gels and found that there was no change in conductance during gelation in some cases while in others marked changes could be observed and no general relationship could be arrived at for inorganic gel forming mixtures. However Robert and Malan (101) used the conductivity measurements to ascertain the problem of the gel structure in the case of lyophilic colloids. They observed a gradual decrease in the conductance of gelatin during gelation with a maximum decrease of 4-8%. They further observed that the conductance of Kcl and KcNS was appreciably lowered in the presence of gelatin, and was of the same order as was in the sol and gel state. On the basis of their results they regarded the gelatin gel to have fibrillar structure.

The changes in conductivity of lyophobic colloidal solutions during dialysis has been a subject of investigations in recent years by Datar (102), Desai, Barve and Paranjpe (103), and Vora and Desai (104). In such cases a decrease in conductance of the sols accompanied by a decrease in their stability during dialysis was observed.

Very recently Malik and Ali (105) studied the variations in conductivity during sol-gel transformation of ferric tungstate and found that the variations in conductivity were not appreciable.

pH measurements:

This property has not been much used in studying sol-gel transformation in inorganic colloids although extensive use is made in studying the mechanism of coagulation of lyophobic colloids having H^+ as the central ion and in explaining the base exchange properties of soils and hydrogen clays. Mention may be made of the work of Freundlich (106) on the gelation of ferric hydroxide sol in which he observed that the time of solidification changes hundred fold upon a change of pH less than a unit. Dhar and Satya Prakash (107) studied the variation in pH while preparing jellies by the addition of electrolytes to various sols. Kruyt and Postma (108) have studied the changes in pH values of the silicic acid during dialysis. Mata Prasad and Hattiangadi (109) have shown that during gelation of silicic acid sol when the mixtures are alkaline, the pH value increases during and after gelation. Study on the variation in pH during gelation helps in giving an insight on the composition and chemical behaviour of the sol under study. Recently Malik and Ali (110) studied pH changes during sol-gel transformation of ferric tungstate gel. From these studies they could infer that normal tungstates undergo conversion into para tungstates.

The effect of hydrogen ion concentration has been investigated in connection with clays by R. Bradfield (111), in the adsorption of clays by Marker and Gordon (112). Kraemer (113) has studied the influence of hydrogen ions on the formation of manganese arsenate jelly.

3. Adsorption:

A number of workers have studied the phenomenon of adsorption. Adsorption consists in the concentration or accumulation of substances at surfaces or interfaces. The adsorbing phase is called the adsorbent, and the adsorbed phase, the adsorbate. If the atoms or molecules of one phase penetrate among the atoms or molecules of the second more or less uniformly, the phenomenon is termed absorption or solution, to distinguish it from the surface phenomenon. Since matter in colloidal state presents an enormous surface relative to the mass, adsorption is probably the most common and important phenomenon encountered in colloid or surface chemistry.

The two types of adsorption viz., physical adsorption and chemisorption are known. The forces causing physical adsorption are similar to those that cause the condensation of a gas to form a liquid. The heat evolved upon adsorption is small, and the adsorption is completely reversible. In chemisorption the heat evolved is considerably larger, and it may be considered that a surface compound is formed. Since this is true only a single adsorbed layer may be formed whereas in physical adsorption the adsorbed layer may be several molecules thick.

For a given weight of adsorbent with a given surface area the amount of material adsorbed depends on the pressure (or concentration) of the material around the adsorbent. The higher the pressure or concentration, the greater the amount that can be adsorbed. When an adsorbing material is placed in contact with a gas or a solution, the amount adsorbed will gradually increase, and the concentration of the surrounding molecules will decrease until the rate of desorption becomes equal to the rate of adsorption, and, thus, an equilibrium is established. If the concentration of gas or solution is increased, the weight of adsorbed substance will increase to a new equilibrium value, and, if the concentration is decreased, the adsorbent will lose adsorbed substance to its surroundings until equilibrium is again established.

Several equations have been devised to represent adsorption data. The equation given below, which does not have any theoritical basis but is empirical has been found useful, and is known as Freundlich (1910) adsorption isotherm. This equation was verified by Keenan and Holmes (114). The equation is mathematically expressed as $x/m=KC^n$, where x is the amount adsorbed on mass m of adsorbent, C the concentration of the adsorbate at the stage at which adsorption attains equilibrium, where K and n are constants $(n<1)$. The constants may be determined by plotting log x/m versus log C, since $\log x/m = n \log C + \log K$. A more significant isotherm is that of Langmuir (115) which was derived originally by a simple theory for the case of physical adsorption of a gas on a plane solid surface, assuming that a layer only one molecule thick could be adsorbed. This isotherm is expressed by the equation

$x/m = Kc/1+K_1c$ where K and K_1 are constants, x/m, the amount of material adsorbed per unit weight of adsorbent, c the concentration of the adsorbate at the stage at which adsorption attains equilibrium. The above equation can also be represented as $x = abc/1+ac$, the linear form of which is $\frac{c}{x/m} = 1/ab + c/b$. The constants can be determined by plotting m/x against $^1/c$. The intercept is 1/b and the slope 1/ab.

Neither the Freundlich nor the Langmuir equation is capable of representing the S-shaped (Sigmoid) isotherms which are obtained when the adsorption of vapours on a porous solid is studied at relatively high vapour pressures (approaching saturation). A more complicated equation is used which is the isotherm of Brunauer, Emmett, and Teller (116). This equation was arrived at on the assumption (confirmed by Harkins and Jura (117)) that multimolecular adsorption can take place. This equation is

$$\frac{p/p_o}{x(1-p/p_o)} = \frac{1}{x_m c} + \frac{(c-1)}{x_m c}\frac{p}{p_o}$$

where x is the amount of vapour adsorbed at a partial pressure p, p_o is the saturation pressure, x_m the amount of vapour which would be required to form a monomolecular layer over the surface, and c is a constant. This B.E.T. equation represents fairly satisfactorily the adsorption of water by textiles, silica gel, etc., and of many vapours by finely divided powders. It is very much used for determining the surface areas of powders. According to this equation a plot of $p/x(p_o-p)$ versus p/p_o should give a straight line with a slope of $c-1/x_m c$ and an intercept of $1/x_m c$, where c is a constant at a given temperature. The surface area accupied by a single molecule of adsorbate on the surface may be estimated from the density of the liquefied adsorbate. From the measured value of x_m the surface area of the adsorbent may be calculated. This method is widely used in the study of solid catalysts and adsorbents.

4. Interaction of dyes with lyophobic colloids:

Most of the existing literature deals with the applied aspect of the problem. References on fundamental work are few and far between.

The references on the adsorption of dyes by the hydrous oxides or on the formation of colour lakes by the dyes of the alizarin class exist in the chemical literature (118). The adsorption of dyes by the hydrous oxides of iron, aluminium, chromium, and tin is the basis of the process of mordant dyeing. Giles, Ealson and Mckay (119) studied the mechanism of adsorption of cationic dyes by alumina. In this study a range of cationic dyes was applied to alkaline chromatographic alumina powder and the nature of adsorption was interpreted from the shape of the adsorption isotherms. Ghosh and Coworkers (120) studied the adsorption of crystal violet on hydrous ferric oxide. Gyani (121) studied the adsorption of night blue, methylene blue and crystal violet by the silica gel with the help of colorimetric techniques and found that 80% of the initial dye concentration got adsorbed on the silica gel. According to him the extent of adsorption of dyes on silica gel is more closely related to their chemical nature than to their molecular size or molecular weight. Blank, Rosington and Weinland (122) studied the adsorption of organic compounds on portland cement and found that in some cases Langmuir and Freundlich adsorption isotherms are obtained. Brooks (123) studied the mechanism of methylene blue dye adsorption on siliceous minerals found in petroleum reservoir formations, according to him in the case of clays (montmorillonite and Kaolinite) the saturation dye adsorption capacity must be attributed to two mechanisms: first, to cation exchange resulting from isomorphous substitution in the alumino silicate lattice and, second, to an adsorption mechanism which might be either physical (Vander Waals) adsorption or chemisorption (hydrogen bonding) with the surface SiOH and AlOH of the alumino silicate lattice, the dye adsorption on silica is due to the physical or chemisorption mechanisms alone.

Kehrin and Thewis (124) studied the precipitation of colloidal solutions of Benzopurpurin 10B with ferric chloride solutions and with ferric oxide sols. The precipitates were analysed and it was shown that salt formation was involved. This was confirmed by measurements of electrophoretic mobility. Kelvin and Thewis (125) also studied the theoritical considerations of the iron treatment of waste water containing dyes, in which they have theoritically discussed the purification of dye waste liquors by the treatment of waste water with iron salts. The colloidal nature of the process is stressed and the results of some experiments with indigo carmine and ferric chloride solutions of various concentrations have been reported.

Trause and Shikata (126) studied the fixation of basic dyes by zinc ferrocyanide (127) in the direct printing of fabrics. Weiser (118) reported that lakes are formed by the addition of sodium alizarate to positively charged hydrous oxide sols stabilized by preferential adsorption of hydrogen ion.

Statement of the problem:

The following aspects of the dye-lyophobic colloidal systems have been studied.

(i) Interaction of acid and basic dyes with ferric oxide, alumina and arsenic sulphide sols and the quantitative determination of their binding.

(ii) Sol-gel transformation of ferric oxide, alumina and silicic acid in presence of acid and basic dyes.

(iii) Adsorption of the acid and basic dyes by silicic acid, ferric oxide and alumina gels.

The interpretation of the available data on the slow coagulation, acclimatisation and ionic antagonism of cobalt, nickel, manganese and zinc ferrocyanides has been included in the 'Appendix'.

INTERACTION OF ARSENIOUS SULPHIDE SOL WITH ACID AND BASIC DYES

Dyes usually behave as ordinary electrolytes in aqueous solutions (1) although many are found to exist as colloids and electrolytes at the same time. The addition of suitable electrolytes to dye solutions (salting out process), at the correct concentration, has the following effect:

(a) in dilute solutions the addition of ions of opposite charge maintains or intensifies the colloidal character of the original solution:

(b) in concentrated solution a precipitate is formed which upon isolation represents the concentrated dye.

The nature of very dilute aqueous solutions has been a subject of recent study by Mitra (2), who observed that acid dyes like indigo carmine, methyl orange could be coagulated by the addition of electrolytes while the basic dyes like malachite green could not be coagulated by electrolytes. He concluded that the acidic dyes except sodium alizarate or alizarin are colloidal in aqueous solutions and that most of the basic dyes are completely electrolytic where as the rest are partially colloidal in the aqueous solutions.

The other aspect worth mentioning, about the behaviour of the dyes in aqueous solutions is their interaction with colloidal material. The most common example is the dyeing of mordant cloth where colour lakes are formed with dyes and the hydrous oxides. Other examples include the diffusion of dyes into gels (gelatin, agar or soap) studied by Trause and Shikata (3), the fixation of basic dyes by zinc ferrocyanide (4) in the direct printing of fabrics. Karezag (5) studied the adsorption of dyes by colloids and made the interesting observation that the colour base of the dye is a manifestation of the chemical effect of the electrical energy on the surface of the colloidal particle: to what he named as electropic adsorption. According to him this type of adsorption is limited to negatively charged colloids and is independent of the charge on the dye. In other cases adsorption of the type like hydrolytic (6), chemisorption (7) or chemical compound formation (8) have been cited in the literature.

From the view point of the interaction of the dyes with colloidal material, one interesting study, viz., investigations dealing with the interaction of dyes with colloidal solutions has not yet been equally taken. Ordinarily with hydrophobic colloids effects similar to the coagulation of sols by the addition of electrolytes or mutual interaction between oppositely charged colloidal solutions are expected to be observed but it is quite probable that useful data concerning the extent of binding of the dye by the sol particles or some information on the nature of the micelles in hydrophobic colloidal solutions may also be obtained.

Klotz (9) studied spectrophotometrically the binding of dyes with hydrophillic colloids. This very method was extended to the metal sulphides using the following sol-dye combinations.

(a) methylene blue and arsenic sulphide sol; (b) malachite green and arsenic sulphide sol; (c) alizarin sulphonic acid and arsenic sulphide sol; (d) methyl orange and arsenic sulphide sol.

EXPERIMENTAL

1.(a) The alizarin sulphonic acid (sod. salt), methyl orange (sod. salt), methylene blue (cl^-) and malachite green (cl^-) were either B.D.H or Merck products. The solution were prepared by dissolving in double distilled water.

(b) Preparation of Arsenic sulphide sol: Arsenic sulphide sol (10) was prepared by slowly bubbling H_2S gas in a saturated solution of AS_2O_3. The excess of H_2S was removed from the sol by bubbling purified hydrogen gas till the sol was free from the smell of H_2S. The sol was filtered and stored in a conical flask. The concentration of the sol was estimated by coagulating a known volume of the sol with hydrochloric acid and filtering it through a sintered glass crucible and weighing as As_2S_3 after drying at 100°C in an electric oven.

(c) Preparation of Buffers: Walpole buffers (11) were prepared by mixing sodium acetate (0.2M) and Hcl (0.2M) in different proportions to get solutions of required pH.

2. Apparatus and Technique: The absorption spectra of the solutions were measured with a Bausch and Lomb 'spectronic 20'. The molar extinction coefficient was calculated from the relationship $\epsilon = \frac{1}{c.d} \log_{10} \frac{I_o}{I}$, where I_o is the intensity of the light passing through the solvent, I the intensity of the light passing through the solution, c, the molar concentration of the solute, and

d, the thickness of the absorption cell in centimeter.

Viscosity measurements:

Viscosity measurements were carried out by modified Scarpa's method as given in chapter IV.

Cataphoretic measurements:

Burton's (12) recommended by Freundlich (13) for determining the cataphoretic velocity of colloidal particles was employed. The mobility of the particle is independent of its size and form and is related to potential as follows

$$\zeta = \frac{4\pi\eta u}{H D}$$

where η is the viscosity of the medium in which the particles move, D is the dielectric constant of the medium, H is the potential gradient of the applied field in electrostatic unit, u is the velocity of the particles in cm/sec under the applied field.

A U tube with a little of water in its bottom was taken. The dye-sol mixture was introduced slowly in the U tube by its side tube, so that in both the limbs there was a column of water above the sol boundary. Platinized platinum electrodes (0.81 sq. cm.) were immersed in both the limbs so that the electrodes dipped in the water. A current of 120 volts was passed through the U tube by connecting the electrodes to a rectifier and potential divider (Low voltage unit, Type LV 55, 300 V,). After fixed intervals of times the displacements of the boundary in the two limbs were noted. The current was reversed and the displacement noted after the same interval of time. The mean of the readings was taken as the displacement in that time. ζ-potential was calculated by the above given relation. The viscosity of the sol-dye mixture was also measured.

pH measurements:

The variation in hydrogen ion concentration during the course of investigations was determined with the help of Cambridge bench pH meter.

Conductivity measurements:

The conductivity measurements were carried out by T.W.T conductivity bridge.

The following sets were used for measuring the variations in viscosity, pH, conductivity, ζ-potential

Set No.1:

(a) Arsenic sulphide sol (0.7400 gms. As_2S_3/litre, pH = 3.68, conductance = 2.25 x 10^{-4}mhos) + malachite green (1.0 x 10^{-3}M, pH = 3.28, conductance = 4.9 x 10^{-4}mhos). Each mixture contains 25 cc of the sol and varying amounts (0 cc, 0.2 cc, 0.4 cc, 0.6 cc, 0.8 cc, 1.0 cc, 1.5 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(b) Buffer solution (same pH as of sol) + malachite green (1.0 x 10^{-3}M) mixture. Each mixture contains 25 cc of the buffer and varying amounts (0 cc, 0.2 cc, 0.4 cc, 0.6 cc, 0.8 cc, 1.0 cc, 1.5 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(c) 0 cc, 0.2 cc, 0.4 cc, 0.6 cc, 0.8 cc, 1.0 cc, 1.5 cc of malachite green (1.0 x 10^{-3}M). Total volume made upto 30 cc by double distilled water.

Set No.2:

(a) Arsenic sulphide sol (0.7400 gms. As_2S_3/litre, pH = 3.68, conductance = 2.25 x 10^{-4}mhos) + methylene blue (1.0 x 10^{-3}M, pH = 5.24, conductance = 5.55 x 10^{-4}mhos). Each mixture contains 25 cc of the sol and varying amounts (0 cc, 0.1 cc, 0.3 cc, 0.4 cc, 0.5 cc, 1.0 cc, 2.0 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(b) Buffer solution (same pH as of sol) + methylene blue (1.0×10^{-3}M) mixture. Each mixture contains 25 cc of the buffer and varying amount (0 cc, 0.1 cc, 0.3 cc, 0.4 cc, 0.5 cc, 1.0 cc, 2.0 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(c) 0 cc, 0.1 cc, 0.3 cc, 0.4 cc, 0.5 cc, 1.0 cc, 2.0 cc of methylene blue (1.0×10^{-3}M). Total volume made upto 30 cc by double distilled water.

Set No.3:

(a) Arsenic sulphide sol (0.7400 gms. As_2S_3/litre, pH = 3.68, conductance = 2.25×10^{-4}mhos) + methyl orange (2.0×10^{-3}M, pH = 5.92, conductance = 2.38×10^{-4}mhos). Each mixture contains 25 cc of the sol and varying amounts (0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(b) Buffer solution (same pH as of sol) + methyl orange (2.0×10^{-3}M) mixture. Each mixture contains 25 cc of the buffer and varying amounts (0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc) of the dye. Total volume made upto 30 cc by double distilled water.

(c) 0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc of the methyl orange (2.0×10^{-3}M). Total volume made upto 30 cc by double distilled water.

Set No.4:

(a) Arsenic sulphide sol (0.7400 gms. As_2S_3/litre, pH = 3.68, conductance = 2.25×10^{-4}mhos) + alizarin sulphonic acid (4.0×10^{-2}M, pH = 2.98, conductance = 1.20×10^{-2}mhos). Each mixture contains 10 cc of the sol and varying amounts (0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc) of the dye. Total volume made upto 20 cc by double distilled water.

(b) Buffer solution (same pH as of sol) + alizarin sulphonic acid (4.0×10^{-2}M) mixture. Each mixture contains 10 cc of the buffer and varying amounts (0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc) of the dye. Total volume made upto 20 cc by double distilled water.

(c) 0 cc, 1.0 cc, 2.0 cc, 3.0 cc, 4.0 cc, 5.0 cc of alizarin sulphonic acid (4.0×10^{-2}M). Total volume made upto 20 cc by double distilled water.

The above sets could not be employed for absorption studies since the constituents of the mixtures were concentrated. Dilute solutions both of the sol and the dye were used. The following sets were employed to determine the binding of the dye.

Set No.5:

(a) 5 cc of sol (0.0110 gms. As_2S_3/litre) + a very small quantity of dye (0.5 cc of 1.5×10^{-4}M aliz. s. acid, 0.5 cc of 0.0451×10^{-3}M methyl orange, 0.5 cc of

0.0314×10^{-3}M methylene blue and 0.5 cc of 0.0196×10^{-3}M malachite green), total volume was made upto 10 cc by the addition of double distilled water.

(b) 1, 2, 3, 4 and 5 ccs of 1.5×10^{-4}M aliz. s. acid + 5 cc sol, 2, 3, 4 and 5 ccs of 0.0451×10^{-3}M methyl orange + 5 cc sol, 2, 3, 4 and 5 ccs of 0.0314×10^{-3}M methyl blue + 5 cc sol, 2, 3, 4 and 5 ccs of 0.0196×10^{-3}M malachite green + 5 cc sol. The total volume was made upto 10 cc by the addition of double distilled water.

(c) Solutions of varying concentrations of dyes (1.5×10^{-4}M aliz. s. acid, 0.0451×10^{-3}M methyl orange, 0.0314×10^{-3}M methylene blue and 0.0196×10^{-3}M malachite green were taken.

A period of about twelve hours was allowed to attain equilibrium before carrying out absorption experiments. The Walpole buffers having the same pH as the sols were prepared for the required pH ranges and experiments were performed under similar conditions as given above.

Sets 5 (a), 5 (b) and 5 (c) were used to determined ϵ_B, ϵ_{app} and ϵ_F respectively in Klotz's equation (9)

$$\alpha = \frac{\epsilon_{app} - \epsilon_B}{\epsilon_F - \epsilon_B}$$

where ϵ_{app} is the apparent molar extinction coefficient, ϵ_B is the molar extinction coefficient of the bound dye and

ϵ_F is the molar extinction coefficient of the free dye.

The pH metric, conductometric, Viscometric and cataphoretic studies were done with sets No. 1, 2, 3, and 4.

VARIATIONS IN pH.

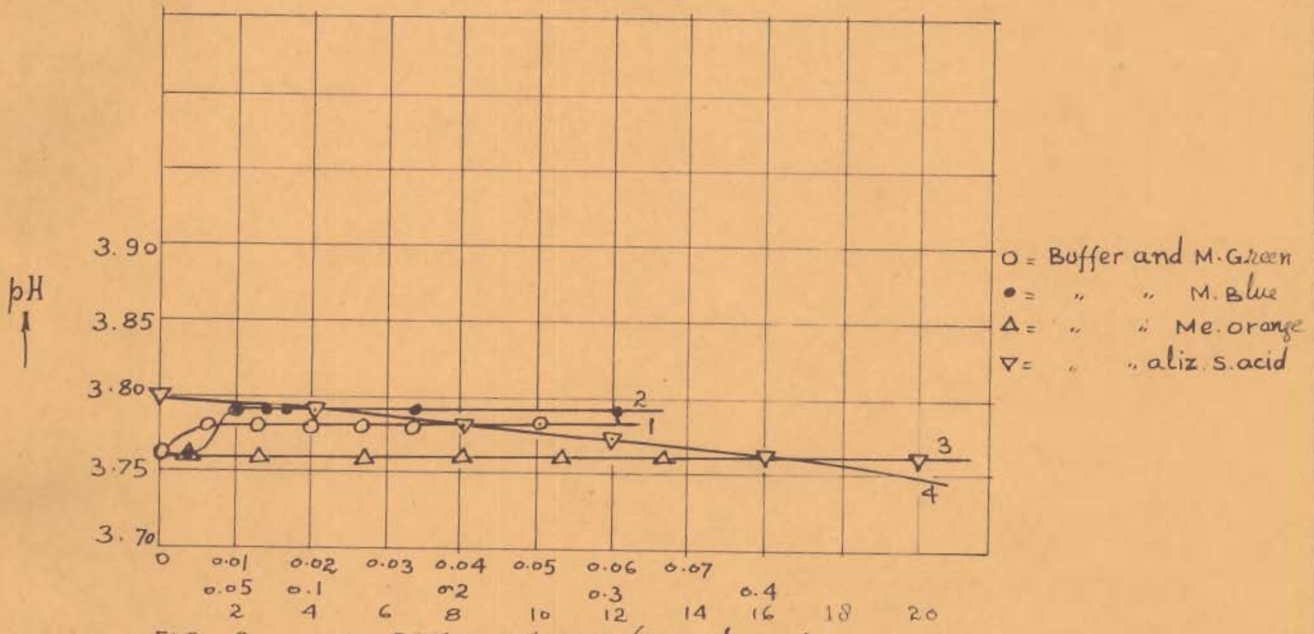


FIG_2 → CONC. OF DYE (m M/LITRE)

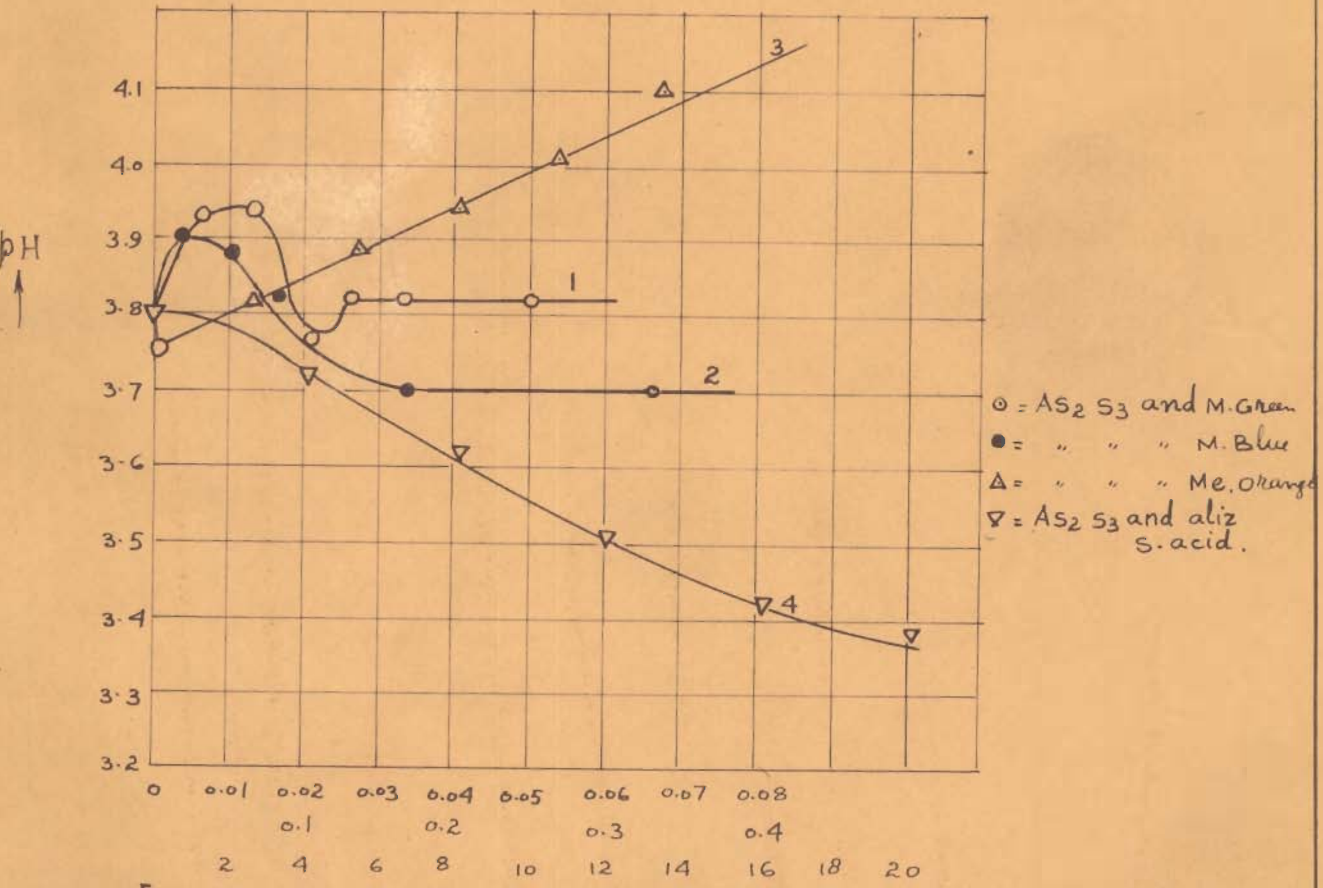


FIG-1 → CONC. OF DYE (mM/LITRE)

TABLE No. 1.

Variations in pH, viscosity, conductivity, ζ-potential of As_2S_3; buffer and dispersion medium by the addition of malachite green.

Volume of dye	Set No. 1 (a)				Set No.1 (b)			Set No.1(
	pH sol+dye mixture	Viscosity sol+dye mixture (centi-poise	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise
0 cc	3.76	0.7201	2.15×10^{-4}	2.541×10^{-7}	3.76	0.7420	3.15×10^{-2}	0.7155
0.2"	3.93	0.7201	1.85×10^{-4}	2.840×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
0.4"	3.94	0.7201	1.82×10^{-4}	2.989×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
0.6"	3.77	0.7202	2.12×10^{-4}	2.392×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
0.8"	3.82	0.7271	2.05×10^{-4}	2.264×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
1.0"	3.82	0.7281	2.05×10^{-4}	2.115×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
1.5"	3.82	0.7353	2.05×10^{-4}	1.679×10^{-7}	3.78	0.7424	2.68×10^{-2}	0.7158
	Fig.(1) curve 1	Fig.(3) curve 1	Fig.(5) curve 1	Fig.(7) curve 1	Fig.(2) curve 1	Fig.(4) curve 1	Fig.(6) curve 1	Fig.(4) curve 5

VARIATIONS IN VISCOSITY.

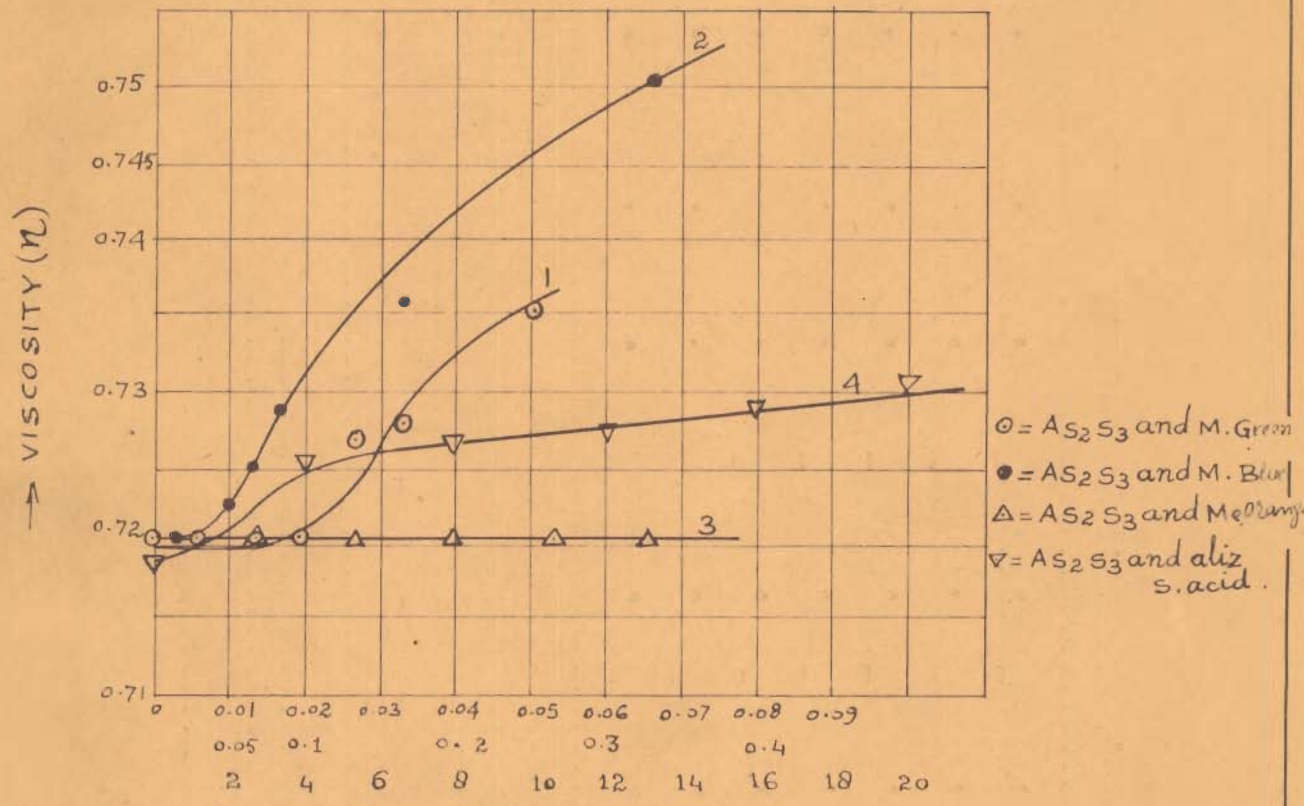


FIG- 3

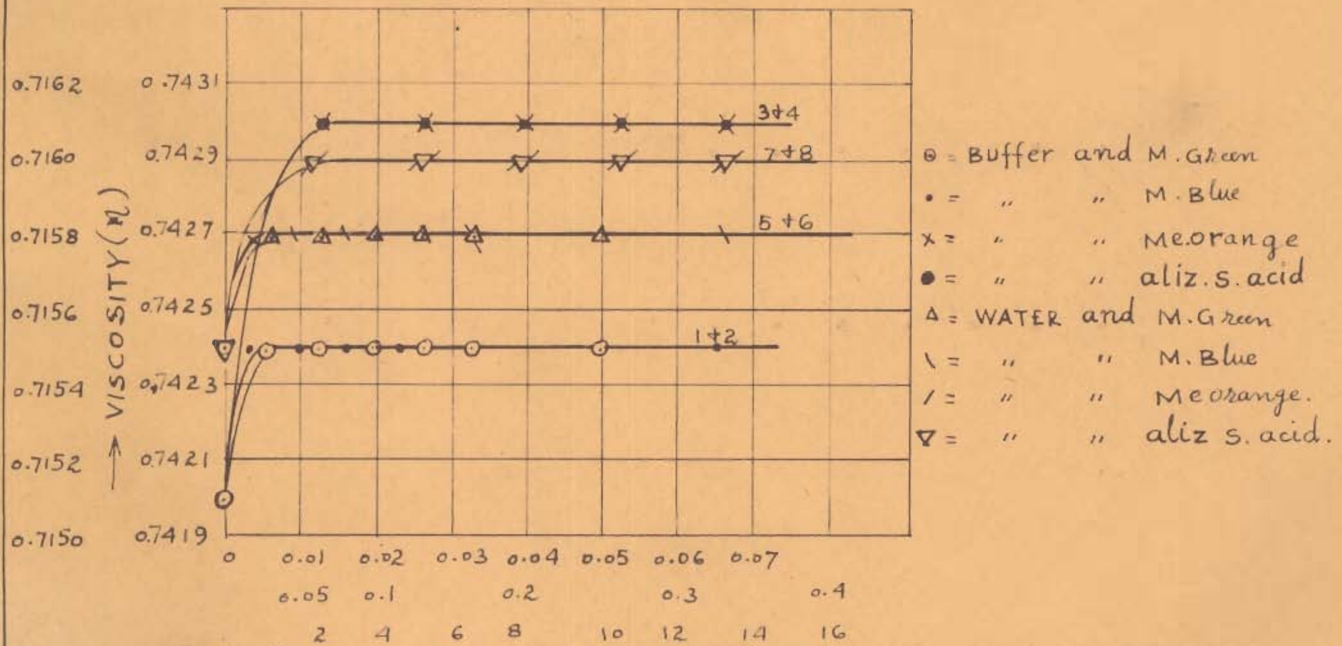


FIG- 4

TABLE NO.2.

Variations in pH, viscosity, conductivity, ζ-potential of As_2S_3; buffer and dispersion medium by the addition of methylene blue.

Volume of dye	Set No. 2 (a)				Set No.2 (b)			Set No.2 (c)
	pH sol+dye mixture	Viscosity sol+dye mixture (centi-poise	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise
0 cc	3.76	0.7201	2.15×10^{-4}	2.541×10^{-7}	3.76	0.7420	3.15×10^{-2}	0.7155
0.1"	3.90	0.7201	2.15×10^{-4}	2.690×10^{-7}	3.76	0.7424	2.65×10^{-2}	0.7158
0.3"	3.88	0.7224	2.18×10^{-4}	2.575×10^{-7}	3.79	0.7424	2.65×10^{-2}	0.7158
0.4"	3.82	0.7249	2.35×10^{-4}	2.345×10^{-7}	3.79	0.7424	2.65×10^{-2}	0.7158
0.5"	3.82	0.7288	2.45×10^{-4}	2.445×10^{-7}	3.79	0.7424	2.65×10^{-2}	0.7158
1.0"	3.70	0.7360	2.55×10^{-4}	2.164×10^{-7}	3.79	0.7424	2.65×10^{-2}	0.7158
2.0"	3.70	0.7509	2.65×10^{-4}	-	3.79	0.7424	2.65×10^{-2}	0.7158
	Fig.(1) curve 2	Fig.(3) curve 2	Fig.(5) curve 2	Fig.(7) curve 2	Fig.(2) curve 2	Fig.(4) curve 2	Fig.(6) curve 2	Fig.(4) curve 6

VARIATIONS IN CONDUCTIVITY

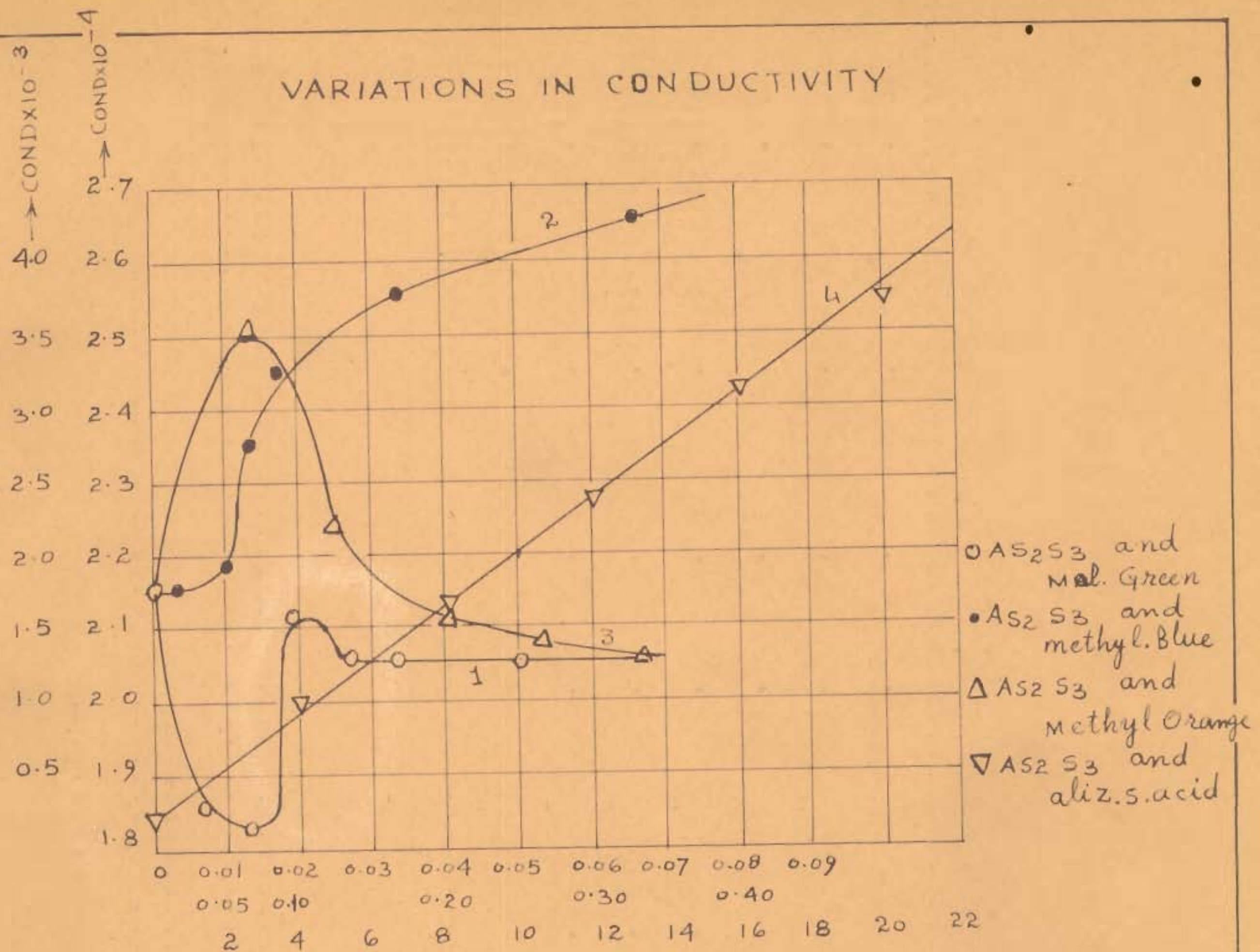


FIG-5 → CONCENTRATION OF DYE (mM/LITRE)

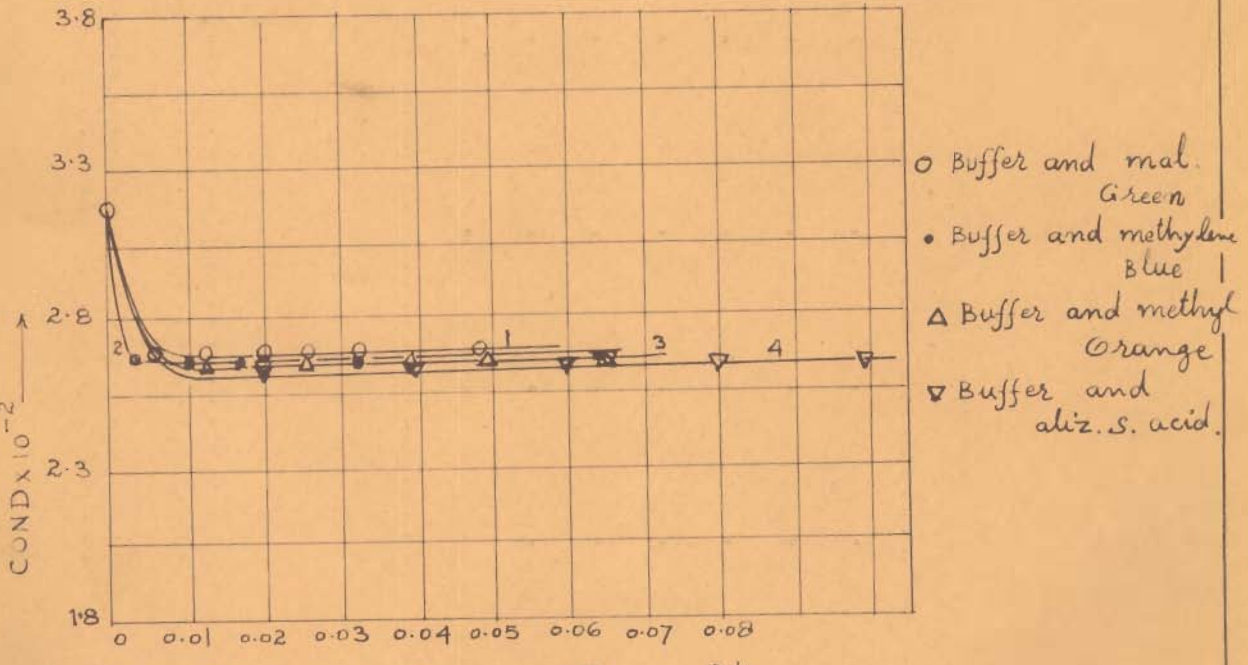


FIG-6 → CONCENTRATION OF DYE (mM/LITRE)

TABLE No.3

Variations in pH, viscosity, conductivity, ζ-potential of As_2S_3; buffer and dispersion medium by the addition of methyl orange.

Volume of dye	Set No. 3 (a)				Set No.3 (b)			Set No.3(c)
	pH sol+dye mixture	Viscosity sol +dye mixture (centi-poise	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise
0 cc	3.76	0.7201	2.15×10^{-4}	2.541×10^{-7}	3.76	0.7420	3.15×10^{-2}	0.7155
1.0"	3.82	0.7201	2.50×10^{-4}	1.495×10^{-7}	3.76	0.7430	2.66×10^{-2}	0.7160
2.0"	3.88	0.7201	2.20×10^{-4}	1.943×10^{-7}	3.76	0.7430	2.66×10^{-2}	0.7160
3.0"	3.94	0.7201	2.10×10^{-4}	2.392×10^{-7}	3.76	0.7430	2.66×10^{-2}	0.7160
4.0"	4.00	0.7201	2.08×10^{-4}	2.840×10^{-7}	3.76	0.7430	2.66×10^{-2}	0.7160
5.0"	4.10	0.7201	2.05×10^{-4}	2.989×10^{-7}	3.76	0.7430	2.66×10^{-2}	0.7160
	Fig.(1) curve 3	Fig.(3) curve 3	Fig.(5) curve 3	Fig.(7) curve 3	Fig.(2) curve 3	Fig.(4) curve 3	Fig.(6) curve 3	Fig.(4) curve 7

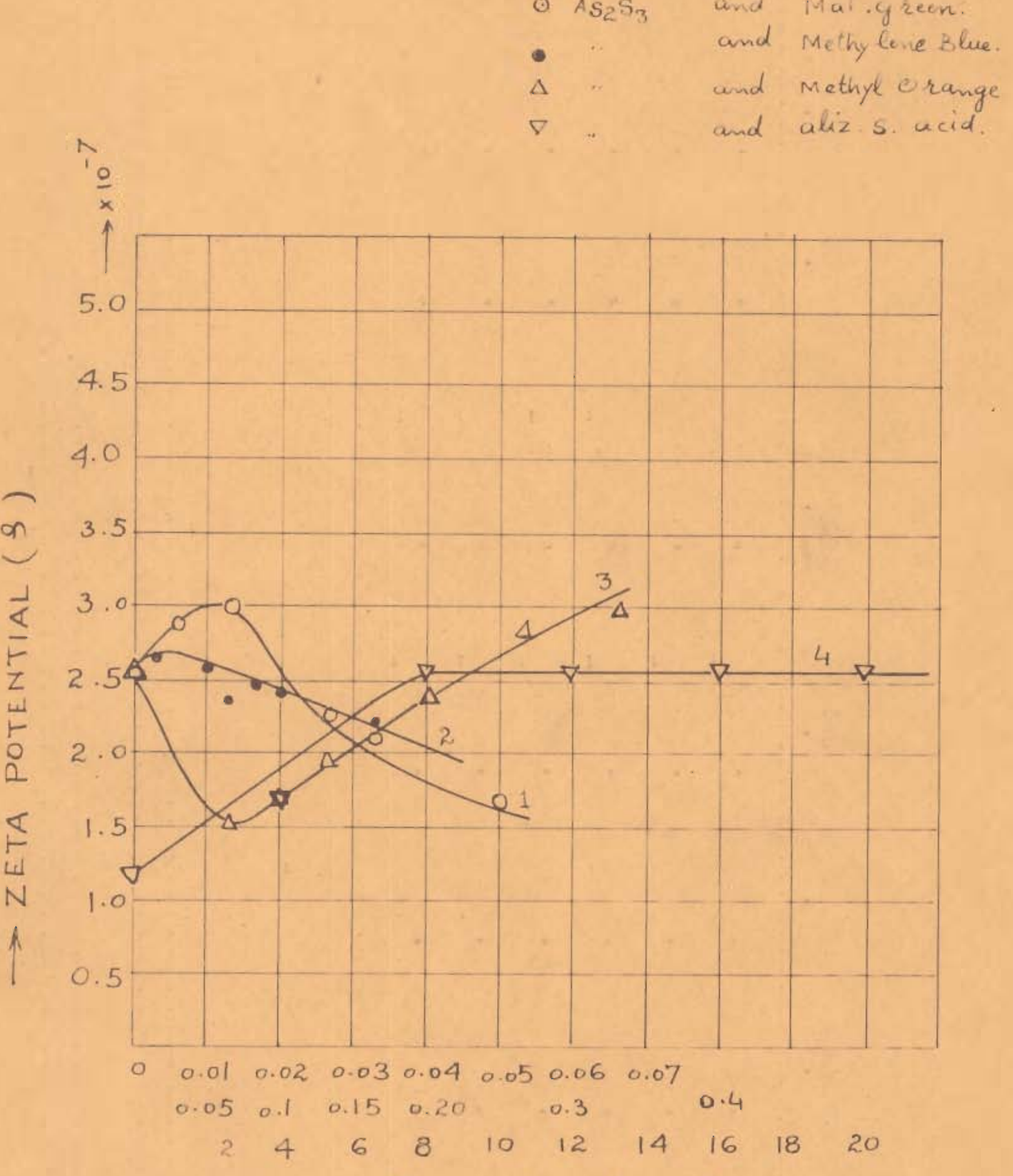


FIG-7. CONC. Of DYE (mM/LITRE)

TABLE No.4

Variations in pH, viscosity, conductivity, ζ-potential of As_2S_3; buffer and dispersion medium by the addition of alizarin sulphonic acid.

Volume of dye	Set No. 4 (a)				Set No. 4 (b)			Set No.4(c)
	pH sol+dye mixture	Viscosity sol+dye mixture (centi-poise	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise
0 cc	3.80	0.7191	0.15×10^{-3}	1.134×10^{-7}	3.80	0.7420	3.55×10^{-2}	0.7155
1.0"	3.72	0.7251	1.00×10^{-3}	1.652×10^{-7}	3.79	0.7430	1.85×10^{-2}	0.7160
2.0"	3.62	0.7266	1.66×10^{-3}	2.543×10^{-7}	3.78	0.7430	1.92×10^{-2}	0.7160
3.0"	3.50	0.7273	2.38×10^{-3}	2.549×10^{-7}	3.77	0.7430	1.98×10^{-2}	0.7160
4.0"	3.42	0.7290	3.12×10^{-3}	2.555×10^{-7}	3.76	0.7430	1.98×10^{-2}	0.7160
5.0"	3.38	0.7311	3.70×10^{-3}	2.563×10^{-7}	3.76	0.7430	1.98×10^{-2}	0.7160
	Fig.(1) curve 4	Fig.(3) curve 4	Fig.(5) curve 4	Fig.(7) curve 4	Fig.(2) curve 4	Fig.(4) curve 4	Fig.(6) curve 4	Fig.(4) curve 8

Verification of Beer Lambert's law

O.D. and conductance were measured at different dilution of the dye solutions. The results are enumerated below.

TABLE No.5

Alizarin sulphonic acid (1.5×10^{-4} M)

Dye	conc. of dye (moles)/litre	O.D. at the maxima of the dye (425 mμ)	Conductance (mhos)
1 c.c. aliz. s. acid + 9 c.c.H_2O	1.5×10^{-5}	0.045	1.72×10^{-5}
2 c.c. aliz. s. acid + 8 c.c.H_2O	3.0×10^{-5}	0.095	2.75×10^{-5}
3 c.c. aliz. s. acid + 7 c.c.H_2O	4.5×10^{-5}	0.16	3.65×10^{-5}
4 c.c. aliz. s. acid + 6 c.c.H_2O	6.0×10^{-5}	0.21	3.90×10^{-5}
5 c.c. aliz. s. acid + 5 c.c.H_2O	7.5×10^{-5}	0.28	4.90×10^{-5}

Figs. (8,9) curves (2,1) respectively

TABLE No.6

Methyl orange (0.0451×10^{-3} M)

Dye	conc. of dye (moles)/litre	O.D. at the maxima of the dye (450 mμ)	Conductance (mhos)
1 c.c.methyl orange +9 c.c.H_2O	0.0451×10^{-4}	0.12	2.05×10^{-5}
2 c.c.methyl orange +8 c.c.H_2O	0.0902×10^{-4}	0.24	2.05×10^{-5}
3 c.c. methyl orange+7 c.c.H_2O	0.1353×10^{-4}	0.36	2.15×10^{-5}
4 c.c.methyl orange +6 c.c.H_2O	0.1804×10^{-4}	0.46	1.75×10^{-5}
5 c.c.methyl orange +5 c.c.H_2O	0.2255×10^{-4}	0.58	1.90×10^{-5}

Figs. (8,9) curves (1,2) respectively

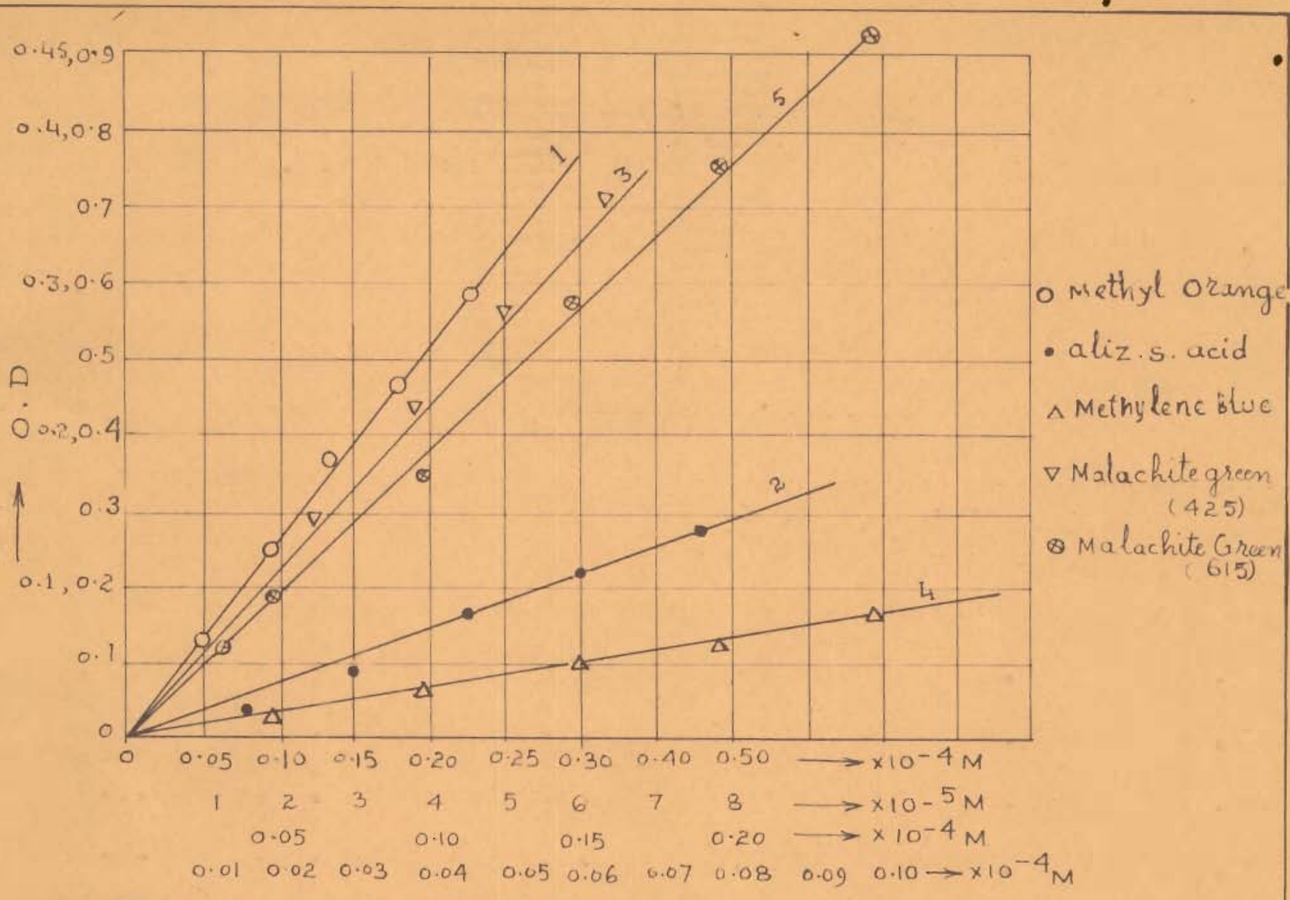


FIG _ 8. → CONC. OF DYE

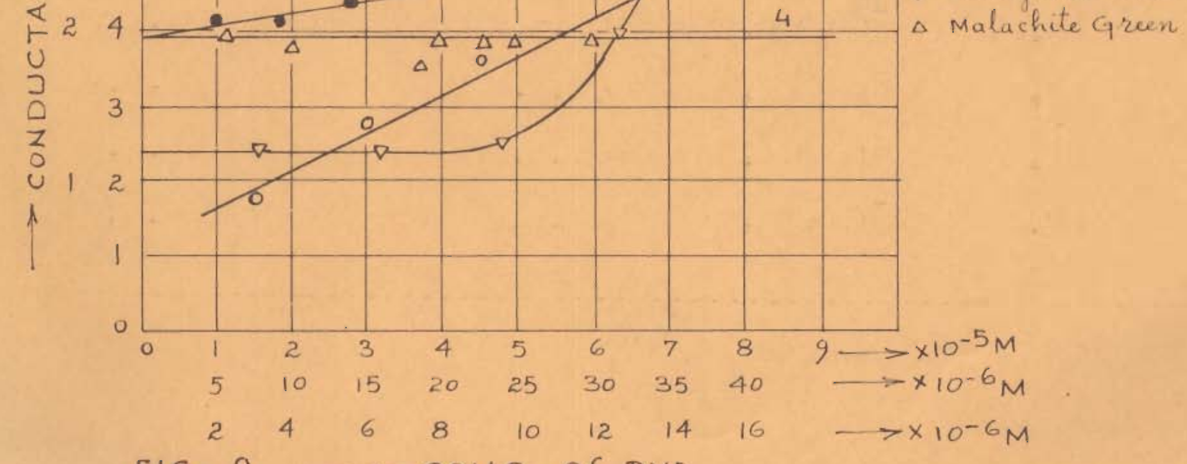


FIG - 9. → CONC. Of DYE

TABLE No.7

Methylene blue (0.0314×10^{-3} M)

Dye	conc. of dye moles/litre	O.D. at the maxima of the dye (650 mμ)	Conductance (mhos)
1 c.c. methylene blue + 9 c.c. H_2O	0.0314×10^{-4}	0.12	2.40×10^{-5}
2 c.c. methylene blue + 8 c.c. H_2O	0.0628×10^{-4}	0.29	2.41×10^{-5}
3 c.c. methylene blue + 7 c.c. H_2O	0.0942×10^{-4}	0.43	2.40×10^{-5}
4 c.c. methylene blue + 6 c.c. H_2O	0.1256×10^{-4}	0.56	3.90×10^{-5}
5 c.c. methylene blue + 5 c.c. H_2O	0.1570×10^{-4}	0.70	6.55×10^{-5}

Figs. (8,9) curves (4,3) respectively

TABLE No.8

Malachite green (0.0196×10^{-3} M)

Dye	conc. of dye (moles)/litre	O.D. at the maxima of the dye (615 mμ)	Conductance (mhos)	O.D. at the maxima of the dye (425 mμ
1 c.c. malachite green + 9 c.c. H_2O	0.0196×10^{-4}	0.09	2.15×10^{-5}	0.012
2 c.c. malachite green + 8 c.c. H_2O	0.0392×10^{-4}	0.17	1.85×10^{-5}	0.030
3 c.c. malachite green + 7 c.c. H_2O	0.0588×10^{-4}	0.285	2.30×10^{-5}	0.045
4 c.c. malachite green + 6 c.c. H_2O	0.0784×10^{-4}	0.37	1.90×10^{-5}	0.06
5 c.c. malachite green + 5 c.c. H_2O	0.0980×10^{-4}	0.46	1.90×10^{-5}	0.08

Figs. (8,9) curves (3,5,4) respectively

TABLE No.9

O.D. of the dyes, sols at different wavelength

conc. of alizarin sulphonic acid = $1.5\text{x}10^{-4}$M

conc. of methyl orange = $0.0451\text{x}10^{-3}$M

Wavelength in mμ	O.D. methyl orange	Wavelength in mμ	O.D. Alizarin s. acid
330	0.16	330	0.46
350	0.23	350	0.41
375	0.47	375	0.43
400	0.80	400	0.54
425	1.0	425	0.56
450	1.1	430	0.54
475	1.0	435	0.52
500	0.66	450	0.41
525	0.26	475	0.24
550	0.06	500	0.16
575	0.01	525	0.13
600	0.01	550	0.10
625	0.01	575	0.10
		600	0.04
		625	0.03
	Fig.(10) curve 3		Fig.(10) curve 4

FIG. 10

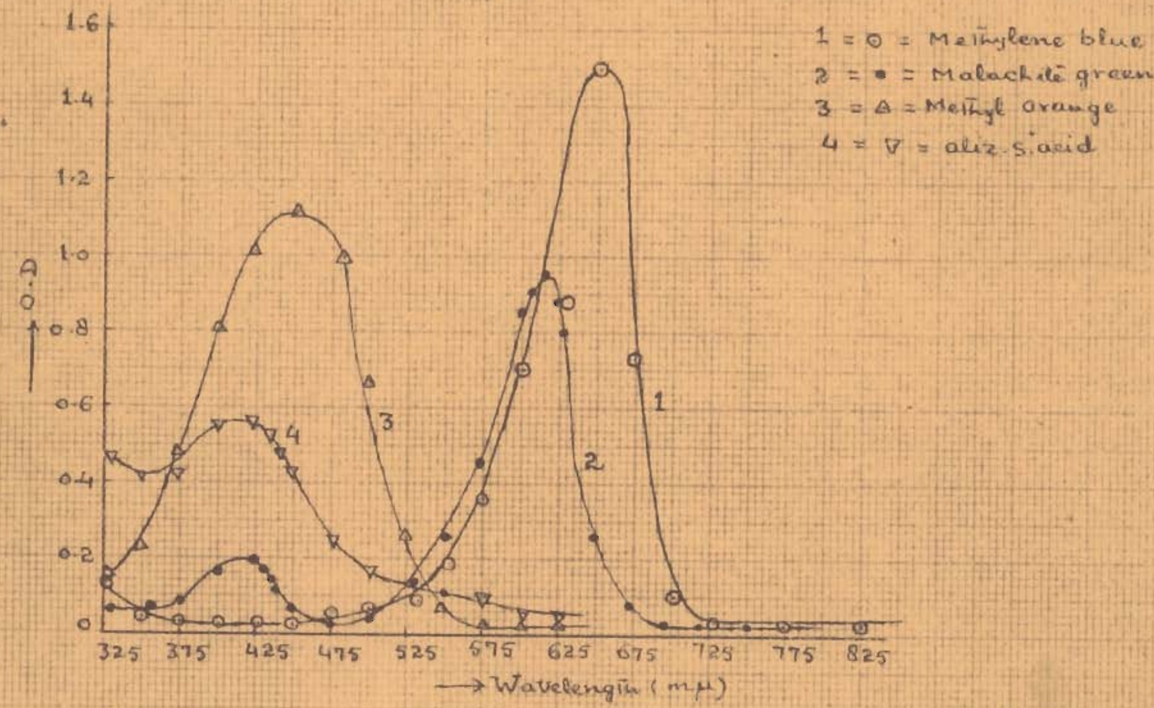

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
O.D
325
375
425
475
525
575
625
675
725
775
825
→ Wavelength (mμ)
1 = ⊙ = Methylene blue
2 = ● = Malachite green
3 = △ = Methyl orange
4 = ▽ = aliz. s. acid
1
2
3
4

FIG. 11

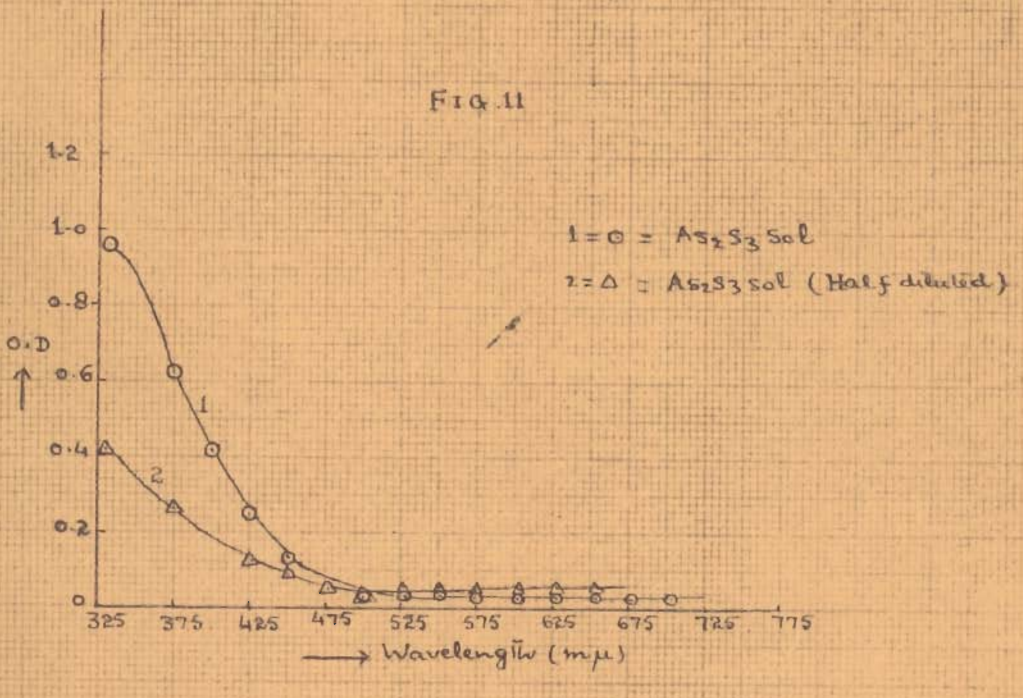

1.2
1.0
0.8
0.6
0.4
0.2
0
O.D
325
375
425
475
525
575
625
675
725
775
→ Wavelength (mμ)
1 = ⊙ = As_2S_3 sol
2 = △ = As_2S_3 sol (Half diluted)
1
2

TABLE No.10

O.D. of the dyes, sols at different wavelength

conc. of methylene blue = 0.0314×10^{-3} M

conc. of malachite green= 0.0196×10^{-3} M

conc. of As_2S_3 sol used for absorption measurements = 0.0110 gms. As_2S_3 per litre.

Wavelength in mμ	O.D. methylene blue	Wavelength in mμ	O.D. malachite green	Wave-length in mμ	O.D. As_2S_3 sol	O.D. sol + water (5 c.c. each)
325	0.15	330	0.06	330	0.95	0.41
350	0.03	350	0.05	350	0.90	0.34
375	0.025	375	0.08	375	0.62	0.26
400	0.02	400	0.16	400	0.42	0.18
425	0.015	425	0.19	425	0.25	0.12
450	0.025	430	0.165	450	0.13	0.08
475	0.045	435	0.14	475	0.07	0.045
500	0.065	440	0.11	500	0.03	0.038
525	0.08	450	0.06	525	0.02	0.035
550	0.165	475	0.025	550	0.02	0.03
575	0.350	500	0.045	575	0.015	0.028
600	0.70	525	0.11	600	0.015	0.02
625	0.90	550	0.25	625	0.015	0.02
650	1.5	575	0.47	650	0.02	0.02
675	0.75	600	0.85	675	0.015	
700	0.12	610	0.90	700	0.010	
725	0.02	615	0.95			
750	0.01	620	0.90			
775	0.01	625	0.80			
800	0.01	650	0.25			
825	0.01	675	0.06			
		700	0.02			
		725	0.01			
		750	0.01			
		775	0.01			
		800	0.01			
	Fig.(10) curve 1		Fig.(10) curve 2		Fig.(11) curve 1	Fig.(11) curve 2

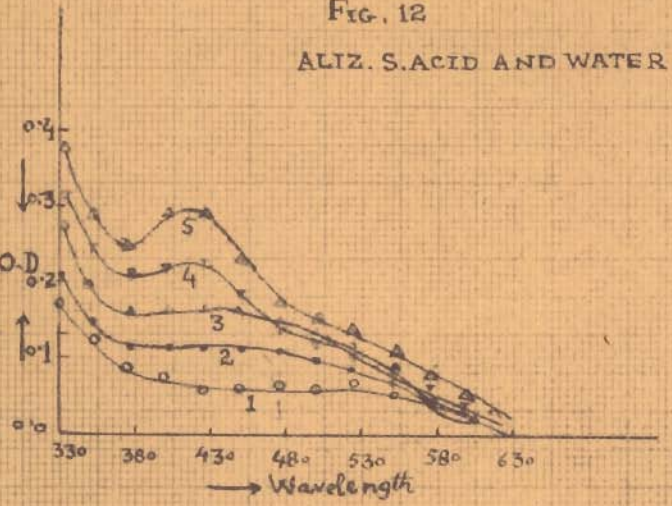


FIG. 12
ALIZ. S. ACID AND WATER

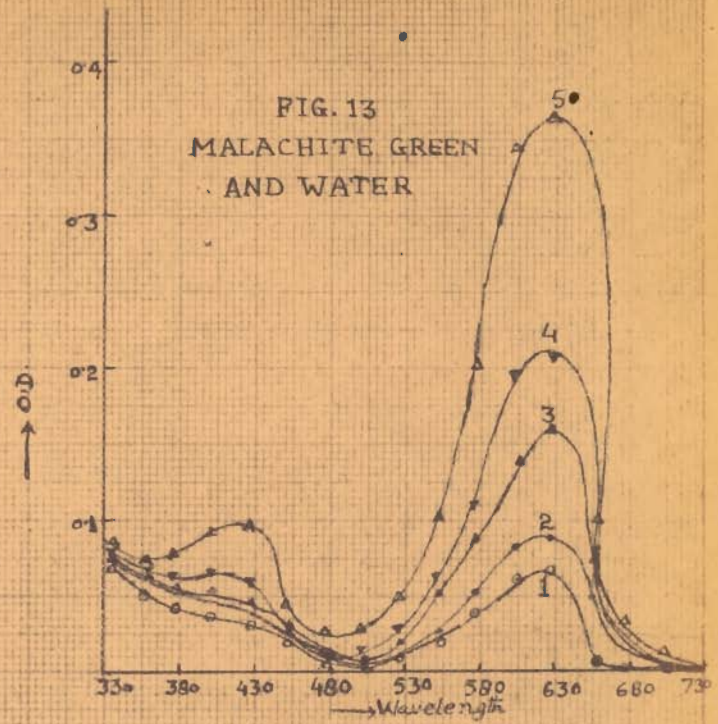


FIG. 13
MALACHITE GREEN
AND WATER

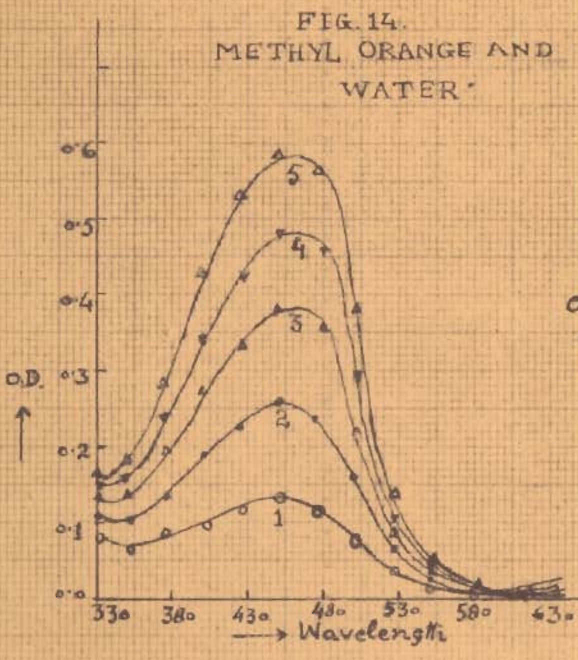


FIG. 14.
METHYL ORANGE AND
WATER

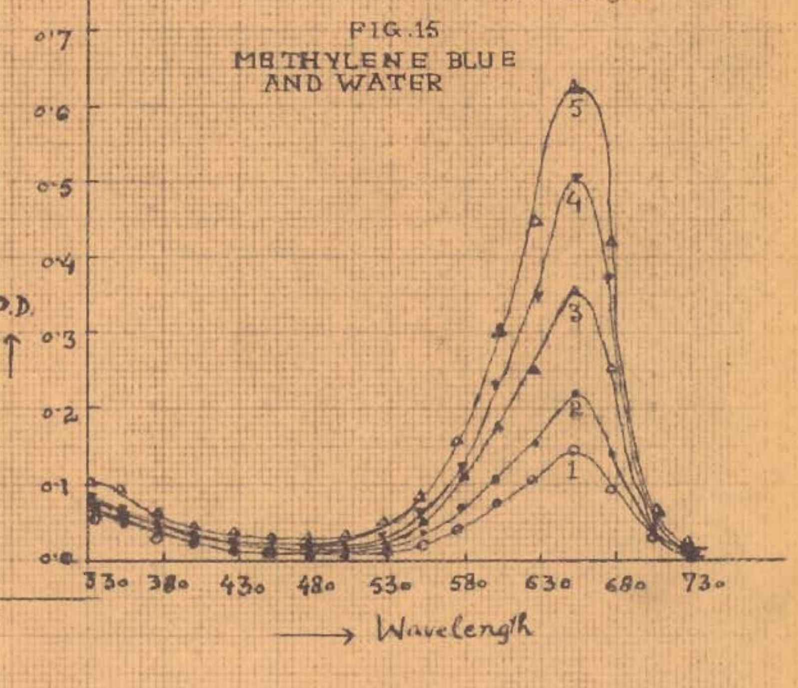


FIG. 15
METHYLENE BLUE
AND WATER

TABLE No.11a

The absorption data of the dyes in presence of sol are given in the following tables

Arsenic sulphide and alizarin sulphonic acid

Absorption spectra of 1.5x10^{-4}M alizarin sulphonic acid in presence of sol, buffer and water

Wavelength in mμ	Set no. 5b(i)			Set no. 5b(ii)			Set no. 5b(iii)		
	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye
330	0.31	0.135	0.17	0.34	0.18	0.20	0.39	0.265	0.27
350	0.25	0.115	0.12	0.30	0.14	0.145	0.34	0.21	0.19
375	0.215	0.08	0.08	0.26	0.11	0.11	0.31	0.17	0.15
400	0.185	0.072	0.07	0.245	0.12	0.11	0.32	0.18	0.16
425	0.145	0.06	0.06	0.22	0.115	0.11	0.275	0.19	0.165
450	0.10	0.05	0.06	0.16	0.12	0.11	0.20	0.15	0.155
475	0.065	0.051	0.07	0.11	0.12	0.105	0.12	0.125	0.14
500	0.045	0.042	0.06	0.07	0.11	0.095	0.078	0.112	0.13
525	0.035	0.035	0.07	0.055	0.09	0.090	0.055	0.095	0.12
550	0.030	0.030	0.055	0.05	0.065	0.065	0.045	0.075	0.08
575	0.030	0.02	0.04	0.045	0.048	0.04	0.04	0.055	0.05
600	0.030	0.015	0.025	0.042	0.04	0.02	0.04	0.04	0.03
625	0.030	0.01	0.015	0.042	0.02	0.015	0.04	0.03	0.015
	Fig.(19) curve 3	Fig.(19) curve 1	Fig.(12) curve 1	Fig.(19) curge 5	Fig.(19) curve 2	Fig.(12) curve 2	Fig.(19) curve 8	Fig.(19) curve 4	Fig.(12) curve 3

TABLE No.11(b)

Wavelength in mμ	Set No.5 b(iv)			Set No.5 b (v)		
	O.D. sol + dye	O.D. buffer+dye	O.D. water+dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye
330	0.45	0.32	0.31	0.52	0.42	0.37
350	0.39	0.25	0.235	0.45	0.30	0.29
375	0.36	0.21	0.20	0.41	0.25	0.24
400	0.37	0.225	0.215	0.43	0.275	0.285
425	0.335	0.23	0.225	0.40	0.28	0.290
450	0.23	0.20	0.180	0.285	0.235	0.225
475	0.13	0.165	0.14	0.17	0.19	0.170
500	0.07	0.15	0.125	0.09	0.17	0.15
525	0.05	0.13	0.11	0.065	0.15	0.135
550	0.045	0.095	0.09	0.055	0.118	0.11
575	0.045	0.065	0.06	0.045	0.078	0.07
600	0.045	0.04	0.035	0.042	0.045	0.04
625	0.050	0.025	0.015	0.042	0.03	0.02
	Fig.(19) curve 9	Fig.(19) curve 6	Fig.(12) curve 4	Fig.(19) curve 10	Fig.(19) curve 7	Fig.(12) curve 5

O.D. of set No.5 a(i) at maxima of sets 5 b (i), 5 b(ii), 5 b(iii), 5 b(iv), 5 b(v) [sol+dye] is 0.06.

TABLE No.12

Arsenic sulphide and methyl orange

Absorption spectra of 0.0451×10^{-3} M methyl orange in presence of sol, buffer and water

Wavelength in mμ	Set no.5 b(i)			Set no.5 b(ii)			Set no.5 b(iii)			Set no.5 b(iv)		
	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye
330	0.365	0.115	0.105	0.445	0.130	0.13	0.385	0.155	0.15	0.44	0.165	0.16
350	0.30	0.11	0.105	0.41	0.135	0.135	0.34	0.162	0.16	0.39	0.19	0.18
375	0.25	0.15	0.135	0.37	0.195	0.19	0.32	0.25	0.24	0.389	0.285	0.29
400	0.21	0.195	0.19	0.322	0.27	0.27	0.321	0.35	0.34	0.42	0.41	0.42
425	0.175	0.225	0.225	0.29	0.33	0.33	0.335	0.43	0.42	0.445	0.52	0.52
450	0.16	0.26	0.255	0.295	0.37	0.375	0.36	0.49	0.48	0.48	0.58	0.58
475	0.14	0.24	0.230	0.24	0.35	0.35	0.35	0.46	0.45	0.46	0.55	0.56
500	0.11	0.155	0.15	0.19	0.22	0.22	0.27	0.30	0.285	0.345	0.355	0.35
525	0.075	0.065	0.06	0.132	0.09	0.085	0.165	0.12	0.11	0.195	0.15	0.14
550	0.045	0.02	0.02	0.087	0.02	0.02	0.075	0.03	0.03	0.085	0.038	0.035
575	0.03	0.01	0.015	0.065	0.01	0.01	0.035	0.01	0.01	0.04	0.012	0.01
600	0.028	0.01	0.01	0.055	0.01	0.01	0.025	0.01	0.01	0.03	0.01	0.01
625	0.029	0.01	0.01	0.058	0.01	0.01	0.025	0.01	0.01	0.032	0.015	0.01
	Fig.(18) curve 1.	Fig.(18) curve 2.	Fig.(14) curve 2.	Fig.(18) curve 3.	Fig.(18) curve 5.	Fig.(14) curve 3.	Fig(18) curve 4.	Fig.(18) curve 7.	Fig.(14) curve 4.	Fig.(18) curve 6.	Fig.(18) curve 8.	Fig.(14) curve 5

O.D. of set No.5a(i) at maxima of sets 5 b(i), 5 b(ii), 5 b(iii), 5 b(iv) [sol + dye] is 0.05

TABLE No.13

Arsenic sulphide and methylene blue

Absorption spectra of 0.0314×10^{-3} M methylene blue in presence of sol, buffer and water

Wavelength in mμ	Set no. 5 b(i)			Set no. 5 b(ii)			Set no. 5 b(iii)			Set no. 5 b(iv)		
	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer + dye	O.D. water+dye	O.D. sol +dye	O.D. buffer+dye	O.D. water + dye
330	0.62	0.04	0.08	0.60	0.05	0.08	0.60	0.06	0.085	0.62	0.075	0.095
350	0.55	0.03	0.06	0.49	0.03	0.06	0.50	0.04	0.055	0.50	0.045	0.06
375	0.44	0.02	0.045	0.26	0.028	0.045	0.37	0.03	0.04	0.37	0.03	0.045
400	0.325	0.015	0.035	0.17	0.02	0.045	0.26	0.025	0.03	0.26	0.02	0.035
425	0.225	0.01	0.025	0.105	0.015	0.025	0.17	0.015	0.02	0.16	0.02	0.025
450	0.155	0.015	0.020	0.07	0.01	0.020	0.11	0.015	0.02	0.10	0.02	0.022
475	0.10	0.018	0.020	0.055	0.018	0.020	0.075	0.022	0.025	0.075	0.025	0.03
500	0.08	0.018	0.022	0.052	0.02	0.02	0.06	0.025	0.025	0.065	0.03	0.03
525	0.07	0.018	0.025	0.06	0.02	0.025	0.065	0.027	0.03	0.07	0.04	0.035
550	0.075	0.025	0.04	0.07	0.04	0.04	0.085	0.055	0.055	0.10	0.07	0.07
575	0.10	0.065	0.07	0.115	0.09	0.082	0.145	0.125	0.12	0.18	0.165	0.15
600	0.135	0.13	0.12	0.175	0.20	0.17	0.23	0.265	0.24	0.30	0.33	0.30
625	0.15	0.18	0.16	0.205	0.28	0.24	0.285	0.36	0.34	0.39	0.45	0.41
650	0.13	0.295	0.22	0.27	0.44	0.35	0.39	0.54	0.50	0.53	0.68	0.62
675	0.10	0.18	0.14	0.18	0.28	0.23	0.27	0.35	0.32	0.35	0.40	0.37
700	0.07	0.02	0.025	0.075	0.035	0.03	0.085	0.045	0.05	0.095	0.05	0.05
725	-	-	0.005	-	-	0.01	-	-	0.01	-	-	0.01
	Fig(16) curve 1.	Fig(16) curve 3	Fig(15) curve 2.	Fig(16) curve 2.	Fig(16) curve 5	Fig(15) curve 3	Fig(16) curve 4.	Fig(16) curve 7	Fig(15) curve 4	Fig(16) curve 6	Fig(16) curve 8	Fig(15) curve 5

O.D. of set No.5a(i) at maxima of sets 5 b(i), 5 b(ii), 5 b(iii), 5 b(iv) [sol + dye] is 0.04 .

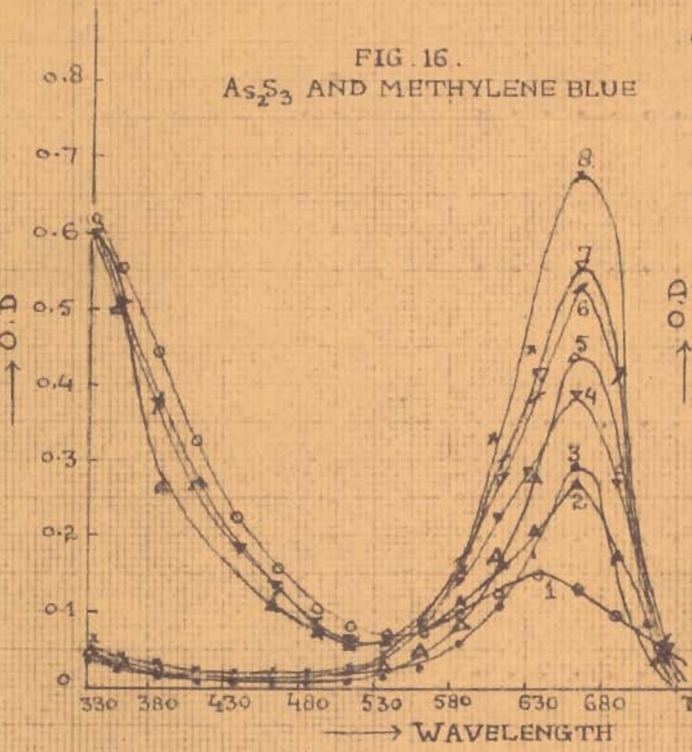


FIG. 16.
As$_2$S$_3$ AND METHYLENE BLUE

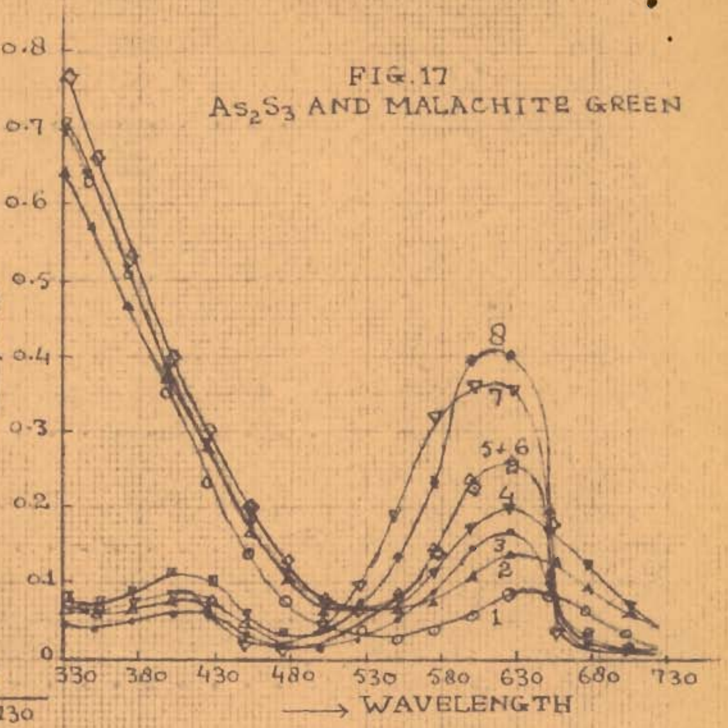


FIG. 17
As$_2$S$_3$ AND MALACHITE GREEN

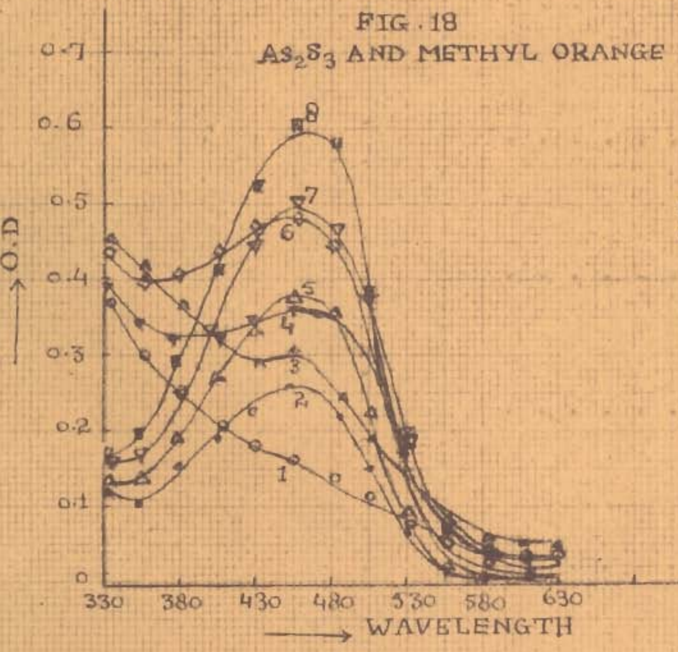


FIG. 18
As$_2$S$_3$ AND METHYL ORANGE

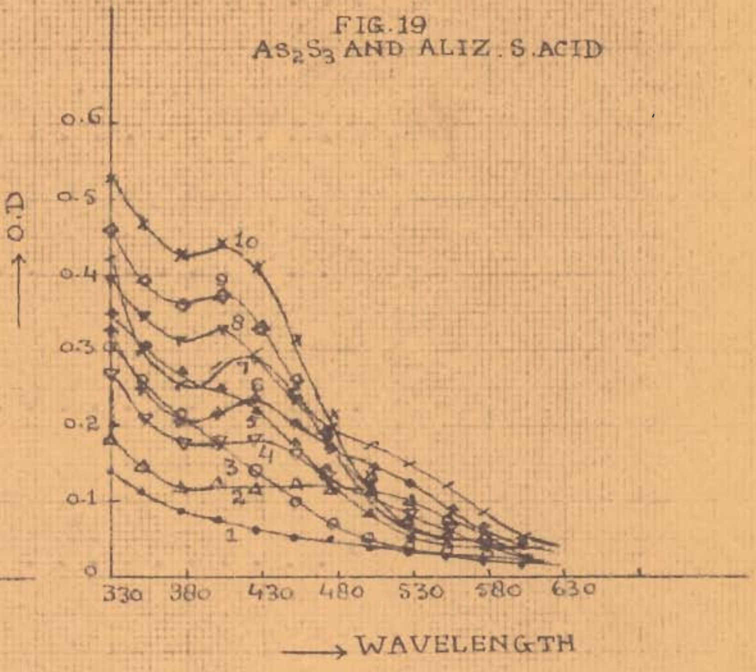


FIG. 19
As$_2$S$_3$ AND ALIZ. S. ACID

TABLE No.14

Arsenic sulphide and malachite green

Absorption spectra of 0.0196×10^{-3} M malachite green in presence of sol, buffer and water

Wavelength in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)		
	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+dye	O.D. buffer + dye	O.D. water + dye
330	0.68	0.04	0.08	0.62	0.055	0.085	0.68	0.065	0.08	0.77	0.07	0.09
350	0.58	0.038	0.07	0.56	0.052	0.07	0.60	0.06	0.07	0.64	0.06	0.075
375	0.44	0.042	0.055	0.44	0.056	0.06	0.46	0.06	0.065	0.48	0.068	0.08
400	0.31	0.05	0.05	0.335	0.07	0.055	0.35	0.08	0.07	0.37	0.10	0.095
425	0.21	0.052	0.04	0.25	0.071	0.05	0.27	0.085	0.065	0.29	0.105	0.10
450	0.13	0.025	0.02	0.17	0.035	0.025	0.18	0.04	0.025	0.185	0.04	0.04
475	0.07	0.015	0.015	0.10	0.02	0.015	0.098	0.02	0.015	0.10	0.025	0.025
500	0.044	0.02	0.014	0.07	0.025	0.010	0.06	0.025	0.02	0.06	0.03	0.03
525	0.03	0.025	0.013	0.06	0.04	0.025	0.058	0.045	0.03	0.062	0.055	0.05
550	0.028	0.05	0.03	0.06	0.08	0.045	0.06	0.10	0.06	0.075	0.12	0.11
575	0.04	0.09	0.05	0.075	0.145	0.085	0.105	0.19	0.11	0.14	0.22	0.21
600	0.06	0.155	0.08	0.105	0.24	0.14	0.17	0.32	0.20	0.22	0.39	0.35
615	0.08	0.160	0.09	0.135	0.250	0.155	0.20	0.335	0.21	0.265	0.395	0.365
625	0.085	0.16	0.09	0.135	0.250	0.16	0.20	0.340	0.21	0.255	0.395	0.365
650	0.090	0.05	0.04	0.120	0.075	0.06	0.16	0.11	0.07	0.19	0.112	0.10
675	0.06	0.01	0.02	0.088	0.015	0.02	0.115	0.03	0.02	0.125	0.02	0.03
700	0.02	0.01	0.01	0.05	0.002	0.01	0.055	0.005	0.01	0.06	0.005	0.01
	Fig(17) curve 1	Fig(17) curve 3	Fig(13) curve 2	Fig(17) curve 2	Fig(17) curve 5	Fig(13) curve 3	Fig(17) curve 4	Fig(17) curve 7	Fig(13) curve 4	Fig(17) curve 6	Fig(17) curve 8	Fig(13) curve 5

O.D. of set No.5a(i) at maxima of sets 5b(i), 5b(ii), 5b(iii), 5b(iv) [sol + dye] = 0.015 .

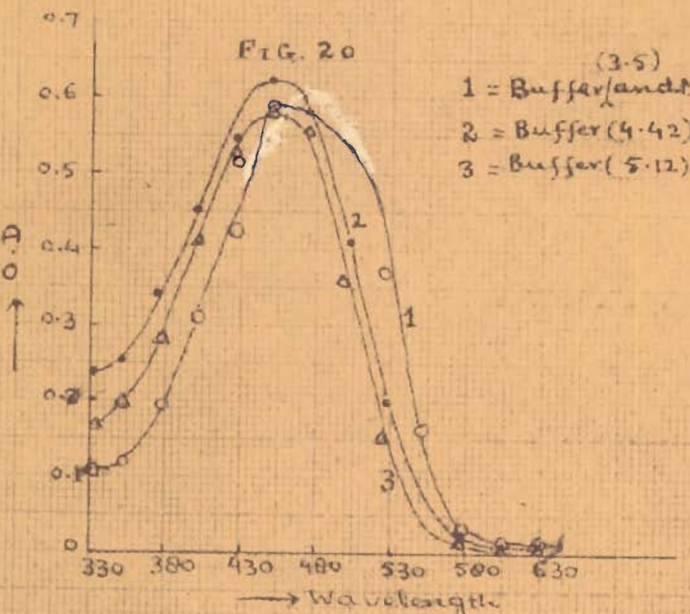


FIG. 20

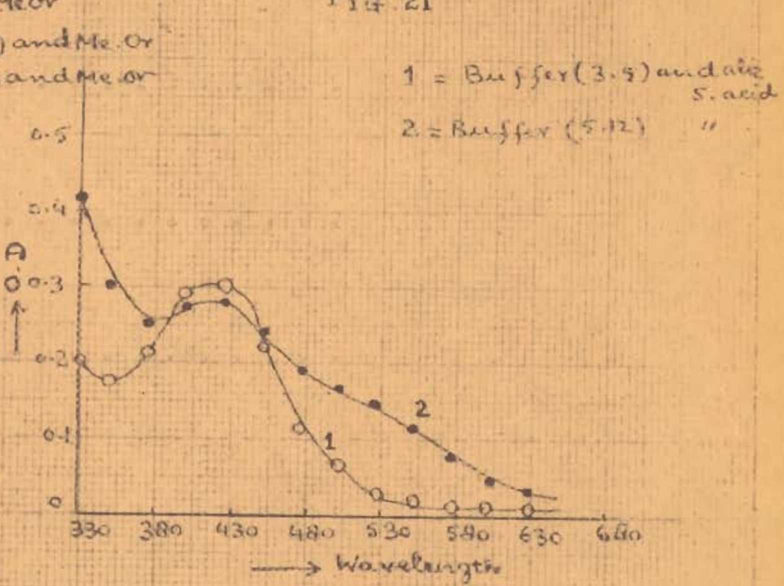


FIG. 21

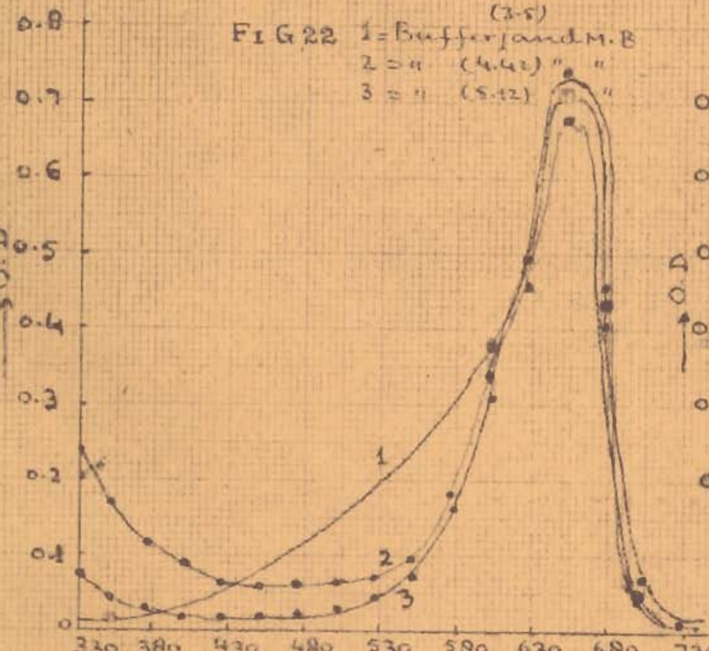


FIG 22

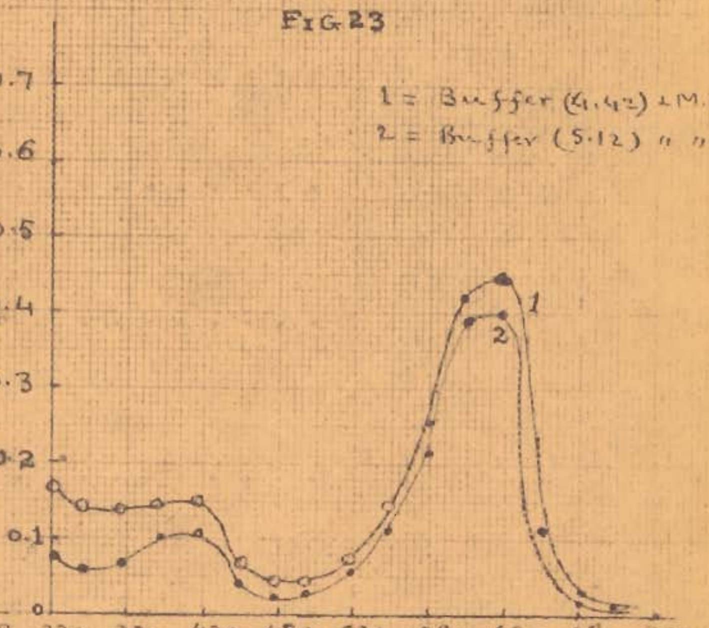


FIG 23

TABLE No.15

Effect of pH on dyes:

Absorption spectra of 1.5×10^{-4} M alizarin s. acid, 0.0451×10^{-3} M methyl orange, 0.0314×10^{-3} M methylene blue and 0.0196×10^{-3} M malachite green in different pH ranges buffer + dye (5 c.c. each), total volume = 10 c.c.

Wavelength in mμ	O.D. buffer (pH=3.5) + methyl orange	O.D. buffer (pH=4.42) + methyl orange	O.D. buffer (pH=5.12) +methyl orange	O.D. buffer (pH=3.5) + aliz. s.acid	O.D. buffer (pH=5.12) + aliz. s. acid	O.D. buffer (pH=3.5) + methylene blue	O.D. buffer (pH=4.42) + methylene blue	O.D. buffer (pH=5.12) + methylene blue	O.D. buffer (pH=4.42) + malachite green	O.D. buffer (pH= 5.12) + malachite green
330	0.115	0.235	0.165	0.20	0.42	0.065	0.24	0.075	0.172	0.07
350	0.12	0.25	0.19	0.185	0.30	0.02	0.17	0.045	0.145	0.06
375	0.195	0.34	0.285	0.215	0.25	-	0.115	0.03	0.144	0.068
400	0.31	0.45	0.41	0.29	0.275	-	0.09	0.02	0.152	0.10
425	0.42	0.54	0.52	0.30	0.28	-	0.06	0.02	0.153	0.105
450	0.60	0.62	0.58	0.225	0.235	-	0.058	0.02	0.072	0.04
475	0.58	0.58	0.55	0.115	0.19	-	0.059	0.025	0.048	0.025
500	0.55	0.41	0.355	0.07	0.17	-	0.061	0.03	0.05	0.03
525	0.37	0.195	0.15	0.03	0.15	-	0.062	0.04	0.075	0.055
550	0.16	0.065	0.038	0.02	0.118	-	0.095	0.07	0.145	0.12
575	0.03	0.02	0.012	0.01	0.078	-	0.18	0.165	0.25	0.22
600	0.01	0.01	0.01	0.01	0.045	0.38	0.36	0.33	0.42	0.39
615	-	-	-	-	0.04	-	-	-	0.45	0.40
625	0.01	0.01	0.01	0.01	0.03	0.49	0.49	0.45	0.44	0.395
650			0.015			0.71	0.73	0.68	0.11	0.112
675						0.43	0.45	0.40	0.03	0.02
700						0.055	0.07	0.05	0.01	0.005
	Fig(20) curve 3	Fig(20) curve 2	Fig(20) curve 1	Fig(21) curve 1	Fig(21) curve 2	Fig(22) curve 2	Fig(22) curve 3	Fig(22) curve 1	Fig(23) curve 1	Fig(23) curve 2

DISCUSSION

The experimental results on the variations in pH, ζ-potential, viscosity and conductivity of arsenic sulphide sol on gradual addition of the acid and the basic dyes present several important features worth considering. An analysis of the various data bring to light one very interesting fact and it is that although the behaviour of the basic dyes (malachite green and methylene blue) towards arsenic sulphide sol is almost similar, the behaviour of the acid dyes, viz., methyl orange and alizarin sulphonic acid is different from each other. For example, it is observed that the ζ-potential, viscosity and conductivity continuously increases with increase in the concentration of the alizarin sulphonic acid dye while almost a reverse behaviour is observed with methyl orange. The same dissimilarity is observed regarding variations in pH (tables 3,4 , page 50,51).

Another interesting fact which emerges out from these results is that the acidic and basic dyes differ amongst themselves in their behaviour towards the sol. It is thus observed that the variation in ζ-potential (a slight increase followed by a decrease), viscosity (constancy in the initial stages followed by an appreciable increase), pH (initial increase followed by a decrease), are the same with the malachite green and the methylene blue. On the other hand, a decrease in ζ-potential followed by an increase, continuous increase in pH and a constancy in viscosity is shown by methyl orange (figs. 7,1,3 curves 3,3,3 respectively). The case of alizarin sulphonic acid is altogether different as stated earlier and merits separate treatment.

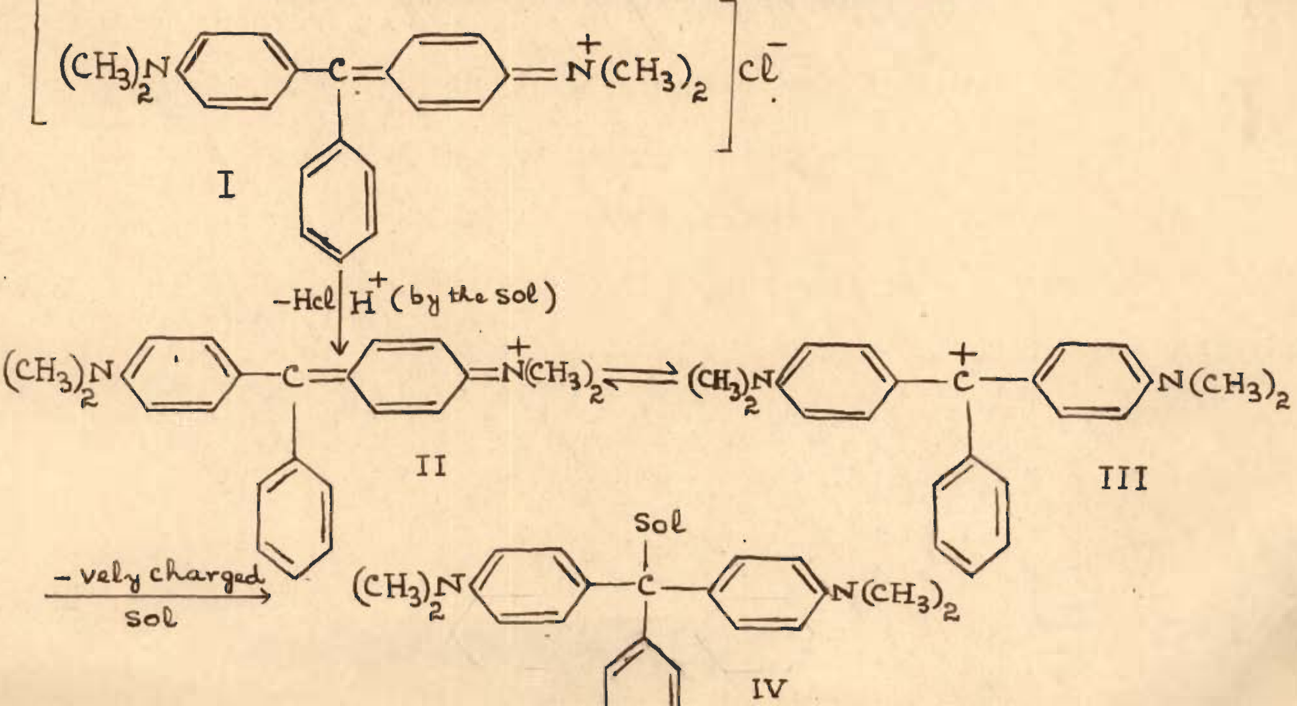
Unlike the ordinary cations and anions the behaviour of the ions of the dye towards lyophobic sols should be very different. Besides considering the charge and sign of the effective ions, due cognizance should be given to factors like, the state of association or aggregation of the dye in solution, the extent of dissociation of the dye salt, structural changes accompanying changes in pH, the shifts in absorption maxima by interaction with the colloidal material, and the adsorbability of the dye by the sol particle The first factor, viz., the association of the dye ions, however, does not seem to be operative here since separate experiments on conductometry, spectrophotometry and viscosity (tables 5,6,7,8 last columns) show that the dyes behave as monomeric in the concentration range employed.

<u>Basic dye-arsenic sulphide sol mixtures</u>:

The dye cations, carrying a charge opposite in sign to that of the sol, should be effective in bringing about the coagulation of the sol. This is what has been actually observed. Sedimentation sets in all the mixtures after a few hours and is complete on keeping them overnight. If the role of the dye cations would have simply been that of decreasing the electrical double layer and consequent release of the counterions, one should expect a continuous decrease in ζ-potential and pH. It is, however, observed that both these increase upto a certain concentration (0.0133×10^{-3}M in the case of malachite green and 0.0100×10^{-3}M in the case of methylene blue). The variations of this type can best be explained by considering that the released hydrogen ions interact with the dyes to either increase their dissociation (and, therefore, their effectiveness as coagulants) or change their structure, or both. Further-more the big dye cation (normal or oriented state) take the place of the small exchangeable hydrogen ions thereby stabilizing the sol. In this manner when sufficient dye has been used up the free hydrogen ions are made available in the dye-sol mixtures and the pH starts decreasing after a certain stage. The initial increase in ζ-potential would have kept the sol in a stable state for long and would have not brought about any change in its value but for the fact that the dye in presence of released H^+ assumes a structure quite susceptible to interaction (chemical compound formation or adsorption) with the negatively charged particles, and the resulting product no more remains in the colloidal state.

The following mechanism may be proposed for the malachite green dye:

Arsenic sulphide and malachite green

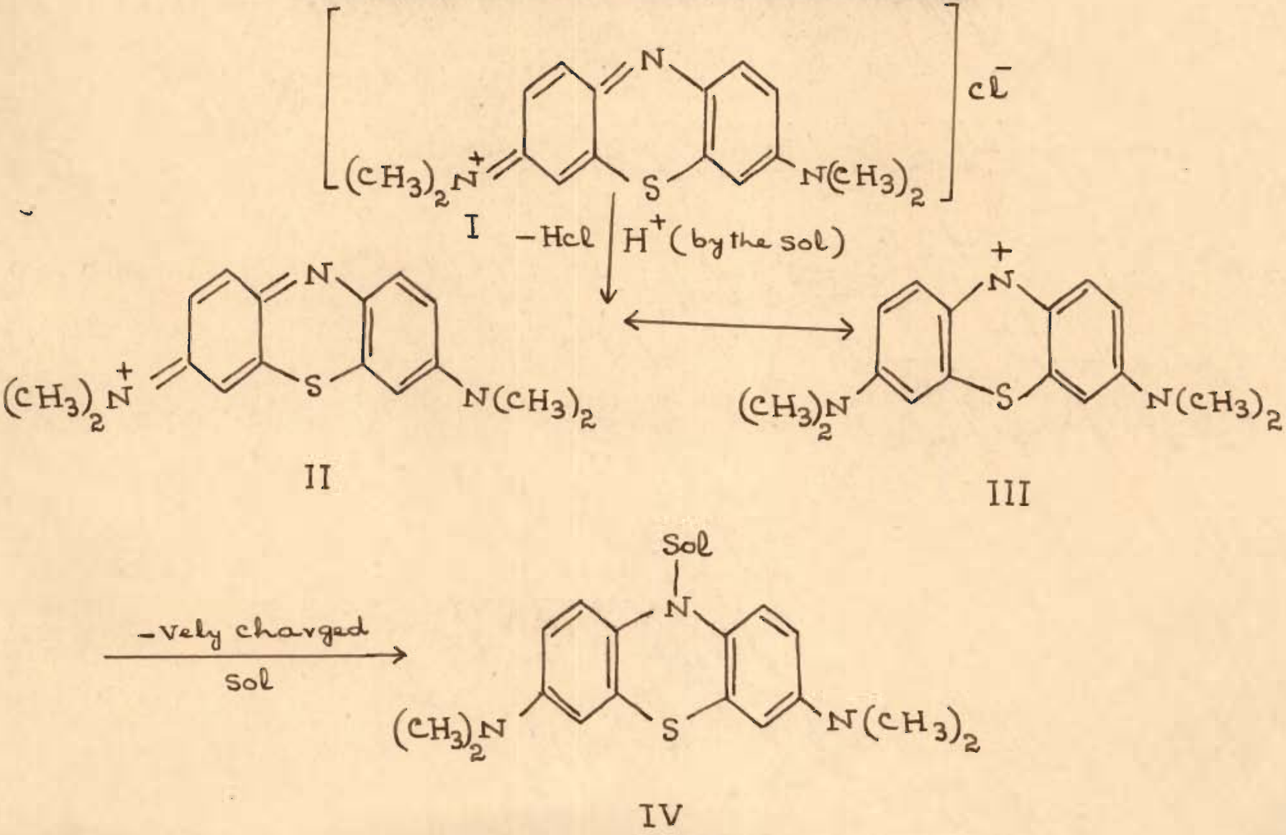


The H^+ ion released from the sol brings about enhanced dissociation of the dye and a resonance between structure II (quinonoid) and III (benzenoid) of the dye takes place. It is only when III (benzenoid) is reached in presence of hydrogen ions that the interaction (physical or chemical) between the dye and the negatively charged sol takes place resulting in the coagulation of the sol.

The possibility of the formation of a stoichiometric compound between the sol and the dye although remote cannot be completely ruled out, especially in view of the fact that after the addition of a certain amount of the dye an abrupt change in conductance, pH, viscosity and ζ-potential takes place (fig.5,1,3,7. curves 1,2. respectively).

In the case of methylene blue a similar mechanism may be proposed.

Arsenic sulphide and methylene blue



The possibility of the stoichiometric interaction of the methylene blue dye can also be postulated here since an abrupt change in viscosity, PH, conductance and ζ-potential also takes place here after the addition of a certain amount of the dye to the sol (0·3cc.). The methylene blue dye differs from malachite green in as much as the former is a phenothiazine derivative while the latter is a triphenyl methane dye. The attachment of arsenic of the sol with sulphur in the dye cannot, however, be visualized since this would necessitate m-quinonoid structure for III which is unlikely. The interaction between the sol and the methylene blue appears to involve electrostatic binding only. It may further be noted that the sol-basic dye mixtures show abrupt increases (figs. 1, 3, 5, 7.) after adding the requisite amount of the dye needed for their stepwise combination. This behaviour is not realized when electrolytes are added to the arsenic sulphide sol.

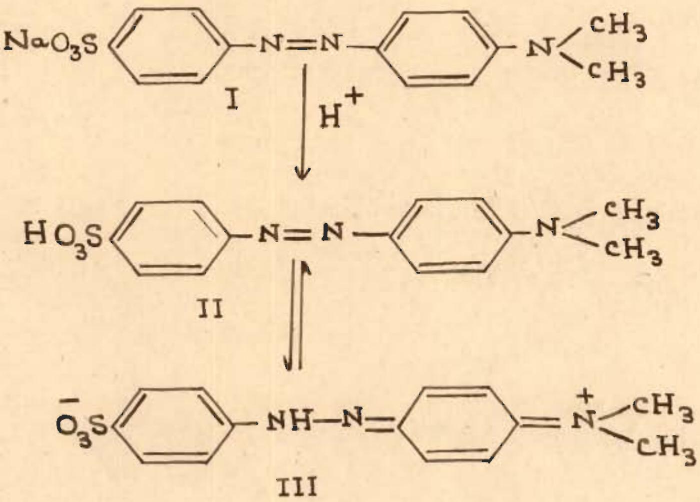
Although it is difficult to assign a composition of the products formed by the interaction of arsenic sulphide and the basic dyes, an approximate idea of the combining ratio can be realized. For the malachite green the molar ratios calculated from the dye-sol mixtures corresponding to abrupt changes (referred to above) is approximately 6 sol: 1 dye while for the methylene blue it is 8 sol:1 dye. These results find support in the studies on the binding of these dyes by the arsenic sulphide sol to be described later.

Acid dye-arsenic sulphide sol mixtures:

(i) Methyl orange:

The effect of the methyl orange dye on the negatively charged sol should result in the stabilization of the latter due to the adsorption of the dye anions by the sol particles resulting in an increase in ζ-potential. This is what has actually been observed except for the fact that there is a large initial fall in the ζ-potential (table 3 , column 5, Fig 7 curve 3). Variations of similar nature are observed in the conductance where an initial increase followed by continuous decrease in conductivity is observed. Further proof of stabilization of the sol also comesforth from the fact that unlike the basic dye-sol mixture, the sol remains in a highly stable state for many days. The viscosity of the various dye-sol mixtures also remain constant irrespective of the amount of the dye added which could happen only when change in the particle size is not contemplated.

The pH of the sol can bring about structural changes in the methyl orange as under:



since compound III is electrically neutral electrostatic binding between the sol and the dye cannot be visualized and, therefore, there should exist little possibility for the formation of adsorption or ordinary complexes of arsenic sulphide with methyl orange.

The abrupt changes in ζ-potential and the conductance on adding the first aliquot of the dye are not easy to explain. It appears that the structural changes in the dye in the acidic medium (pH of As_2S_3 sol = 3.68) described above may be responsible for it. That such variations in viscosity and conductance are likely to occur can be seen from the corresponding data on mixing the dye with buffers of the same pH as of the sol. The decrease in conductance and increase in pH with buffer is due to the fact that hydrogen ions are being used up by the dye.

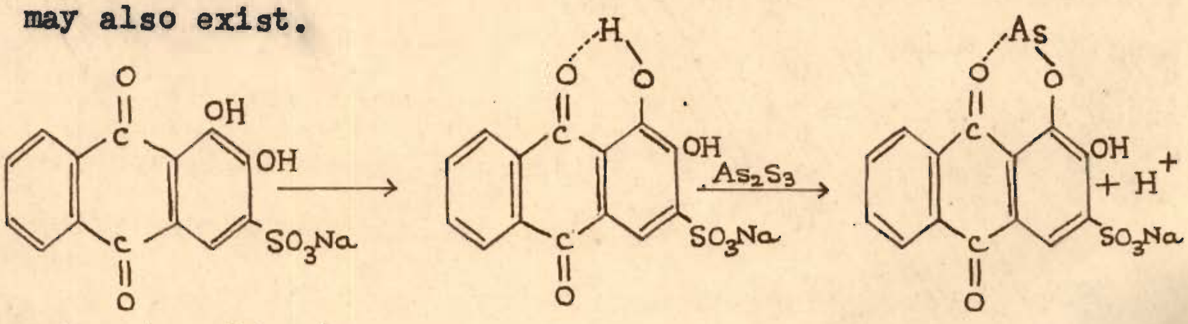
(ii) Alizarin sulphonic acid:

Alizarin lakes are usually formed from positively charged hydrous oxide sols by the process of exchange adsorption. Gels of alumina formed in the absence of chloride ions also adsorb the alizarate ion directly from the solution of the dye. It follows, therefore, that depending on the condition, adsorption of ion may be either exchange adsorption, direct adsorption or both. Chemical interaction or formation of chelates as viewed by Morgan (1924) may also be responsible for lake formation.

The strong adsorbability of alizarin sulphonic acid is reflected not only in the case of hydrous oxide but also in other colloids which may be negatively charged. The data on the variations in ζ-potential, pH, viscosity and conductivity support this view point.

The addition of gradually increasing amount of the alizarate ions to the sol results in the adsorption of these ions by the colloidal micelle (arsenic particles with adsorbed HS^- ions). This could be a direct adsorption or an exchange adsorption but the possibility of the latter being operative is larger since the pH decreases (table no. 4. due to the gradual exchange of HS^- ($HS^- \rightleftharpoons H^+ + \overset{=}{S}$) from the surface of sol particles. Adsorption of the alizarate ions would enhance the stability of the sol with the result that the ζ-potential continuously increases (table no. 4.). The conductivity variations (table no. 4.) also lend support to the view that fairly mobile ions are being exchanged from the sol on the addition of the alizarin sulphonic acid dye.

Mere stabilization of the sol by the dye is not likely to bring about any appreciable change in the viscosity of the sol. It is what has been observed in the case of methyl orange-arsenic sulphide mixtures. The change in viscosity although not as large as structural viscosity can be due to the formation of new particles which may be larger than the original arsenic sulphide particles of the sol. This formation is not easy to see. Besides strong binding of the dye by the arsenic sulphide molecule, the possibility of the formation of an arsenic chelate through hydrogen bonding between 1-hydroxyl and the 10 adjacent carbonyl group (14) may also exist.



alizarin sulphonic acid

The extent of binding of the dyes by arsenic sulphide sol: Spectrophotometric evidence:

From the experimental results it is seen that by the addition of small amount of dye (alizarin sulphonic acid having maxima at 425 mμ) to the constant volume of As_2S_3 brings about a shift in maxima from 425 mμ to 400 mμ (fig.19), and in the case of methyl orange (having maxima at 450 mμ) no shift in maxima is observed but optical density values in sol-dye mixture are less than buffer-dye mixture, while in the case of methylene blue (very low conc. of dye set 5b(i), (sol+dye)) the shift in maxima is from 650 to 625 mμ but with increasing concentration of dye the maxima (650 mμ) remains the same although the O.D. values in dye sol mixtures are very much less than buffer dye mixtures. In the case of malachite green (maxima at 615 mμ) shift in maxima takes place from 615 to 650 mμ(for set 5b(i), (sol+dye)) but with increasing concentration of the dye solution the maxima remains the same(615 mμ) but O.D. values for sol-dye mixtures are appreciably less than O.D.values of buffer-dye mixtures.

From the above observations sufficient proof of the binding of the dyes by sol particles accompanied by structural changes is made available. Quantitative data on the extent of binding obtained by applying Klotz equation are summarized below:

Klotz gave the equation $\alpha = \dfrac{\epsilon_{app} - \epsilon_B}{\epsilon_F - \epsilon_B}$ where α is the fraction of the dye which is free or extent of binding, ϵ_{app} is the apparent molar extinction coefficient of the bound dye and ϵ_B is the molar extinction coefficient of the

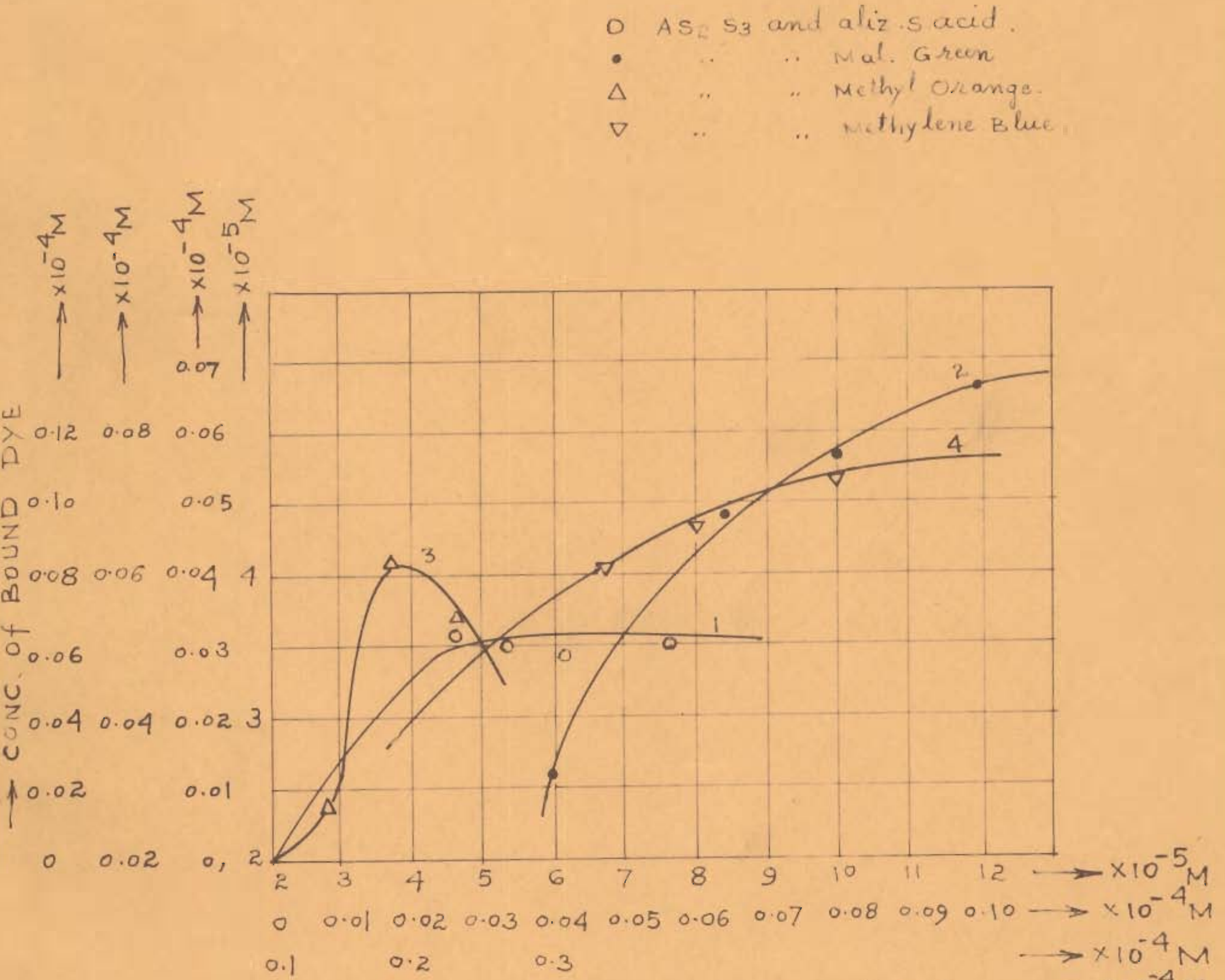


FIG _ 24. → INITIAL CONC. OF DYE

bound dye and ϵ_F is the molar extinction coefficient of the free dye.

TABLE No. 16

Arsenic sulphide and malachite green

Data for the binding of malachite green with arsenic sulphide sol:

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
$0.0392x10^{-4}$M	43361	0.71	$0.0278x10^{-4}$M	$0.0114x10^{-4}$M
$0.0588x10^{-4}$M	22959	0.23	$0.0135x10^{-4}$M	$0.0453x10^{-4}$M
$0.0784x10^{-4}$M	25510	0.30	$0.0235x10^{-4}$M	$0.0549x10^{-4}$M
$0.0980x10^{-4}$M	26020	0.32	$0.0313x10^{-4}$M	$0.0667x10^{-4}$M

Fig. (24) curve (2)

TABLE No. 17.

Arsenic sulphide and methylene blue

Data for the binding of methylene blue with arsenic sulphide sol:

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
$0.0628x10^{-4}$M	23883	0.0165	$0.0010x10^{-4}$M	$0.0618x10^{-4}$M
$0.0942x10^{-4}$M	28661	0.130	$0.0130x10^{-4}$M	$0.0812x10^{-4}$M
$0.1256x10^{-4}$M	31050	0.24	$0.0301x10^{-4}$M	$0.0955x10^{-4}$M
$0.1570x10^{-4}$M	33757	0.32	$0.0502x10^{-4}$M	$0.1068x10^{-4}$M

Fig.(24) curve (4.)

TABLE No. 18

Arsenic sulphide and alizarin sulphonic acid

Data for the binding of alizarin sulphonic acid with arsenic sulphide sol:

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
4.5×10^{-5}M	7111	0.208	0.936×10^{-5}M	3.57×10^{-5}M
6.0×10^{-5}M	6166	0.429	2.574×10^{-5}M	3.426×10^{-5}M
7.5×10^{-5}M	5733	0.530	3.975×10^{-5}M	3.525×10^{-5}M

Fig.(24) curve (1)

TABLE No. 19

Arsenic sulphide and methyl orange

Data for the binding of methyl orange with arsenic sulphide sol:

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
0.135×10^{-4}M	21851	0.80	0.108×10^{-4}M	0.027×10^{-4}M
0.180×10^{-4}M	19955	0.66	0.119×10^{-4}M	0.0614×10^{-4}M
0.2255×10^{-4}M	21286	0.76	0.1713×10^{-4}M	0.0542×10^{-4}M

Fig.(24) curve (3)

From the data on the bound dye the moles of arsenic sulphide bound per dye mole can be calculated. The results are summarised in the following table.

Dyes	conc. of bound dye	moles of As_2S_3 combined per mole of dye
Malachite green	0.0453×10^{-4}M	9.9
	0.0549×10^{-4}M	8.0
	0.0667×10^{-4}M	6.7
Methylene blue	0.0812×10^{-4}M	5.7
	0.0955×10^{-4}M	4.6
	0.1068×10^{-4}M	4.1

Dyes	conc. of bound dye	moles of As_2S_3 combined per mole of dye
Alizarin sulphonic acid	3.426×10^{-5}M	7.3
	3.525×10^{-5}M	8.3
Methyl orange	0.027×10^{-4}M	1.2
	0.0614×10^{-4}M	1.1
	0.0542×10^{-4}M	1.2

From thise data an approximate idea of the size of the arsenic sulphide micelles can be had provided it is assumed that 1 dye molecule is bound to one sol particle. The range being: from 7 to 10 micelles consisting of 1 molecule of malachite green to 10 molecules of arsenic sulphide and 4 to 6 in the case of methylene blue. The close similarity of these data with those obtained from ζ-potential, pH, viscosity and conductivity (page 66) for malachite green and methylene blue is very significant.

From the plots between initial concentration of the dye (fig. 24 curves 1,2,3,4.) and the bound dye the order of binding of the four dyes for the arsenic sulphide sol comes out to be methylene blue (0.106×10^{-4}M dye/mole) > malachite green (0.066×10^{-4}M dye/mole) > methyl orange (0.061×10^{-4}M dye/mole) > alizarin sulphonic acid (3.42×10^{-5}M dye/mole).

INTERACTION OF DYES WITH HYDROUS OXIDE SOLS (Fe AND Al)

It is well known that hydrous oxides like those of iron, chromium and aluminium are well known to possess a high adsorptive capacity. Mokuskin and Esin, White, Gorden and Porter studied the association of several dyes (1) by these hydrous oxides. Weiser (2) and Sen (3) also made a comparative study of adsorption capacity of the hydrous oxides of chromium, aluminium and iron for different inorganic ions. They are of opinion that the adsorption process depends on valency of ion, pH of the medium, chemical activity and reactivity of the adsorbent, etc.

The alizarin lakes of the hydrous oxides are ordinarily formed by an exchange adsorption process in which the relatively strongly adsorbed alizarate ion displaces a more weakly adsorbed ion, such as chloride, from the hydrous oxide. The addition of sodium alizarate above the coagulation value reverses the charge on the sol, owing to preferential adsorption of alizarate ion. This was confirmed by Ackerman (4), Bancroft and Farnham (5), Biltz (6), who showed further that the negatively charged lake was precipitated by an excess of sodium alizarate.

Opposed to the adsorption mechanism is the view of Morgan (7) i.e. many mordant dyes, specially of the alizarin class, have been found to form chelate metallic compounds, and others may form metallic salts of the dye anion (8). It is not known to what extent the above described phenomena connected with the lake formation process can be accounted for on the chelate compound theory. Valko (9) regards adsorption as merely the first step in the taking up of a dye by a fibre. This is followed in time by chemical union in the modern sense between dye molecules and fibre molecules.

Most of the work cited in the literature is of the qualitative nature and nothing has been done so far to determine quantitatively the extent of binding of dyes to sols. With this aim in view physico-chemical studies (pH-metric, conductometric, viscometric, cataphoretic and spectrophotometric) were undertaken using typical anionic (alizarin sulphonic acid and methyl orange) and cationic (methylene blue and malachite green) dyes with ferric hydroxide and aluminium hydroxide sols.

EXPERIMENTAL

I.(a) The B.D.H or Merck product of dyes, alizarin sulphonic acid (sod. salt), methyl orange (sod. salt), methylene blue (cl^-) and malachite green (cl^-) were dissolved in double distilled water.

(b) Preparation of aluminium hydroxide sol:

The method described by H.B. Weiser (10) was followed for the preparation of colloidal solution of alumina. 10 gms. of $Alcl_3$ (E. Merck) was dissolved in 500 c.c. of conductivity water and the resulting solution was heated to boiling. Aluminium hydroxide was precipitated with slight excess of ammonia and mixture was boiled for five minutes. The precipitate was taken in centrifuge tube and suspended in conductivity water. The suspension was centrifuged for fifteen minutes. The supernatant liquid was poured off and conductivity water was again added and precipitate was washed. The process of washing was repeated many times. The precipitate is then transferred to a 500 c.c. pyrex beaker and suspended with conductivity water. The suspension is then heated to boiling. The precipitate of $Al(OH)_3$ was peptized to alumina sol by adding gradually 0.2 N Hcl (in 1 c.c. portion) boiling the solution for ten minutes between each addition. The pH of alumina sol was lowered to 2.00 by the addition of requisite amount of 0.1 N Hcl solutions. The sol was dialysed to a pH 3.16. The concentration of colloidal solution was determined gravimetrically (11) as Al_2O_3 by precipitating Al as $Al(OH)_3$ in the pH range 7-7.5 and heating the precipitate to Al_2O_3.

(c) Preparation of ferric hydroxide sol:

Although a number of methods have been suggested by Pean de St. Gilles (12), Giolitti (13), and Graham (14) for the preparation of ferric hydroxide sol, the method recommended by Krecke (15) was employed.

250 c.c. of double distilled water was heated to boiling in a 500 c.c. Pyrex beaker and to this was added 2-3 drops of a 30% ferric chloride solution, gradually with constant stirring. The colloidal solution, brick red in colour obtained this way was dialysed while still hot. Its pH was adjusted to 2.5 by dialysis and measured by Cambridge pH meter.

Estimation of the sol (16): 25 c.c. of the sol was taken in a clean beaker and it was evaporated to dryness on a water bath. The dried mass was dissolved in minimum amount of conc. HNO_3 and then diluted with water. NH_4OH was added gradually till complete precipitation of ferric hydroxide occurs. The precipitate was filtered, washed, ignited and weighed as Fe_2O_3.

(d) Preparation of buffers:

Walpole buffers were prepared for the investigations (vide chapter I page 40).

(2) Apparatus and technique:

Viscosity and cataphoretic measurements: (Vide chapter I page 41).

pH and conductivity measurements: (Vide chapter I page 42.)

The following sets (1 to 4) were used for measuring the variations in viscosity, pH, conductivity, ζ-potential.

Set No.1:

(a) Ferric oxide sol (1.0840 gms Fe_2O_3/litre, pH=2.5, conductance = 2.10x10^{-3} mhos) + methyl orange (2.0x10^{-3}M, pH = 5.92, conductance = 2.38x10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (0 c.c., 1 c.c., 2 c.c., 3 c.c., 4 c.c., 5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + methyl orange (2.0x10^{-3}M). Each mixture contains 25 c.c. of the buffer and varying amounts (0 c.c., 1 c.c., 2 c.c., 3 c.c., 4 c.c., 5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(c) 0 c.c., 1 c.c., 2 c.c., 3 c.c., 4 c.c., 5 c.c. of methyl orange (2.0x10^{-3}M). Total volume was made upto 30 c.c. by double distilled water.

Set No.2:

(a) Ferric oxide sol (same conc. as in set No.1, pH=3.0)+ alizarin sulphonic acid (1.0x10^{-2}M, pH = 3.54, conductance = 3.53x10^{-3} mhos). Each mixture contains 20 c.c. of the sol and varying amounts (0.1, 0.2, 0.3, 0.35, 0.50 and 1.0 c.cs) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + alizarin sulphonic acid (1.0x10^{-2}M) mixture. Each mixture contains 20 c.c. of the buffer and varying amounts (0.1, 0.2, 0.3, 0.35, 0.50 and 1.0 c.cs) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(c) 0.1, 0.2, 0.3, 0.35, 0.50 and 1.0 c.cs of alizarin sulphonic acid (1.0×10^{-2} M). Total volume made upto 30 c.c. by double distilled water.

Set No.3:

(a) Ferric oxide sol (same conc. and same pH as in set No.1) + malachite green (1.0×10^{-3} M, pH = 3.28, conductance = 2.95×10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (1, 2, 3, 4, 5 c.cs) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of the sol) + malachite green (1.0×10^{-3} M) mixture. Each mixture contains 25 c.c. of the buffer and varying amounts(1, 2, 3, 4, 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(c) 1, 2, 3, 4, 5 c. cs of malachite green (1.0×10^{-3} M). Total volume made upto 30 c.c. by double distilled water.

Set No.4:

(a) Ferric oxide sol (same conc. and same pH as in set No.1) + methylene blue (1.0×10^{-3} M, pH = 5.26, conductance = 3.45×10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (1, 2, 3, 4, 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of the sol) + methylene blue (1.0×10^{-3} M). Each mixture contains 25 c.c. of the buffer and varying amounts (1, 2, 3, 4, 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(c) 1, 2, 3, 4, 5 c.cs of methylene blue (1.0×10^{-3} M).

Total volume made upto 30 c.c. by double distilled water.

The above sets could not be employed for absorption studies since the constituents of the mixtures were concentrated. Dilute solutions both of the sol and the dye were used. The following sets were employed to determine the binding of the dye.

Set No.5:

a (i) 5 c.c. of the sol (0.0142 gms Fe_2O_3/litre) + a very small quantity of dye (0.5 c.c. of 1.5×10^{-4}M alizarin sulphonic acid, (ii) 0.5 c.c. of 0.0451×10^{-3}M methyl orange, (iii) 0.5 c.c. of 0.0314×10^{-3}M methylene blue and (iv) 0.5 c.c. of 0.0196×10^{-3}M malachite green), total volume was made upto 10 c.c. by the addition of double distilled water.

(b) 5 c.c. sol + 1 c.c., 2 c.c. of 1.5×10^{-4}M alizarin sulphonic acid; 1 c.c., 2 c.c., 3 c.c., 4 c.c. and 5 c.c. of 0.0451×10^{-3}M methyl orange + 5 c.c. sol; 1 c.c., 2 c.c., 3 c.c., 4 c.c. and 5 c.c. of 0.0314×10^{-3}M methylene blue + 5 c.c. sol; 1 c.c., 2 c.c., 3 c.c., 4 c.c. and 5 c.c. of 0.0196×10^{-3}M malachite green + 5 c.c. sol. The total volume was made upto 10 c.c. by the addition of double distilled water.

For comparison similar studies were done by taking 5 c.c. buffer of the same pH as of the sol and same amount of dye as above. The experiments with dispersion medium alone were also performed.

(c)i Solutions of varying concentrations of dyes (1.5×10^{-4}M alizarin sulphonic acid, (ii) 0.0451×10^{-3}M methyl orange, (iii) 0.0314×10^{-3}M methylene blue and (iv) 0.0196×10^{-3}M malachite green) were taken.

Set No.6:

5 c.c. sol+5 c.c. water.

Aluminium hydroxide sol:

Set No.1

(a) Alumina sol (8 gms Al_2O_3 /litre, pH = 3.16, conductance = 0.88×10^{-2} mhos) + alizarin sulphonic acid (4.0×10^{-2}M, pH = 2.98, conductance = 1.2×10^{-2} mhos). Each mixture contains 20 c.c. of the sol and varying amounts (0, 0.3, 0.5, 0.7, 0.9, 1.0, 1.3 and 1.5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + alizarin sulphonic acid (4.0×10^{-2}M). Each mixture contains 20 c.c. of the buffer and varying amounts (o, 0.3, 0.5, 0.7, 0.9, 1.0, 1.3 and 1.5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(c) 0, 0.3, 0.5, 0.7, 0.9, 1.0, 1.3 and 1.5 c.cs of alizarin sulphonic acid (4.0×10^{-2}M). Total volume was made upto 30 c.c. by double distilled water.

Set No.2:

(a) Alumina sol (pH = 3.4, $\Lambda = 0.75\times10^{-2}$) + methyl orange ($2.0\times10^{-3}$M, pH = 5.92, conductance = 2.38×10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (1, 2, 3, 4 and 5 c.cs) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + methyl orange (2.0×10^{-3}M). Each mixture contains 25 c.c. of the buffer and varying amounts (1, 2, 3, 4 and 5 c.cs) of the dye. Total volume was made upto 30 c.c. by double distilled water.

(c) 1, 2, 3, 4 and 5 c.cs of methyl orange (2.0x10^{-3}M) Total volume was made upto 30 c.c. by double distilled water.

<u>Set No.3</u>:

(a) Alumina sol (under similar conditions as given in set No.2) + malachite green (1.0x10^{-3}M, pH = 3.28, conductance = 4.9x10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (1, 2, 3, 4 and 5 c.cs) of dye. Total volume made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + malachite green (1.0x10^{-3}M). Each mixture contains 25 c.c. of the buffer and varying amounts (1, 2, 3, 4 and 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(c) 1, 2, 3, 4 and 5 c.cs of malachite green (1.0x10^{-3}M). Total volume made upto 30 c.c. by double distilled water.

<u>Set No.4</u>:

(a) Alumina sol (under similar conditions as in set No.2) + methylene blue (1.0x10^{-3}M, pH = 5.24, conductance = 5.55x10^{-4} mhos). Each mixture contains 25 c.c. of the sol and varying amounts (1, 2, 3, 4, 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(b) Buffer solution (same pH as of sol) + methylene blue (1.0x10^{-3}M). Each mixture contains 25 c.c. of the buffer and varying amounts (1, 2, 3, 4 and 5 c.cs) of the dye. Total volume made upto 30 c.c. by double distilled water.

(c) 1, 2, 3, 4 and 5 c.cs of methylene blue (1.0×10^{-3}M). Total volume made upto 30 c.c. by double distilled water.

The following sets were employed to determine the binding of the dyes with sols.

Set No.5:

(a)i 5 c.c. of the sol (4.0 gms. Al_2O_3 /litre) + a very small quantity of dye (0.5 c.c. of 1.5×10^{-4}M alizarin sulphonic acid, (ii) 0.5 c.c. of 0.0451×10^{-3}M methyl orange, (iii) 0.7 c.c. of 0.0314×10^{-3}M methylene blue and (iv) 0.7 c.c. of 0.0196×10^{-3}M malachite green), total volume was made upto 10 c.c. by the addition of double distilled water.

(b) 5 c.c. sol + 1, 2, 3, 4 and 5 c.cs of 1.5×10^{-4}M alizarin sulphonic acid; 1, 2, 3, 4 and 5 c.cs of 0.0451×10^{-3}M methyl orange + 5 c.c. sol; 1, 2, 3, 4 and 5 c.cs of 0.0314×10^{-3}M methylene blue + 5 c.c. sol; 1, 2, 3, 4 and 5 c.cs of 0.0196×10^{-3}M malachite green + 5 c.cs sol. The total volume was made upto 10 c.c. by the addition of double distilled water.

(c)i Solutions of varying concentrations of dyes (1.5×10^{-4}M alizarin sulphonic acid, (ii) 0.0451×10^{-3}M methyl orange, (iii) 0.0314×10^{-3}M methylene blue and (iv) 0.0196×10^{-3}M malachite green) were used.

The mixture of above sets were placed overnight to attain equilibrium before carrying out absorption experiments. The Walpole buffers having the same pH as the sols were prepared for the above investigations and experiments were performed under similar conditions. For the variations in pH and for the verification of Beer Lamberts law similar sets as given in chapter No.1(page 52,53) were employed.

Sets 5(a), 5(b) and 5(c) were used to determine ϵ_B, ϵ_{app} and ϵ_F respectively in Klotz's equation.

The pH metric, conductometric, viscometric and cataphoretic studies were done with sets 1, 2, 3 and 4.

TABLE No.1

Ferric oxide sol

Variations in pH, viscosity, conductivity, ζ-potential of Fe_2O_3 sol; buffer and dispersion medium by the addition of methyl orange.

Tempt. = 35°C ± 0.1°C, pH of sol = 2.5

Conc. of dye mM/lit.	Set No.1 (a)				Set No.1(b)			Set No.1(c)
	pH sol+dye mixture	Viscosity sol+dye mixture (centi-poise)	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise)
0	2.60	0.7150	1.90×10^{-3}	1.695×10^{-7}	2.60	0.7360	3.05×10^{-2}	0.7155
0.0666	1.66	0.7153	1.80×10^{-3}	1.388×10^{-7}	2.71	0.7369	2.50×10^{-2}	0.7160
0.1333	1.64	0.7168	1.78×10^{-3}	1.391×10^{-7}	2.72	0.7369	2.58×10^{-2}	0.7160
0.2000	1.64	0.7199	1.74×10^{-3}	1.242×10^{-7}	2.72	0.7369	2.58×10^{-2}	0.7160
0.2666	1.64	0.7244	1.72×10^{-3}	1.249×10^{-7}	2.73	0.7369	2.58×10^{-2}	0.7160
0.3333	1.64	0.7244	1.72×10^{-3}	1.249×10^{-7}	2.74	0.7369	2.58×10^{-2}	0.7160
	Fig(32) curve 1	Fig(25) curve 1	Fig(27) curve 1	Fig(29) curve 1	Fig(33) curve 4	Fig(26) curve 1	Fig(28) curve 1	Fig(36) curve 1

1.

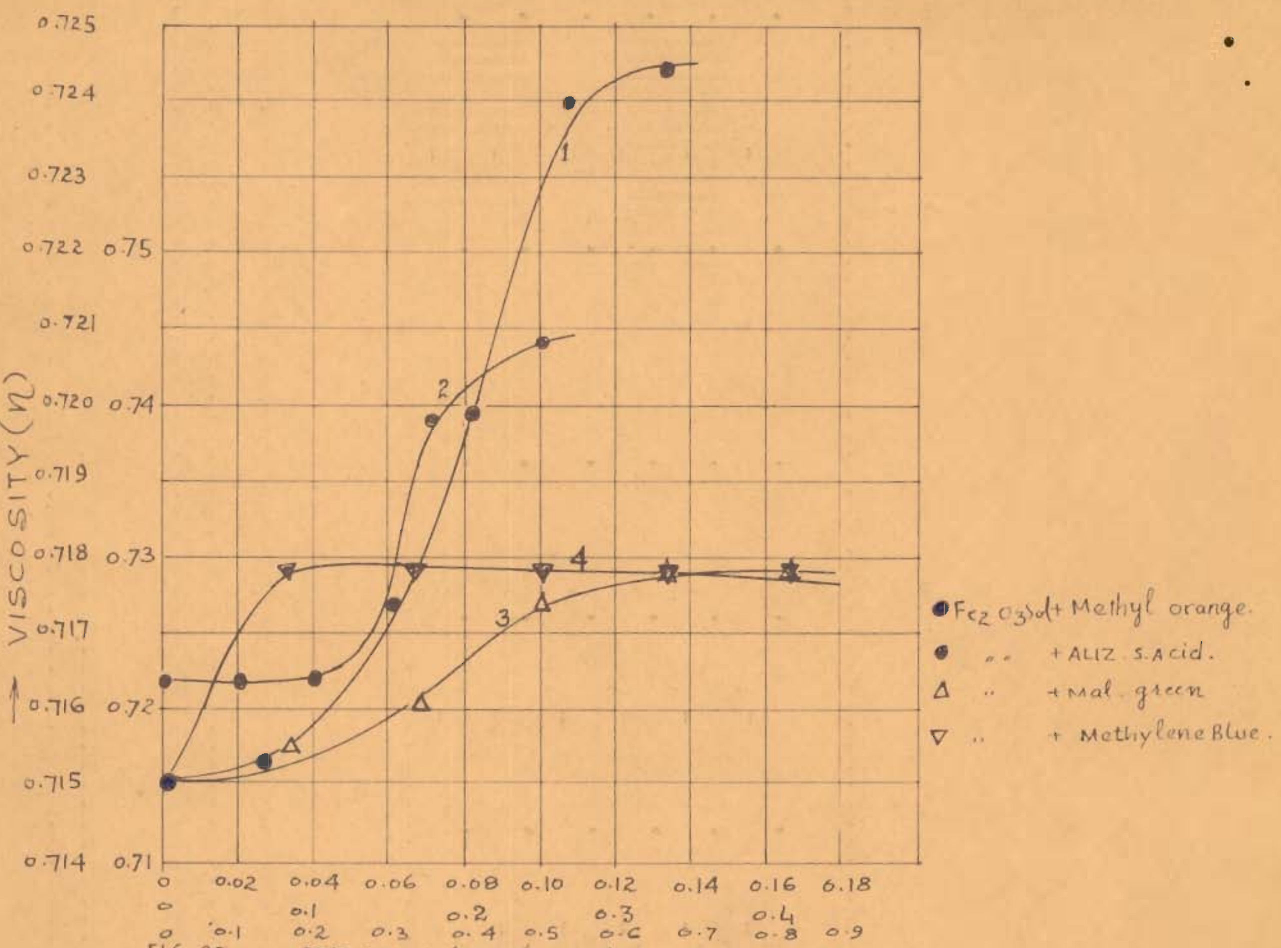


FIG. 25. → DYE CONC. (mm/LITRE)

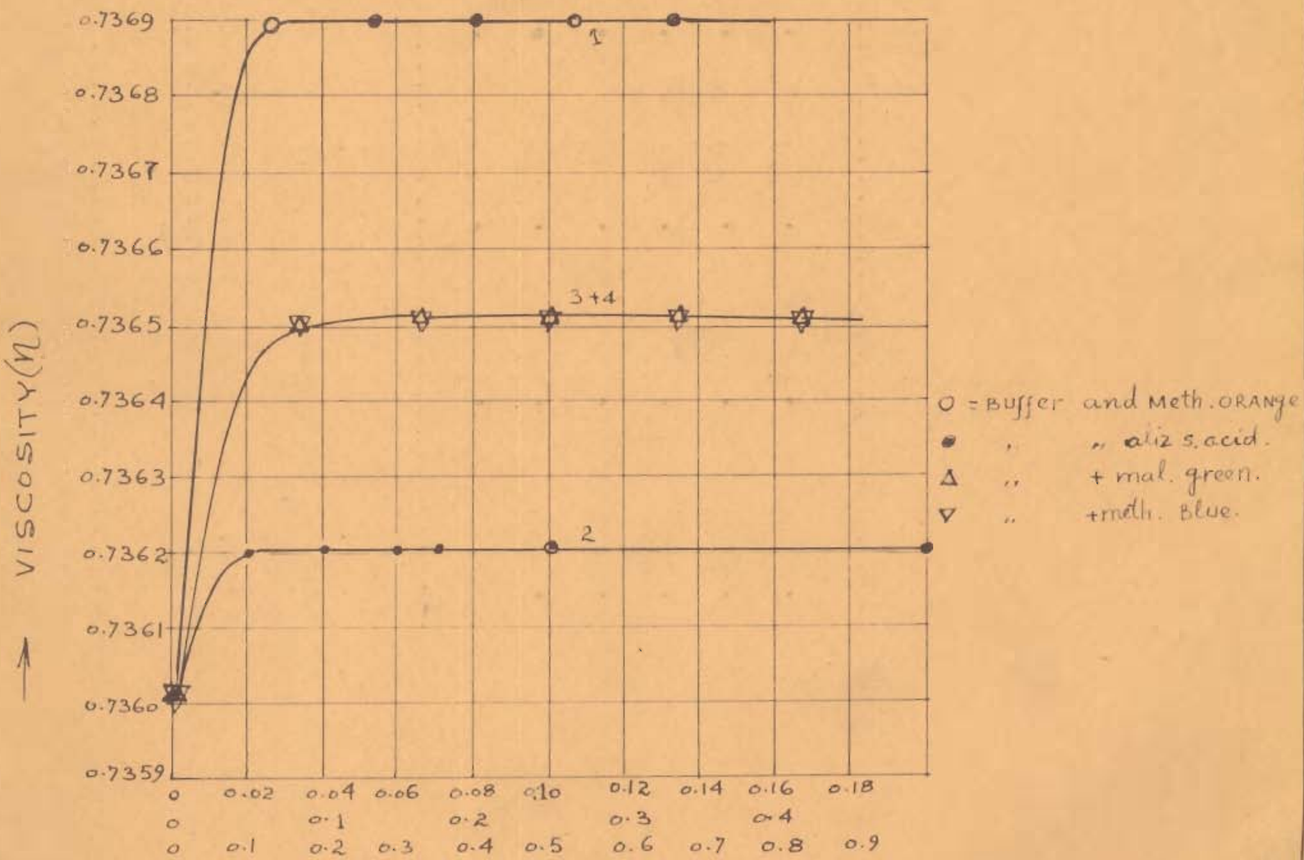


FIG. 26. → DYE CONC. (mm/LITRE)

TABLE No.2

Variations in pH, viscosity, conductivity, ζ-potential of Fe_2O_3 sol; buffer and dispersion medium by the addition of alizarin sulphonic acid.

Tempt. = 35°C ± 0.1°C, pH of sol = 3.0

Conc. of dye mM/lit.	Set No.2 (a)				Set No. 2 (b)			Set No.2(c)
	pH sol + dye mixture	Viscosity sol+dye mixture (centipoise)	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centipoise)
0	3.02	0.7219	1.50×10^{-3}	15.56×10^{-8}	3.02	0.7360	3.25×10^{-2}	0.7155
0.1	2.96	0.7219	1.52×10^{-3}	9.313×10^{-8}	3.07	0.7362	2.20×10^{-2}	0.7157
0.2	2.94	0.7219	1.54×10^{-3}	9.225×10^{-8}	3.07	0.7362	2.20×10^{-2}	0.7157
0.3	2.92	0.7270	1.55×10^{-3}	6.218×10^{-8}	3.07	0.7362	2.20×10^{-2}	0.7157
0.35	2.91	0.7391	1.53×10^{-3}	3.186×10^{-8}	3.07	0.7362	2.20×10^{-2}	0.7157
0.50	2.91	0.7444	1.51×10^{-3}	-	3.07	0.7362	2.20×10^{-2}	0.7157
1.0	2.91	-	1.51×10^{-3}	-	3.07	0.7362	2.20×10^{-2}	0.7157
	Fig(32) curve 2	Fig(25) curve 2	Fig(27) curve 2	Fig(29) curve 2	Fig(33) curve 2	Fig(24) curve 2	Fig(28) curve 2	Fig(36) curve 2

VARIATIONS IN CONDUCTIVITY

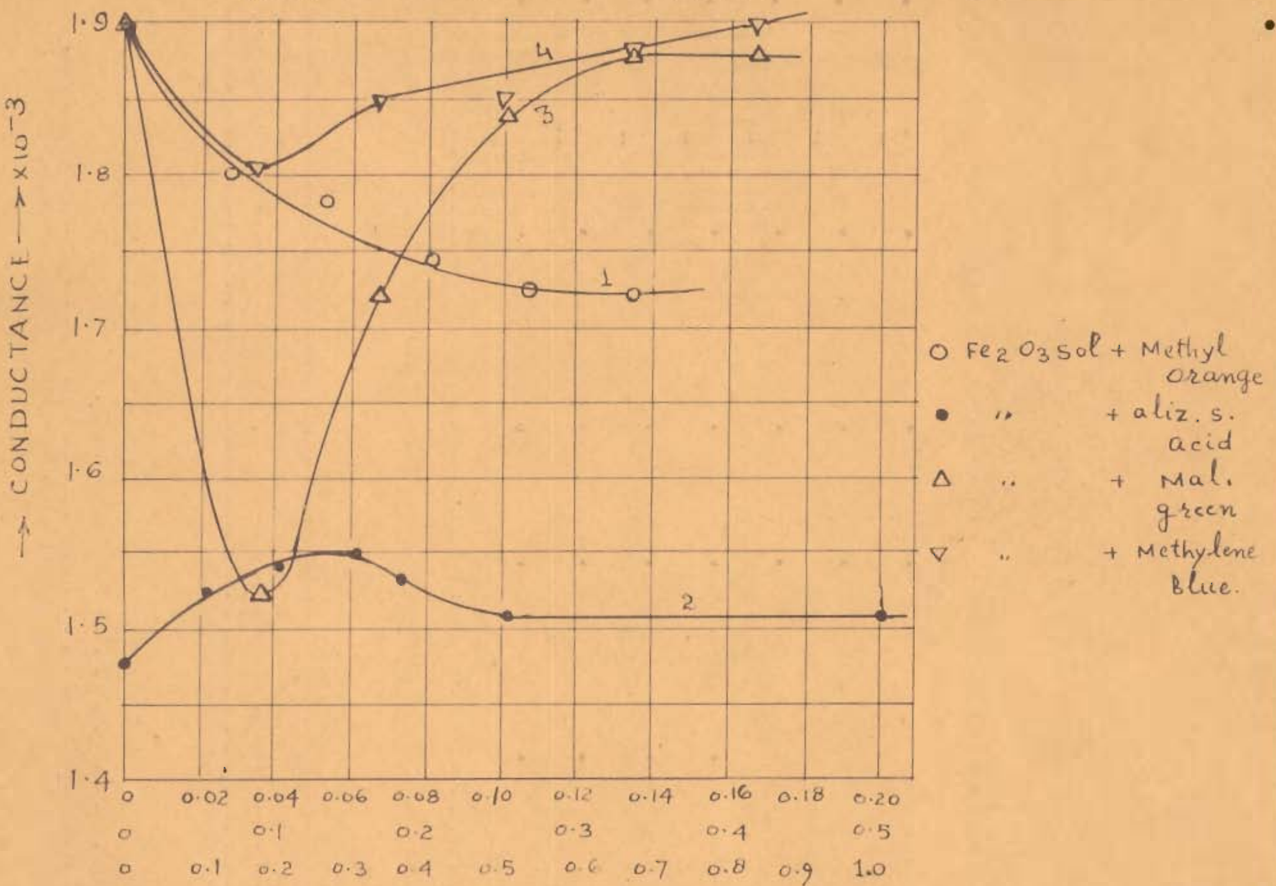


FIG_27. → CONC. OF DYE (mM/LITRE)

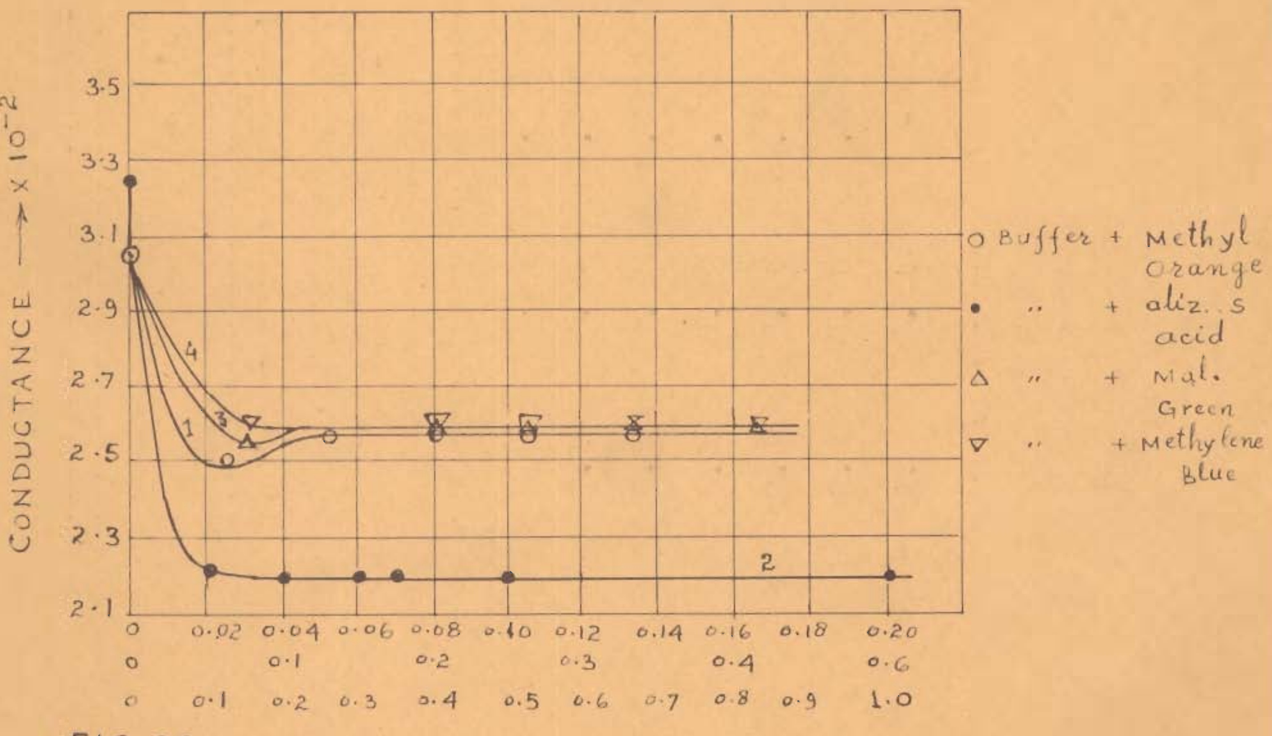


FIG 28. → CONC of DYE (mM/LITRE)

TABLE No.3

Variations in pH, viscosity, conductivity, ζ-potential of Fe_2O_3 sol; buffer and dispersion medium by the addition of malachite green.

Tempt. = 35°C ± 0.1°C, pH of sol = 2.5

Conc. of dye mM/litre	Set No.3 (a)				Set No.3(b)			Set No.3(c)
	pH sol + dye mixture	Viscosity sol + dye mixture (centipoise)	Conductance sol+dye mixture (mhos)	ζ-potential sol+dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (mentipoise)
0	2.60	0.7150	1.90×10^{-3}	1.695×10^{-7}	2.60	0.7360	3.05×10^{-2}	0.7155
0.0333	1.62	0.7155	1.52×10^{-3}	1.541×10^{-7}	2.74	0.7365	2.55×10^{-2}	0.7160
0.0666	1.60	0.7160	1.72×10^{-3}	1.235×10^{-7}	2.74	0.7365	2.60×10^{-2}	0.7160
0.1000	1.60	0.7174	1.84×10^{-3}	1.082×10^{-7}	2.74	0.7365	2.60×10^{-2}	0.7160
0.1333	1.60	0.7178	1.88×10^{-3}	1.083×10^{-7}	2.74	0.7365	2.60×10^{-2}	0.7160
0.1666	1.60	0.7178	1.88×10^{-3}	1.083×10^{-7}	2.74	0.7365	2.60×10^{-2}	0.7160
	Fig(32) curve 3	Fig(25) curve 3	Fig(27) curve 3	Fig(29) curve 3	Fig(33) curve 3	Fig(26) curve 3	Fig(28) curve 3	Fig(36) curve 3

VARIATIONS IN ζ-POTENTIAL

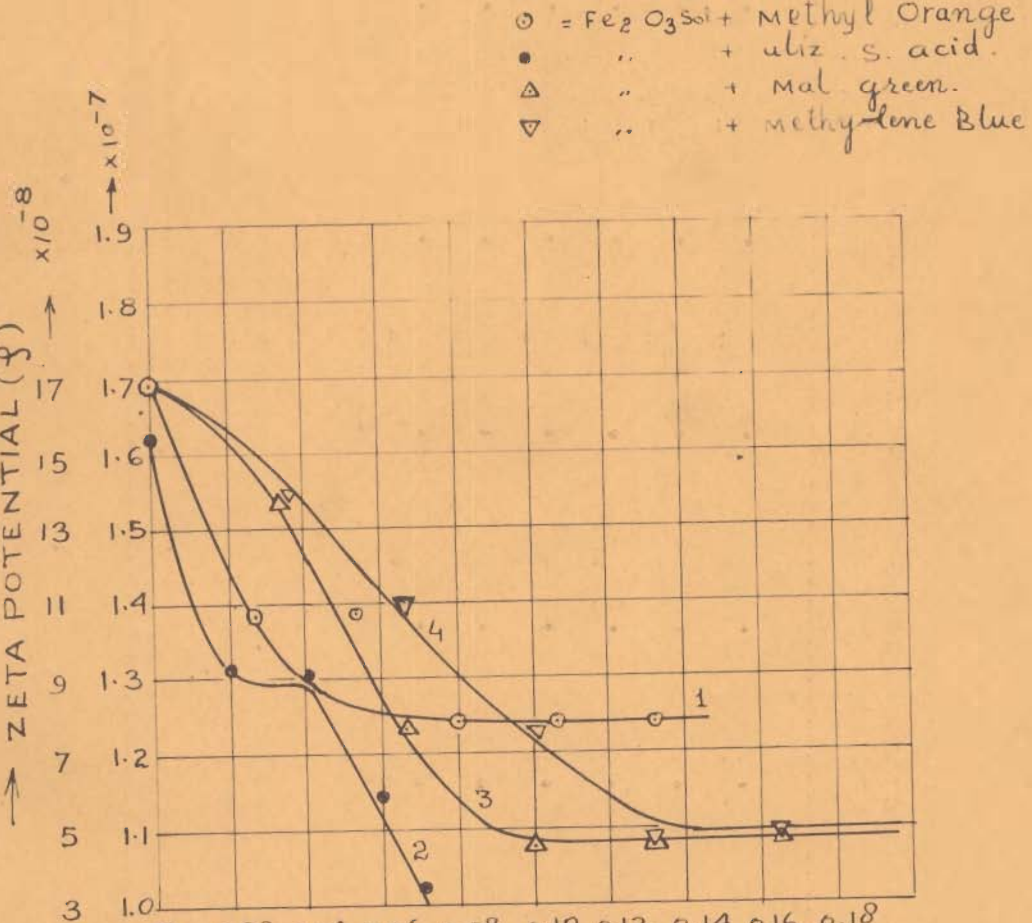


FIG 29. → CONC. OF DYE (mM/LITRE)

TABLE No.4

Variations in pH, viscosity, conductivity, ζ-potential of Fe_2O_3 sol; buffer and dispersion medium by the addition of methylene blue.

Tempt. = 35°C ± 0.1°C, pH of sol = 2.5

Conc. of dye mM/litre	Set No.4(a)				Set No.4(b)			Set No.4(c)
	pH sol+dye mixture	Viscosity sol+dye mixture (centi-poise	Conductance sol + dye mixture (mhos)	ζ-potential, sol+ dye mixture (volts)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centi-poise	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centi-poise)
0	2.60	0.7150	1.90×10^{-3}	1.695×10^{-7}	2.60	0.7360	3.05×10^{-2}	0.7155
0.0333	2.52	0.7178	1.80×10^{-3}	1.547×10^{-7}	2.72	0.7365	2.60×10^{-2}	0.7178
0.0666	2.50	0.7178	1.85×10^{-3}	1.393×10^{-7}	2.72	0.7365	2.60×10^{-2}	0.7178
0.1000	2.49	0.7178	1.85×10^{-3}	1.238×10^{-7}	2.72	0.7365	2.60×10^{-2}	0.7178
0.1333	2.49	0.7178	1.88×10^{-3}	1.082×10^{-7}	2.72	0.7365	2.60×10^{-2}	0.7178
0.1666	2.49	0.7178	1.90×10^{-3}	1.082×10^{-7}	2.72	0.7365	2.60×10^{-2}	0.7178
	Fig(32) curve 4	Fig(25) curve 4	Fig(27) curve 4	Fig(29) curve 4	Fig(33) curve 1	Fig(26) curve 4	Fig(28) curve 4	Fig(36) curve 4

VARIATIONS IN pH.

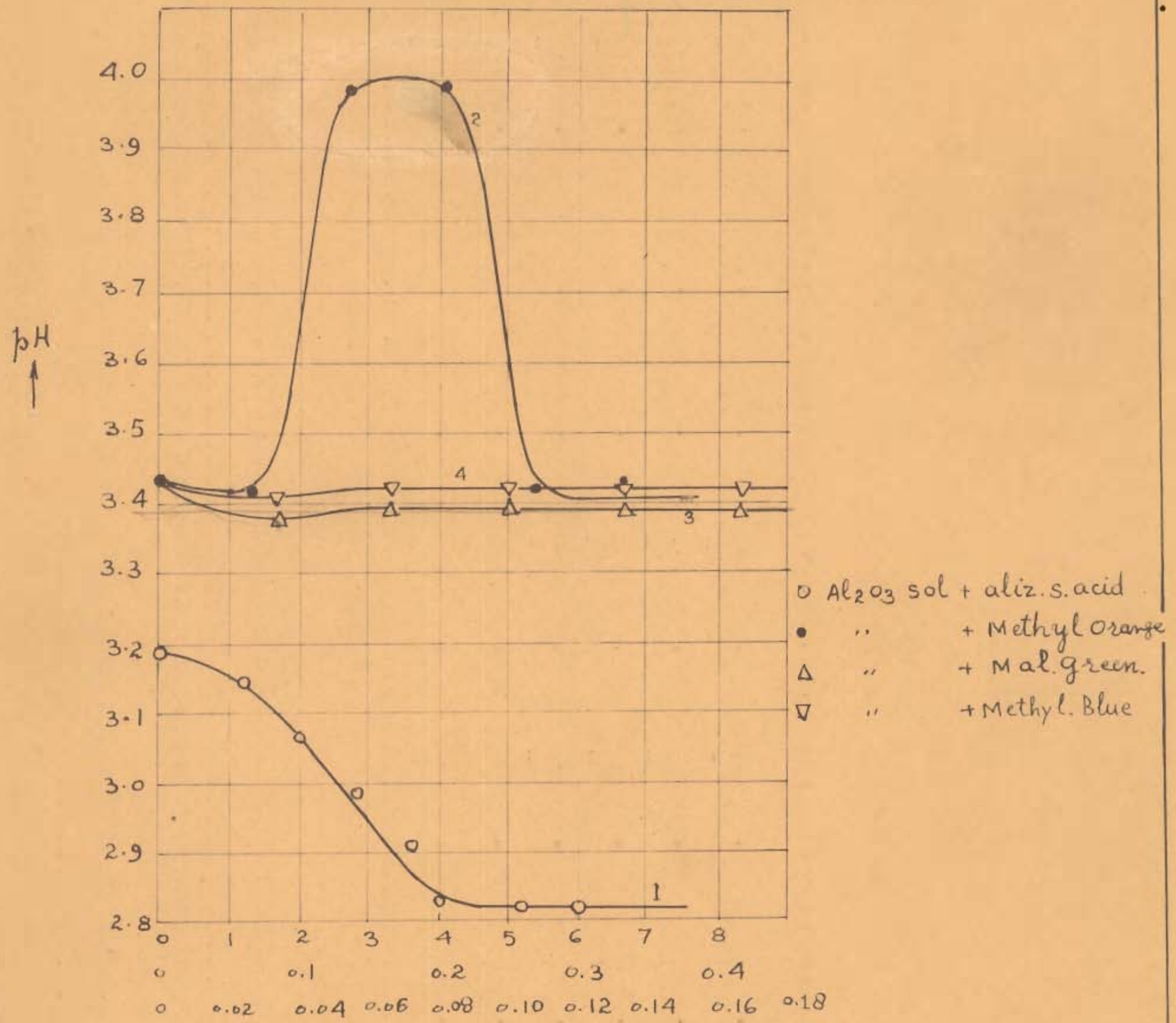


FIG – 30. → CONC. OF DYE (mM/LITRE)

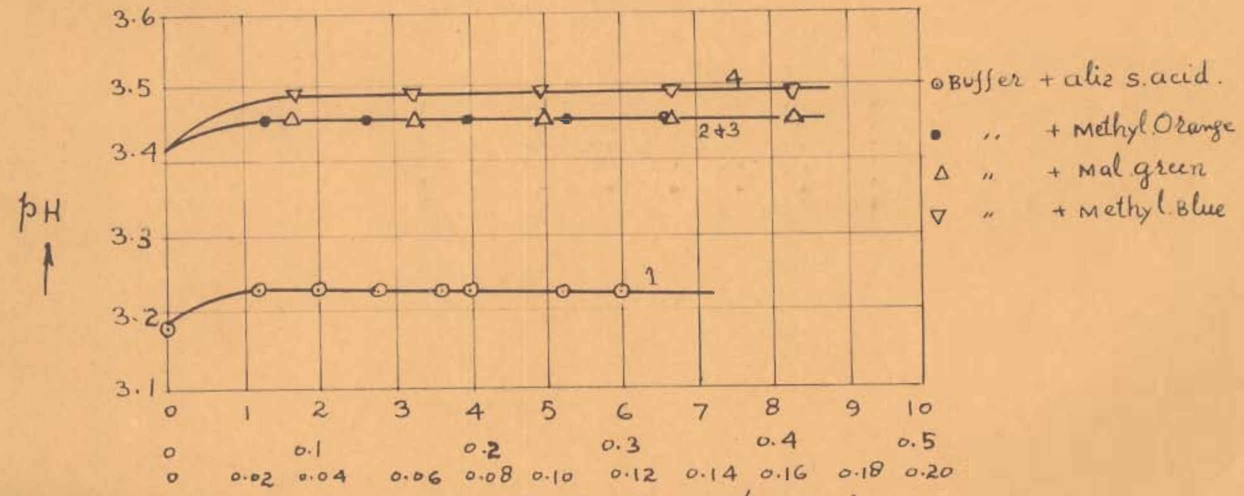


FIG – 31. → CONC. OF DYE (mM/LITRE)

TABLE No.5

Alumina sol:

Variations in pH, viscosity and conductivity of alumina sol, buffer and dispersion medium by the addition of alizarin sulphonic acid.

Tempt. = 35°C ± 0.1°C, pH of sol = 3.16

Conc. of dye mM/litre	Set No. 1 (a)			Set No. 1 (b)			Set No.1(c)
	pH sol + dye mixture	Viscosity sol + dye mixture (centipoise)	Conductance sol + dye mixture (mhos)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture (centipoise)
0	3.18	0.7511	0.60×10^{-2}	3.18	0.7360	4.72×10^{-2}	0.7155
1.2	3.14	0.7679	0.62×10^{-2}	3.23	0.7363	4.00×10^{-2}	0.7157
2.0	3.06	0.8872	0.65×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
2.8	2.98	1.052	0.66×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
3.6	2.91	1.120	0.69×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
4.0	2.82	1.182	0.70×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
5.2	2.82	1.243	0.70×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
6.0	2.82	1.243	0.70×10^{-2}	3.23	0.7363	4.08×10^{-2}	0.7157
	Fig (30) curve 1	Fig (37) curve 1	Fig (34) curve 1	Fig (31) curve 1	Fig (38) curve 1	Fig (35) curve 1	Fig (Same as 36) curve 2

VARIATIONS IN pH.

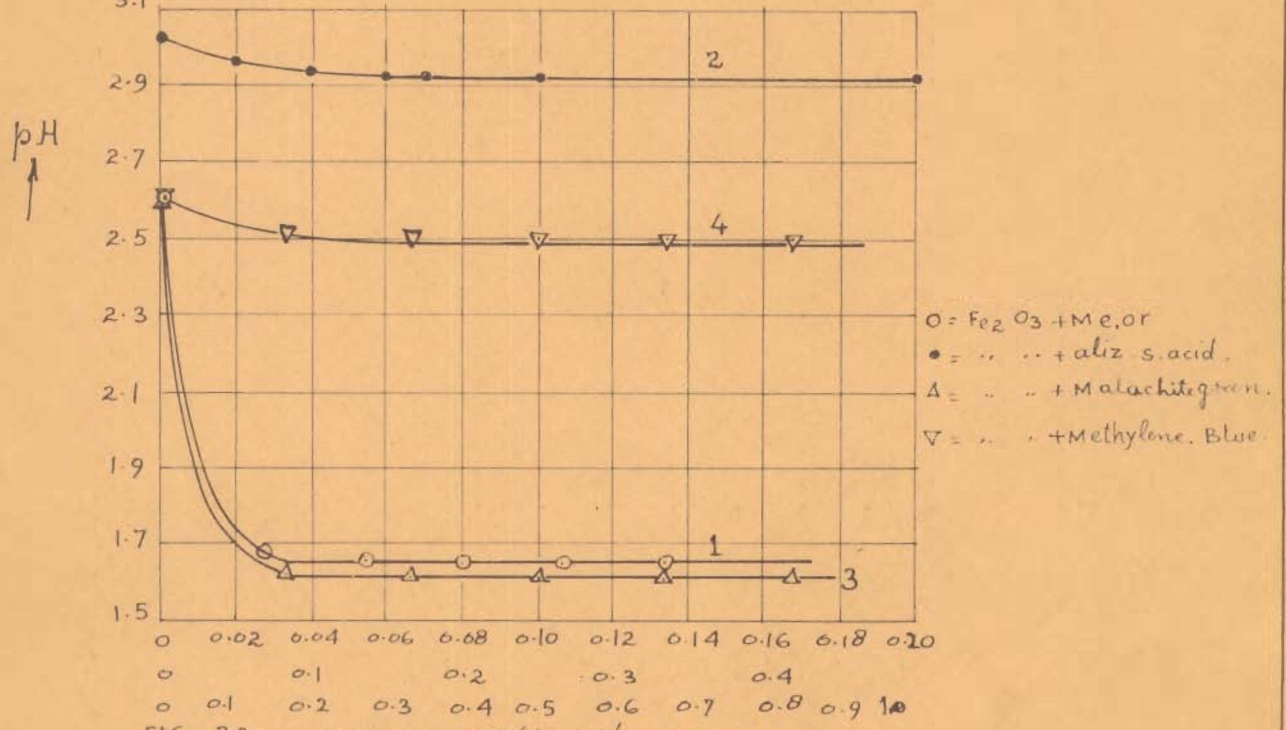


FIG-32. → CONC. OF DYE (mM/LITRE)

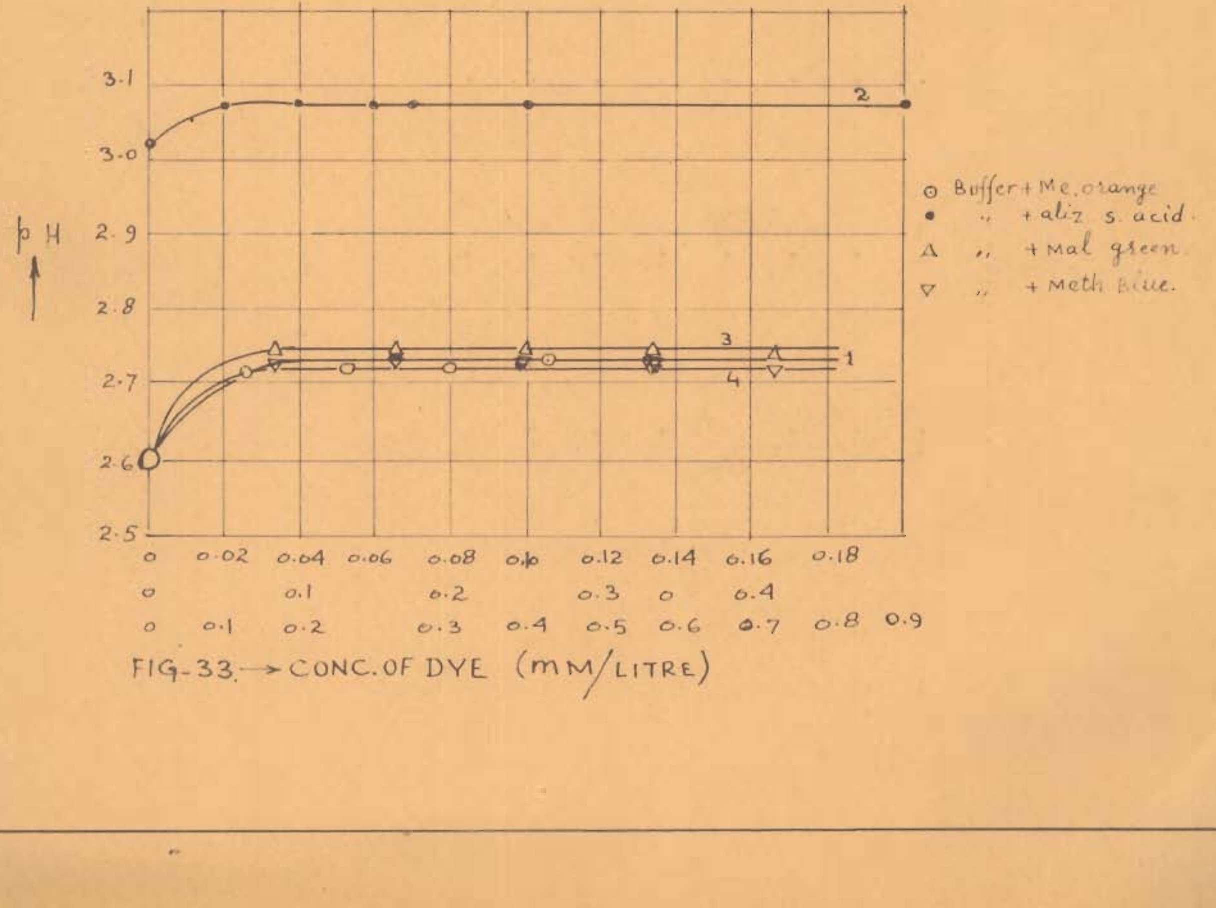


FIG-33. → CONC. OF DYE (mM/LITRE)

TABLE No.6

Variations in pH, viscosity and conductivity of alumina sol, buffer and dispersion medium by the addition of methyl orange.

Tempt. = 35°C ± 0.1°C, pH of sol = 3.40

Conc. of dye mM/litre	Set No. 2(a)			Set No.2 (b)			Set No.2(c)
	pH sol + dye mixture	Viscosity sol + dye mixture (centipoise)	Conductance sol+dye mixture (mhos)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise)	Conductance buffer + dye mixture (mhos)	Viscosity water + dye mixture centipoise)
0	3.42	0.7580	0.75×10^{-2}	3.42	0.7360	3.38×10^{-2}	0.7155
0.0666	3.41	0.7578	0.74×10^{-2}	3.46	0.7365	2.85×10^{-2}	0.7160
0.1333	3.99	0.7610	0.73×10^{-2}	3.46	0.7365	2.85×10^{-2}	0.7160
0.200	3.99	0.7660	0.72×10^{-2}	3.46	0.7365	2.85×10^{-2}	0.7160
0.266	3.42	0.7723	0.72×10^{-2}	3.46	0.7365	2.85×10^{-2}	0.7160
0.333	3.42	0.7896	0.72×10^{-2}	3.46	0.7365	2.85×10^{-2}	0.7160
	Fig(30) curve 2	Fig(37) curve 2	Fig(34) curve 2	Fig(31) curve 2	Fig(38) curve 2	Fig(35) curve 2	Fig(36) curve 1

VARIATIONS IN CONDUCTIVITY

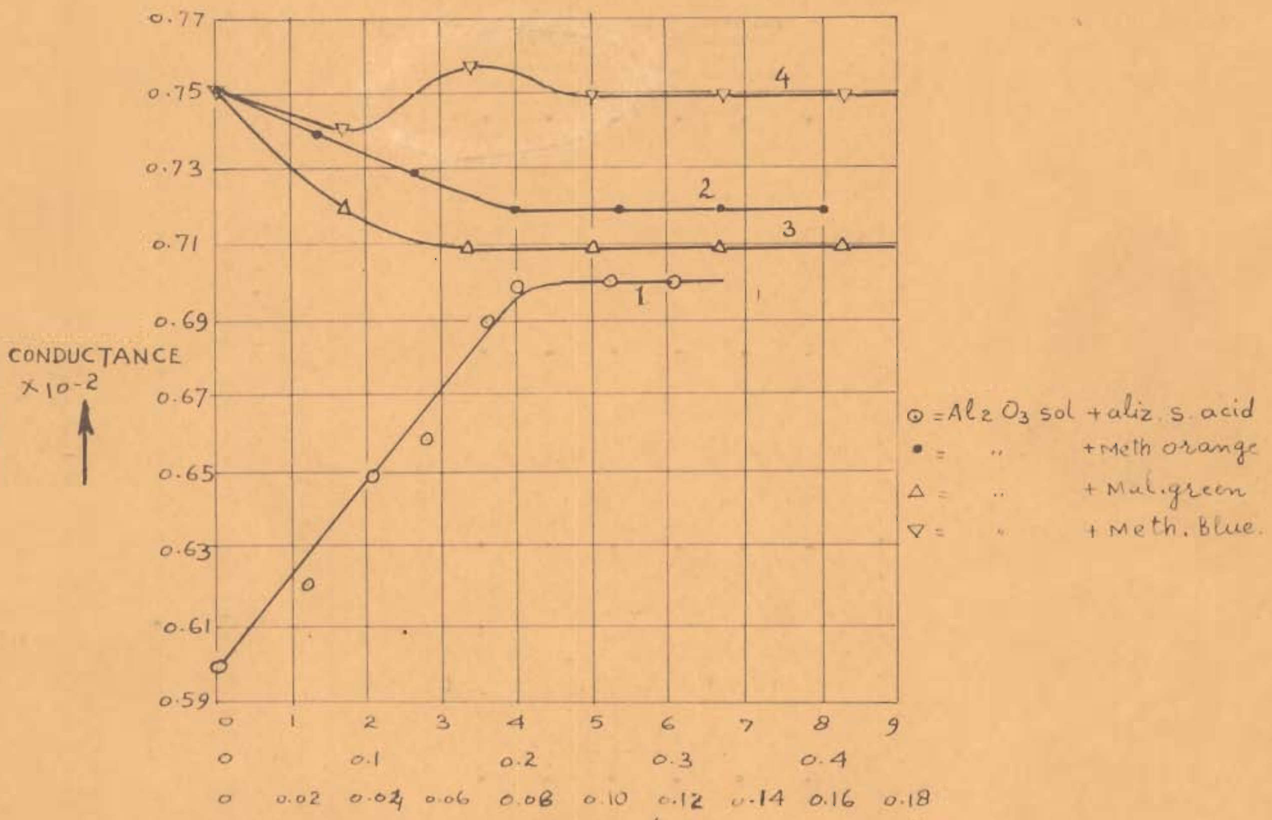


FIG-34. → CONC. OF. DYE (mM/LITRE)

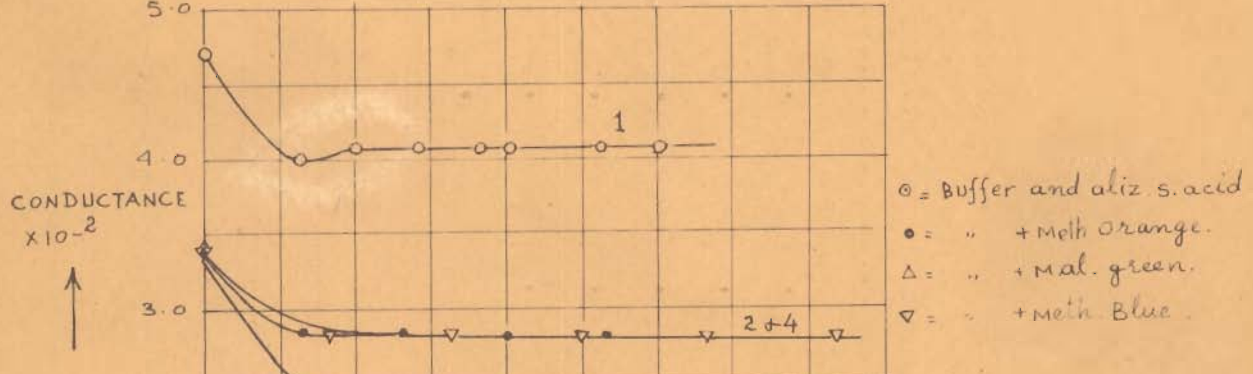


FIG-35. → CONC. OF DYE (mM/LITRE)

TABLE No.7

Variations in pH, viscosity and conductivity of alumina sol, buffer and dispersion medium by the addition of malachite green.

Tempt. = 35°C ± 0.1°C, pH of sol = 3.40

Conc. of dye mM/litre	Set No.3(a)			Set No.3(b)			Set No.3(c)
	pH sol+dye mixture	Viscosity sol+dye mixture (centipoise)	Conductance sol+dye mixture (mhos)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise)	Conductance buffer+ dye mixture (mhos)	Viscosity water + dye mixture (centipoise)
0	3.42	0.7580	0.75×10^{-2}	3.42	0.7360	3.38×10^{-2}	0.7155
0.0333	3.37	0.7523	0.72×10^{-2}	3.47	0.7365	2.38×10^{-2}	0.7160
0.0666	3.39	0.7530	0.71×10^{-2}	3.47	0.7365	2.38×10^{-2}	0.7160
0.1000	3.39	0.7534	0.71×10^{-2}	3.47	0.7365	2.38×10^{-2}	0.7160
0.1333	3.39	0.7551	0.71×10^{-2}	3.47	0.7365	2.38×10^{-2}	0.7160
0.1666	3.39	0.7600	0.71×10^{-2}	3.47	0.7365	2.38×10^{-2}	0.7160
	Fig(30) curve 3	Fig(37) curve 3	Fig(34) curve 3	Fig(31) curve 3	Fig(38) curve 3	Fig(35) curve 3	Fig(36) curve 3

VARIATIONS IN VISCOSITY

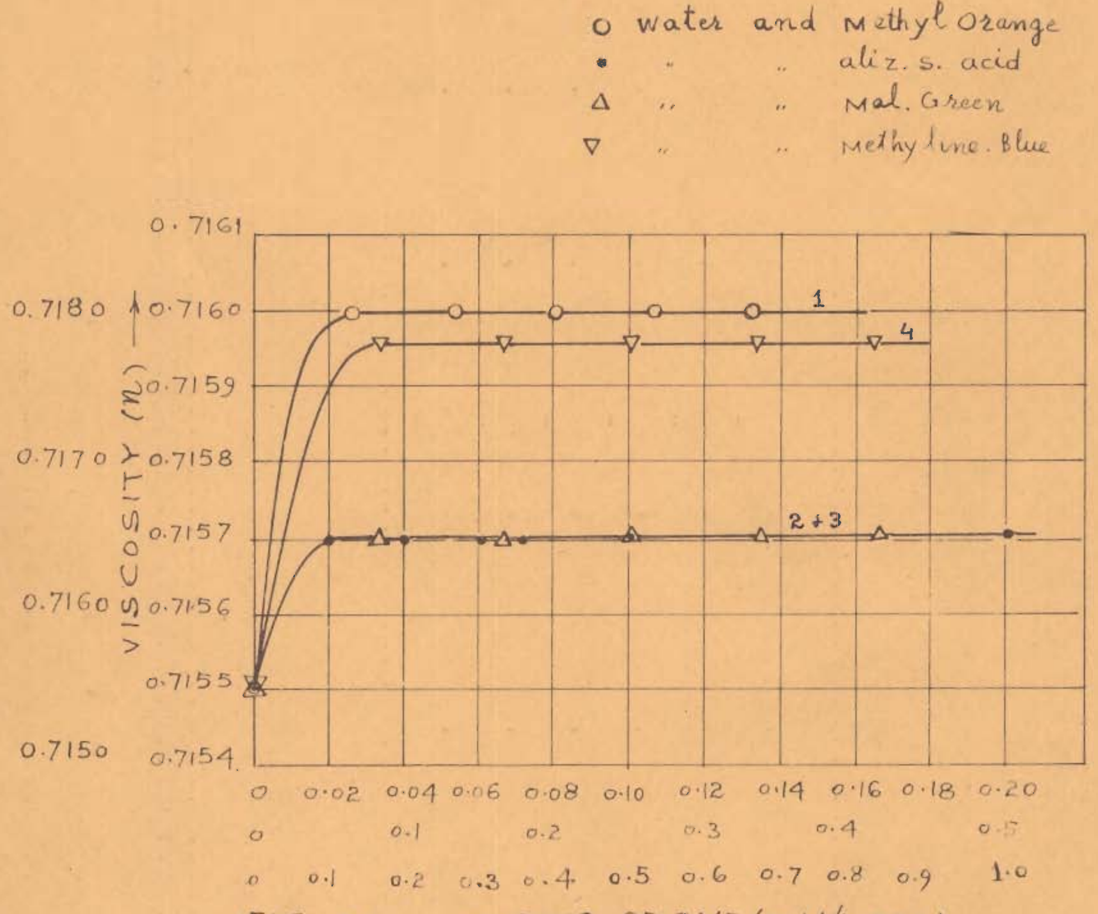


FIG_36. → CONC. OF DYE (mM/LITRE)

TABLE No.8

Variations in pH, viscosity and conductivity of alumina sol, buffer and dispersion medium by the addition of methylene blue.

Tempt. = 35°C ± 0.1°C, pH of sol = 3.40

Conc. of dye mM/litre	Set No.4(a)			Set No.4(b)			Set No.4(c)
	pH sol+dye mixture	Viscosity sol + dye mixture (centipoise)	Conductance sol+dye mixture (mhos)	pH buffer + dye mixture	Viscosity buffer + dye mixture (centipoise	Conductance buffer+ dye mixture (mhos)	Viscosity water + dye mixture (centipoise)
0	3.42	0.7580	0.75×10^{-2}	3.42	0.7360	3.38×10^{-2}	0.7155
0.0333	3.40	0.7539	0.74×10^{-2}	3.49	0.7364	2.82×10^{-2}	0.7178
0.0666	3.42	0.7530	0.76×10^{-2}	3.49	0.7364	2.82×10^{-2}	0.7178
0.1000	3.42	0.7536	0.75×10^{-2}	3.49	0.7364	2.82×10^{-2}	0.7178
0.1333	3.42	0.7530	0.75×10^{-2}	3.49	0.7364	2.82×10^{-2}	0.7178
0.1666	3.42	0.7530	0.75×10^{-2}	3.49	0.7364	2.82×10^{-2}	0.7178
	Fig(30) curve 4	Fig(37) curve 4	Fig(34) curve 4	Fig(31) curve 4	Fig (38) curve 4	Fig (35) curve 4	Fig(36) curve 4

VARIATIONS IN VISCOSITY

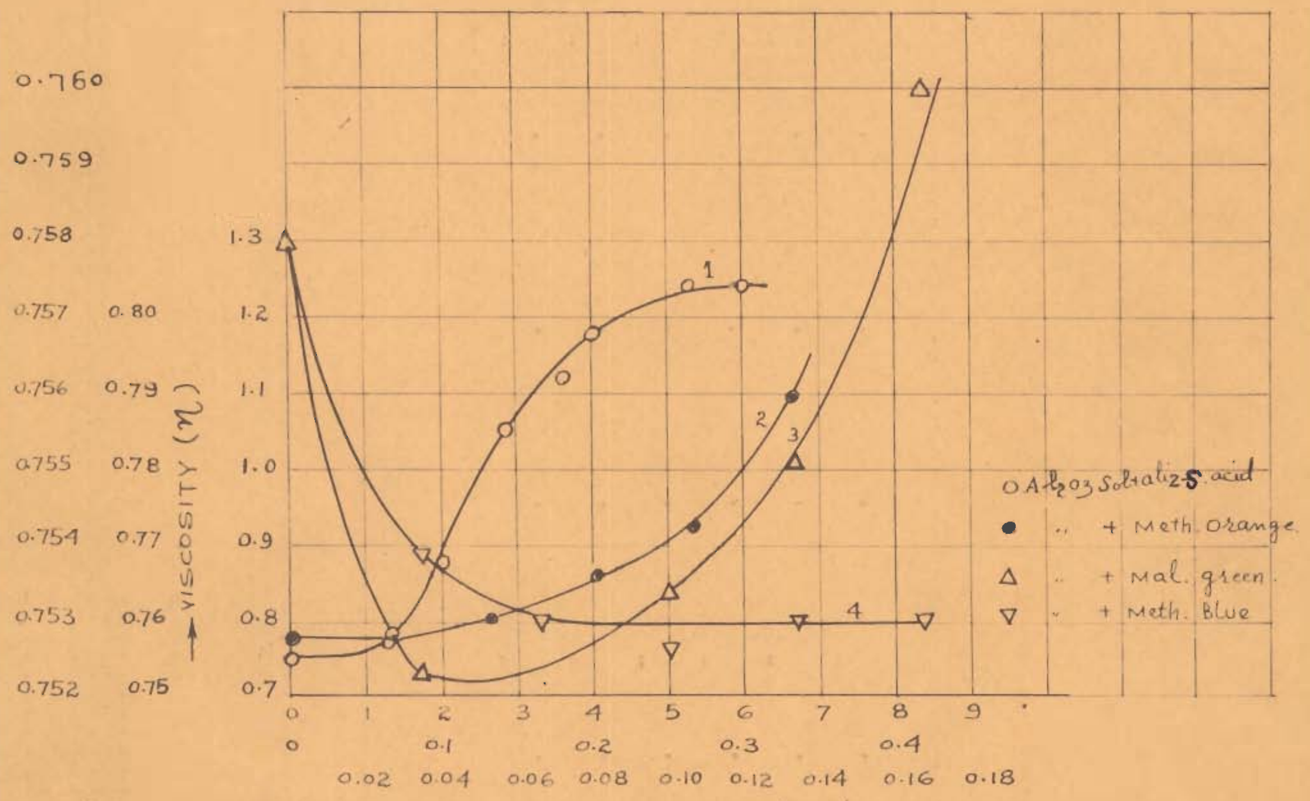


FIG- 37. → CONC. OF Dye (mM/LITRE)

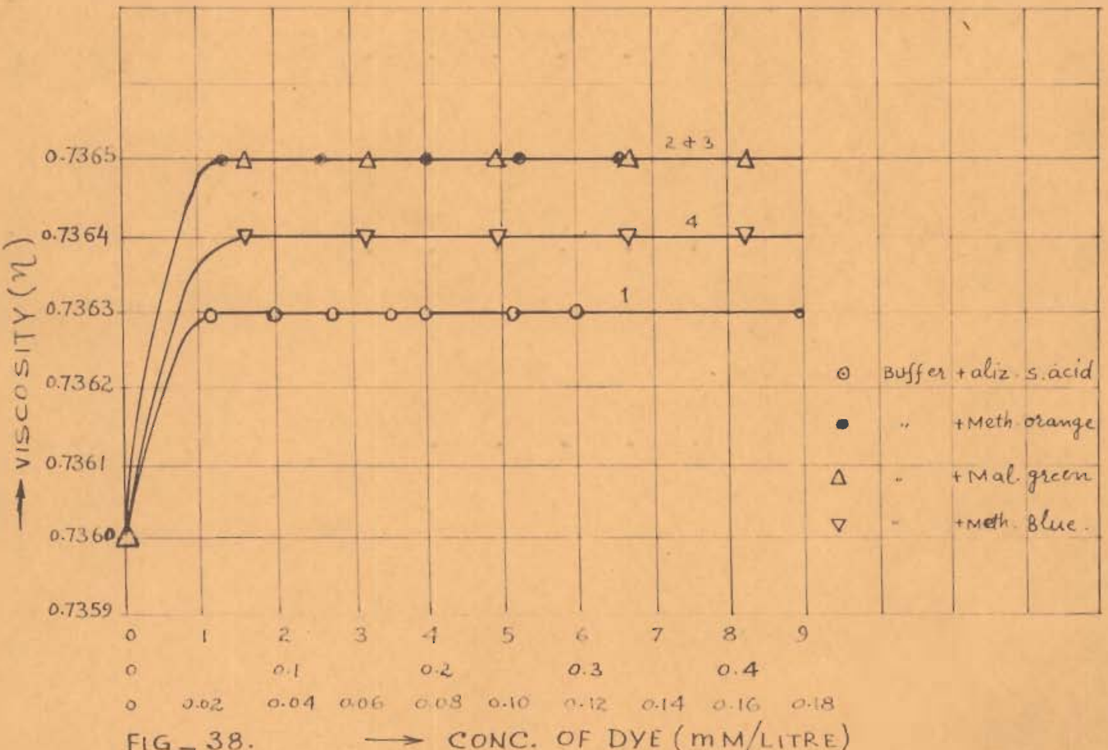


FIG _ 38. → CONC. OF DYE (mM/LITRE)

Data on absorption

TABLE No.9

Optical density of the dyes at different wavelengths

conc. of alizarin sulphonic acid = 1.5×10^{-4} M

conc. of methyl orange = 0.0451×10^{-3} M

Wavelength in mμ	O.D. set No.5 c(i) alizarin s. acid	Wavelength in mμ	O.D. set No.5 c(ii) methyl orange
330	0.46	330	0.16
350	0.41	350	0.23
375	0.43	375	0.47
400	0.54	400	0.80
425	0.56	425	1.0
430	0.54	450	1.1
435	0.52	475	1.0
450	0.41	500	0.66
475	0.24	525	0.26
500	0.16	550	0.06
525	0.13	575	0.01
550	0.10	600	0.01
575	0.10	625	0.01
600	0.04		
625	0.03		

TABLE No.10

Optical density of the dyes and sols at different wavelengths

conc. of methylene blue = 0.0314×10^{-3}M

conc. of malachite green = 0.0196×10^{-3}M

conc. of Al_2O_3 used for absorption measurements = 4.0 gms. Al_2O_3 per litre.

conc. of Fe_2O_3 sol used for absorption measurements = 0.0142 gms. Fe_2O_3 per litre.

Wavelength in mμ	O.D. Set No. 5 c(iii) methylene blue	Wave-length in mμ	O.D. Set No. 5 c(iv) malachite green	Wave-length in mμ	O.D. Al_2O_3 sol	O.D. Fe_2O_3 sol	O.D. Set No.6
325	0.15	330	0.06	330	0.125	1.4	0.80
350	0.03	350	0.05	350	0.11	1.3	0.74
375	0.025	375	0.08	375	0.085	1.0	0.60
400	0.02	400	0.16	400	0.07	0.75	0.44
425	0.015	425	0.19	425	0.06	0.53	0.32
450	0.025	430	0.165	450	0.05	0.37	0.225
475	0.045	435	0.14	475	0.04	0.28	0.165
500	0.065	440	0.11	500	0.03	0.20	0.125
525	0.08	450	0.06	525	0.03	0.14	0.085
550	0.165	475	0.025	550	0.02	0.08	0.05
575	0.350	500	0.045	575	0.02	0.04	0.03
600	0.70	525	0.11	600	0.02	0.03	0.02
625	0.90	550	0.25	615	0.02	0.03	0.02
650	1.5	575	0.47	625	0.02	0.02	0.02
675	0.75	600	0.85	650	0.03	0.03	0.02
700	0.12	610	0.90	675	0.02	0.01	
725	0.02	615	0.95	700	0.01	-	
750	0.01	620	0.90				
775	0.01	625	0.80				
800	0.01	650	0.25				
825	0.01	675	0.06				
		700	0.02				
		725	0.01				
		750	0.01				
		775	0.01				
		800	0.01				

TABLE No.11

Ferric oxide sol and alizarin sulphonic acid

Absorption spectra of 1.5x10^{-4} M alizarin sulphonic acid in presence of sol, buffer and water.

Wave-length in mμ	Set No.5b(i)		Set No.5b(ii)			Set No.5b(iii)		
	O.D. sol+dye	O.D. buffer+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water+dye	O.D. sol+dye	O.D. buffer+dye	O.D. water + dye
330	0.8	0.15	0.85	0.19	0.17	0.95	0.24	0.2
350	0.75	0.13	0.84	0.16	0.12	0.85	0.23	0.145
375	0.62	0.12	0.66	0.145	0.08	0.74	0.21	0.11
400	0.47	0.08	0.51	0.13	0.07	0.58	0.205	0.11
425	0.33	0.07	0.40	0.115	0.06	0.47	0.19	0.11
450	0.27	0.04	0.33	0.09	0.06	0.39	0.145	0.11
475	0.23	0.03	0.29	0.07	0.07	0.33	0.10	0.105
500	0.19	0.02	0.26	0.06	0.06	0.31	0.075	0.095
525	0.14	-	0.215	0.045	0.07	0.24	0.06	0.090
550	0.10	-	0.165	0.04	0.055	-	0.05	0.065
575	0.085	-	0.125	0.028	0.04	-	-	0.04
600	0.065	-	0.090	0.025	0.025	-	-	0.02
625	0.04	-	0.065	0.020	0.015	-	-	0.015

O.D. of set No.5a(i) at the maxima of set No.5b(i), 5b(ii), 5b(iii) [sol+dye] is 0.170.

TABLE No.12

Ferric oxide sol and methyl orange

Absorption spectra of 0.0451×10^{-3} M methyl orange in presence of sol, buffer and water.

Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye
330	0.76	0.15	0.08	0.85	0.18	0.105	0.85	0.20	0.130	0.9	0.22	0.15	0.93	0.235	0.16
350	0.68	0.135	0.07	0.77	0.165	0.105	0.80	0.195	0.135	0.85	0.225	0.16	0.85	0.25	0.18
375	0.55	0.140	0.085	0.66	0.190	0.135	0.70	0.245	0.19	0.77	0.29	0.24	0.82	0.34	0.29
400	0.46	0.145	0.10	0.56	0.23	0.19	0.62	0.305	0.27	0.72	0.38	0.34	0.78	0.45	0.42
425	0.36	0.150	0.115	0.48	0.26	0.225	0.57	0.35	0.33	0.68	0.44	0.42	0.77	0.54	0.52
450	0.30	0.152	0.13	0.395	0.28	0.255	0.54	0.39	0.375	0.66	0.50	0.48	0.75	0.62	0.58
475	0.25	0.145	0.115	0.36	0.265	0.230	0.48	0.375	0.35	0.62	0.48	0.45	0.70	0.58	0.56
500	0.185	0.10	0.07	0.28	0.18	0.15	0.36	0.26	0.22	0.45	0.335	0.285	0.52	0.41	0.35
525	0.115	0.055	0.03	0.165	0.09	0.06	0.21	0.12	0.085	0.265	0.165	0.11	0.29	0.195	0.14
550	0.055	0.022	0.01	0.075	0.035	0.02	0.09	0.05	0.02	0.115	0.055	0.03	0.12	0.065	0.035
575	0.025	0.015	0.01	0.03	0.015	0.015	0.035	0.02	0.01	0.04	0.02	0.01	0.04	0.02	0.01
600	0.015	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01
625	0.015	0.01	0.01	0.015	0.01	0.01	0.015	0.01	0.01	0.015	0.01	0.01	0.015	0.01	0.01

O.D. of set No.5a(ii) is 0.25 and of set No.6 is 0.225.

TABLE No.13

Ferric oxide and methylene blue:

Absorption spectra of 0.0314×10^{-3} M methylene blue in presence of sol, buffer and water.

Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye
330	0.90	0.15	0.075	0.90	0.155	0.08	0.95	0.17	0.08	0.75	0.165	0.085	0.87	0.24	0.10
350	0.80	0.12	0.05	0.85	0.130	0.06	0.87	0.13	0.06	0.66	0.13	0.055	0.78	0.17	0.095
375	0.68	0.10	0.04	0.68	0.10	0.045	0.70	0.115	0.045	0.56	0.11	0.04	0.64	0.115	0.06
400	0.50	0.07	0.03	0.50	0.08	0.035	0.52	0.085	0.045	0.42	0.085	0.03	0.48	0.09	0.045
425	0.35	0.055	0.02	0.355	0.065	0.025	0.37	0.065	0.025	0.31	0.07	0.02	0.35	0.06	0.035
450	0.25	0.04	0.015	0.255	0.05	0.020	0.27	0.05	0.020	0.23	0.06	0.02	0.26	0.058	0.025
475	0.19	0.035	0.01	0.195	0.045	0.020	0.21	0.049	0.020	0.19	0.052	0.025	0.21	0.059	0.022
500	0.145	0.034	0.01	0.15	0.04	0.022	0.165	0.05	0.020	0.15	0.055	0.025	0.165	0.061	0.03
525	0.095	0.03	0.015	0.11	0.035	0.025	0.12	0.045	0.025	0.12	0.052	0.03	0.14	0.062	0.03
550	0.07	0.032	0.02	0.085	0.045	0.04	0.11	0.062	0.04	0.13	0.08	0.055	0.145	0.095	0.035
575	0.065	0.045	0.045	0.095	0.075	0.07	0.135	0.11	0,08	0.185	0.15	0.12	0.215	0.18	0.07
600	0.08	0.075	0.075	0.140	0.140	0.12	0.22	0.22	0.17	0.225	0.285	0.24	0.38	0.36	0.15
625	0.10	0.10	0.110	0.190	0.190	0.16	0.29	0.30	0.24	0.43	0.38	0.34	0.51	0.49	0.30
650	0.17	0.155	0.15	0.28	0.30	0.22	0.44	0.46	0.35	0.62	0.58	0.50	0.75	0.73	0.62
675	0.11	0.095	0.10	0.185	0.19	0.14	0.28	0.295	0.23	0.40	0.365	0.32	0.46	0.45	0.37
700	0.02	0.02	0.02	0.03	0.025	0.025	0.045	0.19	0.03	0.06	0.052	0.05	0.065	0.07	0.05
725	0.01	-	0.01	0.01	-	0.005	0.01	-	0.01	0.015	0.015	0.01	0.015	0.015	0.01
750	-	-	-	-	-	-	-	-	-	0.01	-	-	0.01	-	-

O.D. of set No.5a(iii) at the maxima of set No.5b(i), 5b(ii), 5b(iii), 5b(iv), 5b(v) [sol+dye] is 0.05.

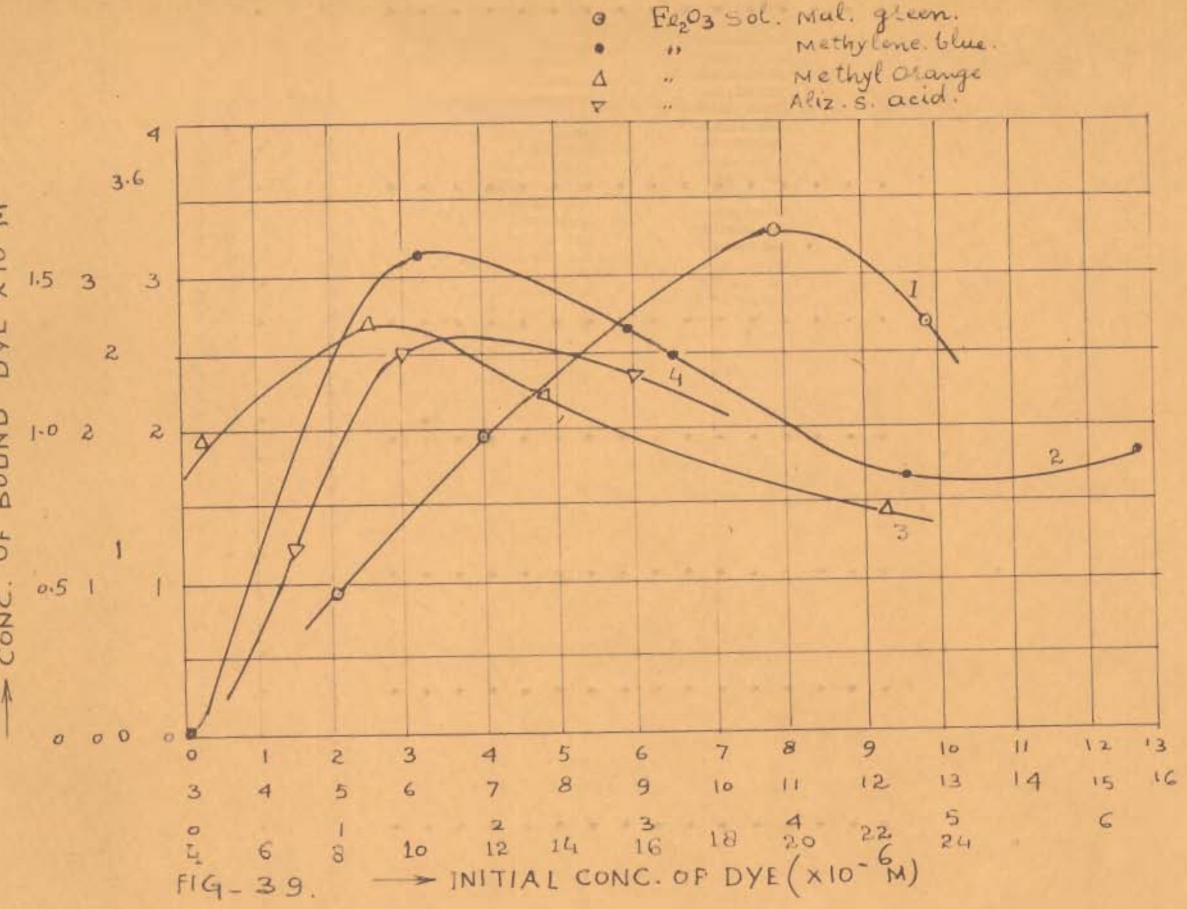
TABLE No.14

Ferric oxide and malachite green

Absorption spectra of 0.0196x10^{-3} M malachite green in presence of sol, buffer and water.

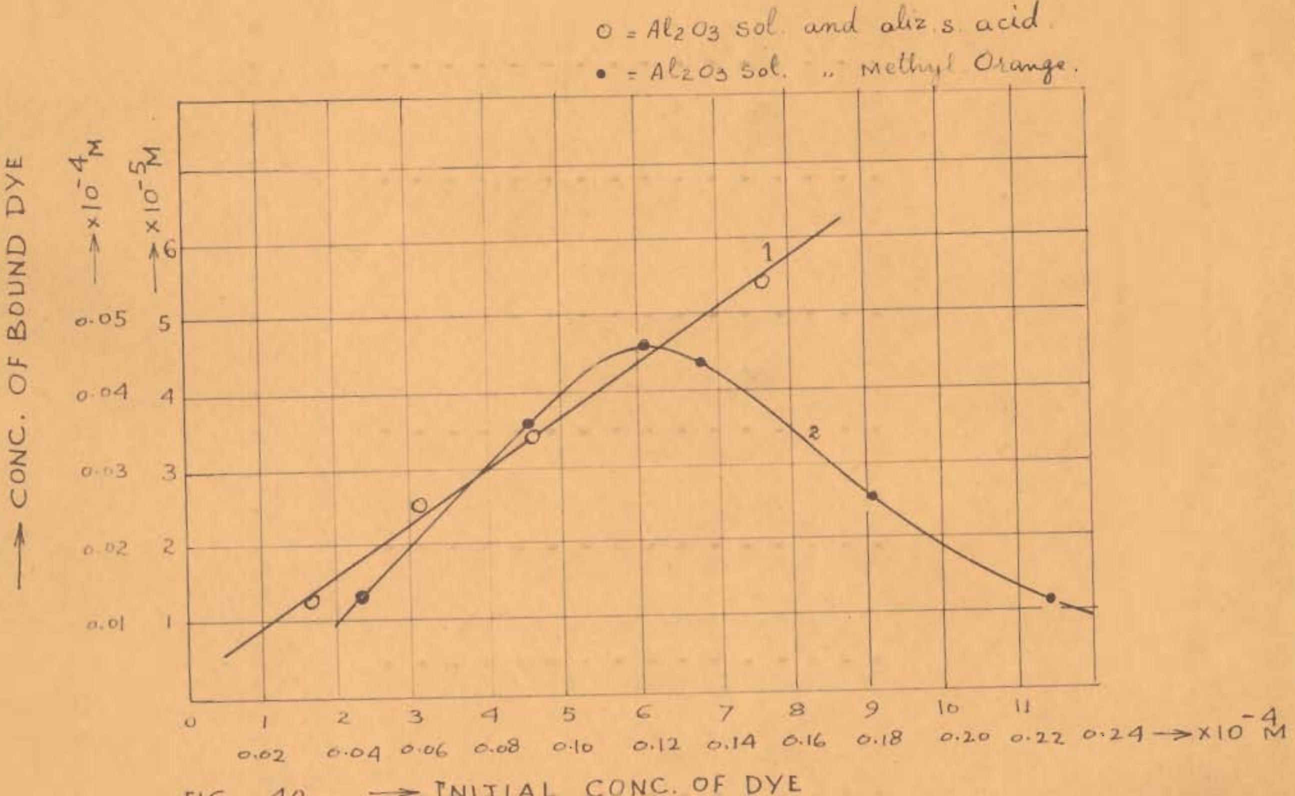
Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye
330	0.75	0.15	0.07	0.5	0.155	0.08	0.17	0.165	0.085	0.07	0.175	0.08	0.08	0.175	0.09
350	0.70	0.135	0.06	0.45	0.14	0.07	0.15	0.15	0.07	0.06	0.15	0.07	0.065	0.145	0.075
375	0.57	0.11	0.045	0.37	0.12	0.055	0.135	0.13	0.06	0.065	0.14	0.065	0.07	0.145	0.08
400	0.43	0.09	0.04	0.30	0.11	0.05	0.125	0.135	0.055	0.085	0.15	0.07	0.10	0.150	0.095
425	0.32	0.08	0.035	0.23	0.06	0.04	0.11	0.130	0.05	0.090	0.135	0.065	0.11	0.155	0.10
450	0.23	0.05	0.02	0.145	0.04	0.02	0.055	0.075	0.025	0.03	0.07	0.025	0.02	0.070	0.04
475	0.16	0.04	0.15	0.105	0.05	0.015	0.04	0.04	0.015	0.02	0.05	0.015	0.02	0.045	0.025
500	0.125	0.03	0.10	0.085	0.07	0.015	0.035	0.045	0.010	0.025	0.055	0.02	0.025	0.05	0.03
525	0.095	0.035	0.015	0.075	0.05	0.015	0.045	0.055	0.025	0.045	0.07	0.03	0.055	0.075	0.05
550	0.075	0.04	0.025	0.08	0.065	0.03	0.075	0.09	0.045	0.10	0.125	0.06	0.12	0.145	0.11
575	0.075	0.06	0.040	0.11	0.11	0.05	0.145	0.16	0.085	0.185	0.21	0.11	0.24	0.25	0.21
600	0.095	0.085	0.065	0.165	0.18	0.08	0.24	0.26	0.14	0.315	0.35	0.20	0.40	0.42	0.35
615	0.095	0.085	0.065	0.165	0.185	0.085	0.245	0.265	0.15	0.32	0.355	0.205	0.425	0.435	0.36
625	0.095	0.085	0.070	0.170	0.19	0.09	0.25	0.28	0.16	0.33	0.36	0.21	0.43	0.44	0.365
650	0.045	0.03	0.010	0.05	0.06	0.04	0.075	0.09	0.06	0.10	0.110	0.07	0.12	0.11	0.10
675	0.02	0.01	0.03	0.015	0.015	0.02	0.02	0.01	0.02	0.02	0.03	0.02	0.03	0.03	0.03

O.D. of set No.5a(iv) at 615 is 0.06.



⊙ Fe_2O_3 sol. Mal. green.
● " Methylene. blue.
Δ " Methyl Orange
▽ " Aliz. S. acid.
→ CONC. OF BOUND DYE × 10^{-6}M
4
3.6
1.5 3 3
2
1.0 2 2
1
0.5 1 1
0 0 0 0
0 1 2 3 4 5 6 7 8 9 10 11 12 13
3 4 5 6 7 8 9 10 11 12 13 14 15 16
0 1 2 3 4 5 6
4 6 8 10 12 14 16 18 20 22 24
→ INITIAL CONC. OF DYE (× 10^{-6} M)
1
2
3
4

FIG-39.



○ = Al_2O_3 sol. and aliz. s. acid.
● = Al_2O_3 sol. " Methyl Orange.
→ CONC. OF BOUND DYE
→ × 10^{-4}M
→ × 10^{-5}M
6
0.05 5
0.04 4
0.03 3
0.02 2
0.01 1
0 1 2 3 4 5 6 7 8 9 10 11
0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22 0.24 → × 10^{-4} M
→ INITIAL CONC. OF DYE
1
2

FIG- 40.

TABLE No.15

Alumina sol and alizarin sulphonic acid:

Absorption spectra of 1.5×10^{-4} M alizarin sulphonic acid in presence of sol, buffer and water.

Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye
330	0.085	0.065	0.17	0.135	0.11	0.20	0.175	0.145	0.27	0.225	0.18	0.31	0.27	0.20	0.37
350	0.060	0.060	0.12	0.085	0.08	0.145	0.105	0.125	0.19	0.14	0.17	0.235	0.165	0.185	0.29
375	0.045	0.060	0.08	0.065	0.080	0.11	0.08	0.135	0.15	0.10	0.19	0.20	0.12	0.215	0.24
400	0.05	0.075	0.07	0.075	0.105	0.11	0.09	0.18	0.16	0.125	0.25	0.215	0.155	0.29	0.285
425	0.06	0.08	0.06	0.11	0.135	0.11	0.15	0.20	0.165	0.20	0.26	0.225	0.25	0.30	0.29
450	0.085	0.065	0.06	0.16	0.130	0.11	0.23	0.165	0.155	0.32	0.19	0.18	0.38	0.225	0.225
475	0.10	0.045	0.07	0.20	0.120	0.105	0.29	0.115	0.14	0.39	0.10	0.14	0.47	0.115	0.17
500	0.095	0.03	0.06	0.19	0.10	0.095	0.285	0.075	0.13	0.375	0.05	0.125	0.45	0.07	0.15
525	0.07	0.025	0.07	0.135	0.07	0.09	0.20	0.05	0.12	0.275	0.03	0.11	0.34	0.03	0.135
550	0.035	0.015	0.055	0.07	0.045	0.065	0.105	0.03	0.08	0.15	0.02	0.09	0.18	0.02	0.11
575	0.01	0.015	0.04	0.025	0.04	0.04	0.035	0.02	0.05	0.05	0.015	0.06	0.06	0.01	0.07
600	0.005	0.01	0.025	0.005	0.03	0.02	0.01	0.020	0.03	0.015	0.015	0.035	0.015	0.01	0.04
625	0.005	0.01	0.015	0.005	0.03	0.015	0.005	0.015	0.015	0.005	0.01	0.015	0.005	0.01	0.02

O.D. of set No.5a(i) at the maxima of sets 5b(i), 5b(ii), 5b(iii), 5b(iv) and 5b(v) [sol + dye] is 0.055.

TABLE No.16

Alumina sol and methyl orange:

Absorption spectra of 0.0451×10^{-3} M methyl orange in presence of sol, buffer and water.

Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye
330	0.08	0.02	0.08	0.095	0.045	0.105	0.115	0.08	0.13	0.135	0.095	0.15	0.15	0.115	0.16
350	0.075	0.015	0.07	0.09	0.05	0.105	0.115	0.075	0.135	0.135	0.095	0.16	0.16	0.12	0.18
375	0.08	0.025	0.085	0.115	0.075	0.135	0.15	0.125	0.19	0.21	0.155	0.24	0.28	0.195	0.29
400	0.09	0.055	0.10	0.15	0.12	0.19	0.215	0.195	0.27	0.29	0.25	0.34	0.36	0.31	0.42
425	0.105	0.08	0.115	0.19	0.172	0.225	0.28	0.27	0.33	0.35	0.34	0.42	0.42	0.42	0.52
450	0.115	0.095	0.13	0.23	0.225	0.255	0.335	0.33	0.375	0.42	0.44	0.48	0.50	0.54	0.58
475	0.12	0.115	0.115	0.25	0.26	0.230	0.37	0.38	0.35	0.46	0.50	0.45	0.56	0.61	0.56
500	0.11	0.10	0.07	0.22	0.225	0.15	0.32	0.34	0.22	0.40	0.44	0.285	0.47	0.55	0.35
525	0.07	0.065	0.03	0.15	0.15	0.06	0.22	0.23	0.085	0.27	0.305	0.11	0.32	0.37	0.14
550	0.03	0.025	0.01	0.065	0.07	0.02	0.10	0.10	0.02	0.115	0.135	0.03	0.135	0.16	0.035
575	0.015	0.010	0.01	0.015	0.010	0.015	0.02	0.025	0.01	0.02	0.03	0.01	0.025	0.03	0.01
600	0.010	0.015	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.005	0.015	0.01	0.005	0.01	0.01
625	0.010	0.015	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.005	0.015	0.01	0.005	0.01	0.01

O.D. of set No.5a(ii) at the maxima of sets 5b(i), 5b(ii), 5b(iii), 5b(iv) and 5b(v) [sol+dye] is 0.075.

TABLE No.17

Alumina sol and methylene blue:

Absorption spectra of 0.0314×10^{-3} M methylene blue in presence of sol, buffer and water.

Wave-length in mμ	Set No. 5b(i)			Set No. 5b(ii)			Set No. 5b(iii)			Set No. 5b(iv)			Set No. 5b(v)		
	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye
325	0.065	0.025	0.08	0.075	0.025	0.085	0.09	0.035	0.09	0.10	0.05	0.095	0.11	0.060	0.10
330	0.060	-	0.075	0.075	0.02	0.08	0.085	0.040	0.08	0.095	0.04	0.085	0.10	0.040	0.095
350	0.05	0.01	0.05	0.055	0.02	0.06	0.06	0.045	0.06	0.065	0.02	0.055	0.065	0.02	0.06
375	0.04	-	0.04	0.045	-	0.045	0.05	-	0.045	0.05	0.01	0.04	0.05	-	0.045
400	0.035	-	0.03	0.035	-	0.035	0.04	-	0.045	0.045	-	0.03	0.04	-	0.035
425	0.025	-	0.02	0.03	-	0.025	0.03	-	0.025	0.03	-	0.02	0.03	-	0.035
450	0.025	-	0.015	0.025	-	0.020	0.03	-	0.02	0.03	-	0.02	0.035	-	0.020
475	0.025	-	0.01	0.03	-	0.020	0.035	-	0.02	0.04	-	0.025	0.04	-	0.03
500	0.02	-	0.01	0.025	-	0.020	0.035	-	0.02	0.04	-	0.025	0.045	-	0.03
525	0.015	-	0.015	0.03	-	0.025	0.040	-	0.025	0.045	-	0.03	0.05	-	0.035
550	0.025	-	0.02	0.04	-	0.04	0.055	-	0.04	0.07	-	0.055	0.085	-	0.07
575	0.04	-	0.045	0.07	-	0.07	0.11	-	0.080	0.145	-	0.12	0.17	-	0.15
600	0.07	0.07	0.075	0.145	0.125	0.12	0.215	0.22	0.17	0.29	0.285	0.24	0.33	0.38	0.30
625	0.095	0.095	0.110	0.20	0.18	0.16	0.30	0.31	0.24	0.39	0.39	0.34	0.46	0.49	0.41
650	0.165	0.15	0.15	0.32	0.285	0.22	0.47	0.46	0.35	0.60	0.58	0.50	0.70	0.71	0.62
675	0.10	0.09	0.10	0.21	0.175	0.14	0.30	0.28	0.23	0.38	0.38	0.32	0.47	0.43	0.37
700	0.02	0.01	0.02	0.03	0.02	0.025	0.04	0.035	0.03	0.05	0.045	0.05	0.06	0.055	0.05
725	0.01	-	0.01	0.01	-	0.005	0.01	-	0.01	0.01	-	0.01	0.01	-	0.01

O.D. of set No.5a(iii) at the maxima of sets 5b(i), 5b(ii), 5b(iii), 5b(iv) and 5b(v) = 0.10. (sol + dye)

TABLE No.18

Alumina sol and malachite green:

Absorption spectra of 0.0196x10^{-3} M malachite green in presence of sol, buffer and water

Wave-length in mμ	Set No.5b(i)			Set No.5b(ii)			Set No.5b(iii)			Set No.5b(iv)			Set No.5b(v)		
	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol+ dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water + dye	O.D. sol + dye	O.D. buffer + dye	O.D. water ++ dye
325	0.065	0.02	-	0.07	0.03	-	0.08	0.03	-	0.085	0.04	-	0.095	-	-
330	0.065	0.010	0.07	0.07	0.01	0.08	0.075	-	0.085	0.08	0.02	0.08	0.09	-	-
350	0.05	0.015	0.06	0.065	0.02	0.07	0.06	0.02	0.07	0.065	0.03	0.07	0.075	-	0.090
375	0.045	0.015	0.045	0.055	0.025	0.055	0.06	0.03	0.06	0.07	0.035	0.065	0.08	-	0.08
400	0.045	0.025	0.04	0.06	0.035	0.05	0.08	0.05	0.055	0.095	0.06	0.07	0.105	0.075	0.095
425	0.045	0.022	0.035	0.060	0.04	0.04	0.085	0.06	0.05	0.10	0.07	0.065	0.115	0.09	0.10
430	0.04	0.02	-	0.06	0.035	-	0.07	0.05	-	0.09	0.065	-	0.10	0.085	-
435	0.045	0.02	-	0.05	-	-	0.065	-	-	0.075	-	-	0.085	-	-
440	0.03	-	-	0.045	-	-	0.060	-	-	0.065	-	-	0.07	-	-
450	0.025	0.01	0.02	0.03	0.015	0.02	0.03	0.02	0.025	0.05	0.03	0.025	0.05	0.03	0.04
475	0.02	0.005	0.015	0.02	0.01	0.015	0.025	0.01	0.015	0.03	0.015	0.015	0.03	0.02	0.025
500	0.015	0.01	0.01	0.025	0.02	0.015	0.03	0.02	0.01	0.035	0.025	0.02	0.04	0.03	0.03
525	0.02	0.015	0.015	0.03	0.025	0.010	0.045	0.035	0.025	0.055	0.045	0.03	0.065	0.055	0.05
550	0.03	0.025	0.025	0.055	0.05	0.03	0.085	0.075	0.045	0.11	0.09	0.06	0.13	0.115	0.11
575	0.055	0.045	0.040	0.105	0.09	0.05	0.155	0.14	0.085	0.20	0.175	0.11	0.24	0.215	0.21
600	0.085	0.07	0.065	0.17	0.16	0.08	0.26	0.24	0.14	0.335	0.315	0.20	0.40	0.37	0.35
610	0.10	-	-	0.2	-	-	0.30	-	-	0.39	-	-	0.47	0.42	-
615	0.10	0.085	-	0.205	0.185	-	0.302	0.285	-	0.395	0.370	-	0.475	0.425	-
620	0.095	-	-	0.195	0.180	-	0.29	0.27	-	0.375	0.360	-	0.46	-	-
625	0.09	0.078	0.070	0.175	0.17	0.09	0.265	0.25	0.16	0.35	0.32	0.21	0.42	0.365	0.365
650	0.035	0.02	0.010	0.06	0.05	0.04	0.08	0.06	0.06	0.12	0.09	0.07	0.14	0.10	0.10
675	0.015	0.005	0.03	0.02	0.01	0.02	0.02	0.015	0.02	0.045	0.018	0.02	0.035	0.02	0.03
700	0.01	-	0.01	0.01	-	0.01	0.01	-	0.01	0.01	-	0.01	0.015	-	-

O.D. of set No.5a(iv) at the maxima of sets 5b(i), 5b(ii), 5b(iii), 5b(iv), 5b(v) [sol + dye] is 0.075 (615 mμ) and 0.045 at 425 mμ.

DISCUSSION

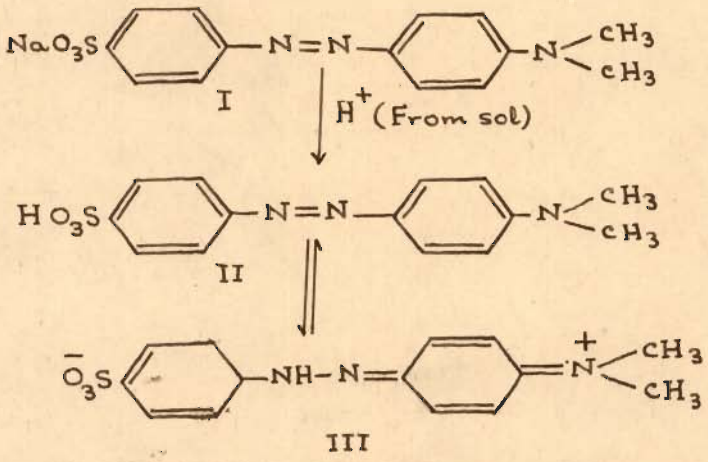
Ferric oxide sol:

The results on the variations in pH, ζ-potential, viscosity and conductivity of ferric oxide sol on the addition of acid and basic dyes differ from those in the case of arsenic sulphide. For example, a decrease in ζ-potential is observed in the case of ferric oxide sol irrespective of the dye used (in the case of arsenic sulphide these variations were dependent on the dye used).

Methyl orange and alizarin sulphonic acid being anion active dyes would easily bring about a decrease in ζ-potential of the positively charged ferric oxide. Besides the adsorption of the acid dye by the hydrous oxide sol would be quite large, a simultaneous release of H^+ ion from the inner part of the double layer is expected to take place. A decrease in pH is, therefore observed in both cases. There is, however, a subtle difference in the behaviour of the two dyes towards these changes. With methyl orange the pH falls down abruptly and then becomes constant while in the case of alizarin sulphonic acid a continuous decrease in pH is observed over a larger concentration range of the dye. As for ζ-potential, the variations are quite small with methyl orange in comparison to alizarin sulphonic acid (table no.1,2, column 5) where a large decrease in ζ-potential is observed. This difference may be explained by taking into consideration two phenomenon, viz., the taking up of the released H^+ by the dyes and the interaction between the hydrous oxide and the dyes.

Addition of methyl orange brings about the following change in the structure of the dye by using the H^+ released from the sol resulting in a constancy in pH (compare with pH variations with buffer):

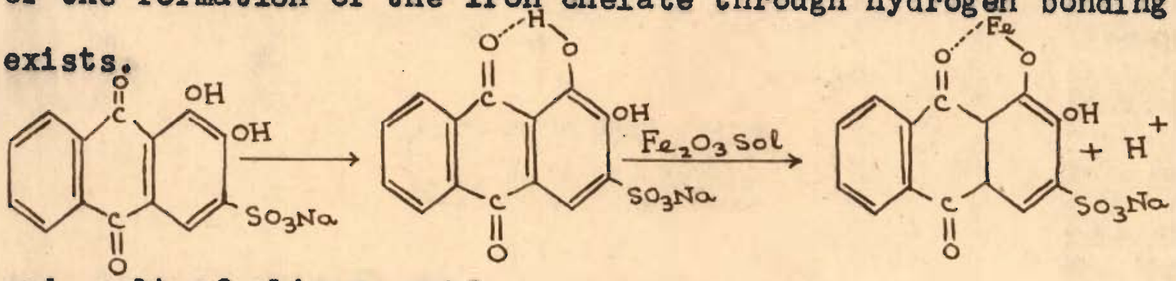
methyl orange:



Such structural changes cannot be visualized in the case of alizarin sulphonic acid with the result that the hydrogen ions released remain unused and the pH continuously decreases (table no. 2 column 2). It is only when sufficient amount of the dye has been added that the pH becomes constant due to the adsorption of H^+ by the coagulum.

The variations in ζ-potential in the case of methyl orange are of the same order as are expected during the coagulation of the sol. The abnormal variations in the case of alizarin sulphonic acid may be attributed to the strong adsorption of the alizarin sulphonic acid dye by ferric hydroxide sol (either through exchange or direct adsorption) resulting in the formation of alizarin lakes.

A similar difference exists with regard to viscosity variations. The variation in viscosity in the case of methyl orange are the same as are expected during coagulation of the sol but an abrupt increase in viscosity is observed on the addition of the alizarin sulphonic acid. It appears that the adsorbed alizarate ions either bring about enhanced hydration of the sol particles or bigger aggregates, contributing to enhanced viscosity, are formed by chemical interaction between the sol particles and the dye. The possibility of the formation of the iron chelate through hydrogen bonding exists.



sod. salt of aliz.s. acid

The variations in conductivity are of the same type in the two cases. With alizarin sulphonic acid where tendency for hydration and subsequent gelation exists the variations in conductivity are very little (table no. 2 , column 4).

The contention that factors other than charge neutralization are operative in the case of the coagulation of sols by dyes is again borne out from the results on the interaction of basic dyes with ferric oxide sol. Normally the cation of the added dye should bring about little variation (or a slight increase) in the ζ-potential of the positively charged ferric oxide sol but the results show that there is a continuous decrease in ζ-potential and only when sufficient amount of the dye has been added that a constancy is observed. It is apparent that both the dyes are strongly adsorbed by the ferric oxide sol.

There is an initial decrease in pH in both cases (although it is much larger in the case of malachite green, pointing towards its greater adsorption) followed by a constancy. Structural changes in the two dyes by taking up the released hydrogen ions as described under arsenic sulphide (page 64,65, chapter I) are likely to take place here also. Adsorption of the dye by the sol particle would result in the formation of bigger aggregates thereby contributing to higher viscosity. Addition of malachite green to ferric oxide brings about coagulation of the sol whereas in the case of methylene blue the sol remains in the suspended state for long. The difference in the mode of viscosity variations in the two cases may be attributed to this behaviour. Similarly the conductivity variations with malachite green, where actual coagulation takes place, are quite appreciable in comparison to methylene blue where very little change in conductivity is observed.

Spectrophotometric evidence:

Shifts in maxima from 425 mμ to 500 mμ and from 450 mμ to 475 mμ take place in the case of alizarin sulphonic acid and methyl orange respectively on mixing these dyes with ferric oxide sol. On the other hand in the case of the basic dyes no shifts in the maxima are observed but the O.D. values are appreciably lowered. From these observations sufficient proof of the binding of the dye by the sol particles accompanied by structural changes in some cases (where shift in maxima is observed) is obtained.

Quantitative data on the extent of binding is obtained by applying Klotz's equation are summarized below:

TABLE No. 19

Ferric oxide sol and alizarin sulphonic acid

Data for the binding of alizarin sulphonic acid with ferric oxide sol:

$\epsilon_F = 3733$, $\epsilon_B = 10000$

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
0.75×10^{-5} M	8666	0.21	0.15×10^{-5} M	0.60×10^{-5} M
1.50×10^{-5} M	9000	0.15	0.22×10^{-5} M	1.28×10^{-5} M
3.0×10^{-5} M	6166	0.61	1.83×10^{-5} M	1.17×10^{-5} M

Fig.(39) curve (4)

TABLE No. 20

Ferric oxide sol and methyl orange

Data for the binding of methyl orange with ferric oxide sol:

$\epsilon_F = 24434$, $\epsilon_B = 11111$

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
4.51×10^{-6} M	18847	0.58	2.61×10^{-6} M	1.90×10^{-6} M
9.02×10^{-6} M	21618	0.70	6.31×10^{-6} M	2.71×10^{-6} M
13.53×10^{-6} M	23281	0.91	11.31×10^{-6} M	2.22×10^{-6} M
18.04×10^{-6} M	25232	1.0	-	-
22.55×10^{-6} M	23725	0.94	21.19×10^{-6} M	1.36×10^{-6} M

Fig.(39) curve (3.)

TABLE No. 21

Ferric oxide sol and methylene blue

Data for the binding of methylene blue with ferric oxide sol:

$\epsilon_F = 47770$, $\epsilon_B = 31847$

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
3.14×10^{-6} M	47770	1.0	3.14×10^{-6} M	0
6.28×10^{-6} M	41401	0.60	3.76×10^{-6} M	2.52×10^{-6} M
9.42×10^{-6} M	44585	0.79	7.44×10^{-6} M	1.98×10^{-6} M
12.56×10^{-6} M	46178	0.90	11.3×10^{-6} M	1.26×10^{-6} M
15.70×10^{-6} M	46496	0.91	14.28×10^{-6} M	1.42×10^{-6} M

Fig.(39) curve (2)

TABLE No. 22

Ferric oxide sol and malachite green

Data for the binding of malachite green with ferric oxide sol:

$\epsilon_F = 45918$, $\epsilon_B = 30612$

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
1.96×10^{-6} M	38265	0.50	0.98×10^{-6} M	0.98×10^{-6} M
3.92×10^{-6} M	38265	0.50	1.96×10^{-6} M	1.96×10^{-6} M
5.88×10^{-6} M	39115	0.55	3.23×10^{-6} M	2.65×10^{-6} M
7.84×10^{-6} M	39540	0.58	4.54×10^{-6} M	3.30×10^{-6} M
9.80×10^{-6} M	41836	0.73	7.15×10^{-6} M	2.65×10^{-6} M

Fig. (39) curve (1)

From the above data the moles of ferric oxide bound per dye can be calculated. The results are as follows:

TABLE No. 23

Data for moles of ferric oxide bound per mole of the dye

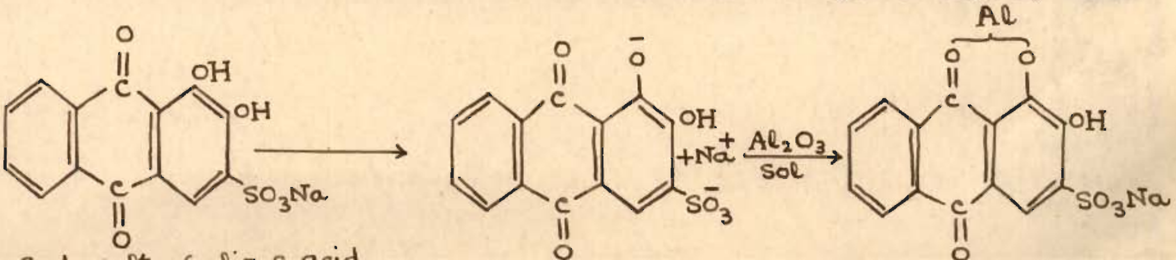
Dyes	conc. of bound dye	moles of ferric oxide bound per mole of the dye
Alizarin sulphonic acid	1.28×10^{-5} M	7.3
	1.17×10^{-5} M	6.8
Methyl orange	1.90×10^{-6} M	47.5
	2.71×10^{-6} M	33.3
	2.22×10^{-6} M	40.7
Methylene blue	1.98×10^{-6} M	45.50
	1.26×10^{-6} M	71.20
	1.42×10^{-6} M	63.20
Malachite green	1.96×10^{-6} M	45.90
	2.65×10^{-6} M	34.07
	3.30×10^{-6} M	27.37
	2.65×10^{-6} M	34.07

Assuming that one dye molecule is bound to one sol particle, an approximate idea of the size range of the ferric oxide ionic micelles can be had from the above data. The range comes out to be 7 moles, 40.5 moles, 59.9 moles and 47.1 moles of Fe_2O_3 per ionic micelle of alizarin sulphonic acid, methyl orange, methylene blue and malachite green respectively.

The plots between the initial concentration of the dye (fig.39 curves1,2,3,4.) and the bound dye do not give straight lines as in the case of proteins (obtained by Klotz). From these the order of binding of the four dyes for the ferric oxide sol comes out to be alizarin sulphonic acid (1.28×10^{-5} M/mole) > malachite green (3.3×10^{-6} M dye/mole) > methyl orange (2.7×10^{-6} M dye/mole) > methylene blue (2.5×10^{-6} M dye/mole). It is thus evident that the adsorption of alizarin sulphonic acid is much higher than the other three dyes (tables 19, 20, 21, 22, Fig.39). Although rest of the dyes got equally adsorbed, malachite green is adsorbed more than either the methylene blue or methyl orange.

Alumina sol:

Unlike ferric oxide or arsenic sulphide sols marked variations in pH, viscosity and conductivity are observed only in the case of alizarin sulphonic acid. With methyl orange only the viscosity variations are worth considering otherwise those in pH and conductance are almost negligible. Basic dyes, viz., malachite green and methylene blue do not influence the various physical properties and even the variations in viscosity are too small to be considered. From these results it may be concluded that of the four alizarin sulphonic acid is appreciably bound to the alumina sol. The variation in viscosity and pH are of the same type as with ferric oxide sol and the same explanation based on the interaction of the alumina with the sulphonic acid dye resulting in the formation of alizarin lakes may also be given here.



The variations in viscosity (table no.6) in the case of methyl orange also provide evidence for the formation of bigger aggregates by the interaction of the dye with alumina. As for the basic dyes they appear only to stabilize the alumina sol.

Spectrophotometric evidence:

Shift in maxima from 425 mμ to 475 mμ takes place only in the case of alizarin sulphonic acid, a similar shift from 425 to 475 mμ is observed (same shift from buffer also) on adding methyl orange (compare ferric oxide sol) to alumina sol but a marked decrease in O.D. value is observed. With malachite green and methylene blue neither a shift in maxima nor a decrease in O.D. takes place thereby indicating the inertness of alumina towards the two dyes.

Quantitative data on the extent of binding is obtained by applying Klotz's equation are summarized below:

TABLE No. 24

Alumina sol and alizarin sulphonic acid

Data for the binding of alizarin sulphonic acid with alumina sol:

$\epsilon_F = 3733$, $\epsilon_B = 7333$

conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
1.5×10^{-5}M	6666	0.185	0.2775×10^{-5}M	1.2225×10^{-5}M
3.0×10^{-5}M	6666	0.185	0.5555×10^{-5}M	2.4450×10^{-5}M
4.5×10^{-5}M	6444	0.246	1.1070×10^{-5}M	3.393×10^{-5}M
6.0×10^{-5}M	6500	0.231	1.386×10^{-5}M	4.614×10^{-5}M
7.5×10^{-5}M	6266	0.296	2.220×10^{-5}M	5.280×10^{-5}M

Fig. (40) curve (1)

TABLE No. 25

Alumina sol and methyl orange

Data for the binding of methyl orange with alumina sol:

$\epsilon_F = 24390$, $\epsilon_B = 33333$

Initial conc. of dye	ϵ_{app}	α	conc. of free dye	conc. of bound dye
0.0451×10^{-4} M	26607	0.75	0.033×10^{-4} M	0.012×10^{-4} M
0.0902×10^{-4} M	27716	0.62	0.055×10^{-4} M	0.035×10^{-4} M
0.1353×10^{-4} M	27346	0.66	0.089×10^{-4} M	0.046×10^{-4} M
0.1804×10^{-4} M	25488	0.87	0.156×10^{-4} M	0.024×10^{-4} M
0.2255×10^{-4} M	24833	0.95	0.2142×10^{-4} M	0.011×10^{-4} M

Fig. (40) curve (2)

From the above data the moles of alumina bound per dye can be calculated. The results are as follows:

TABLE No. 26

Data for moles of alumina bound per mole of dye

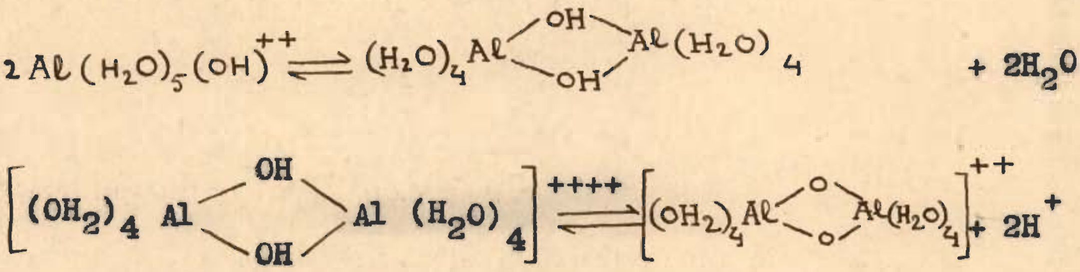
Dyes	conc. of bound dye	moles of alumina bound per mole of dye
Alizarin sulphonic acid	3.393×10^{-5} M	1070.56
	4.614×10^{-5} M	789.26
	5.280×10^{-5} M	686.93
Methyl orange	0.035×10^{-4} M	11416.63
	0.046×10^{-4} M	8686.53
	0.024×10^{-4} M	16648.67

Quantitative data on binding obtained by applying Klotz's equation give average values of number of moles of alumina bound per dye mole as 849 and 12251 with alizarin sulphonic acid and methyl orange respectively. These results indicate two facts:

(i) The alumina ionic micelles are much bigger than the ferric oxide micelles and (ii) the alizarin sulphonic acid dye is much more strongly adsorbed than methyl orange (table no. 24 fig. 40). From the plots between the initial concentration of the dye and the bound dye; the order of binding comes out to be 0.70 (alizarin sulphonic acid) and 0.33 (methyl orange) which indicates that binding in the case of alizarin sulphonic acid > methyl orange (figs 40.).

It is observed that although the bound alizarin sulphonic acid is higher for ferric oxide sol than alumina sol, the alizarin sulphonic acid-alumina mixture is more viscous than the corresponding ferric oxide mixture. The larger variations in the case of alumina may be attributed to the existence of polymeric ol and oxo compounds in the sol. These will be formed with the gradual loss of proton according to the following scheme:

$$Al\,(H_2O)_6^{+++} \rightleftharpoons Al(H_2O)_5(OH)^{++} + H^+$$



A comparison of the pH variations with ferric oxide would reveal that the decrease in pH with the addition of alizarin sulphonic acid is much greater in the case of alumina than ferric oxide. In the latter only ol complexes are formed which show much less tendency for polymerisation in comparison to the ox complexes.

ADSORPTION OF DYES BY ALUMINA, FERRIC OXIDE AND SILICA GELS

References on the adsorption of dyes by the hydrous oxides or on the formation of colour lakes by the dyes of the alizarin class are usually met with in the chemical literature. Mokuskin and Esin, White, Gorden and Porter studied the association of several dyes (1-chapter II) by the dydrous oxides of iron, chromium and aluminium. Giles, Ealson and Mckay (2) studied the mechanism of adsorption of cationic dyes by alumina. In this study a range of cationic dyes was applied to alkaline chromatographic alumina powder and nature of adsorption was interpreted from the shape of the adsorption isotherms. Gyani (3) studied the adsorption of night blue, methylene blue and crystal violet by the silica gel with the help of colorimetric techniques and found that 80% of the initial dye concentration got adsorbed on the silica gel. According to him the extent of adsorption of dyes on silica gel was more closely related to their chemical nature than to their molecular size or molecular weight. For example tertiary basic N groups in dye mols favoured strong adsorption. Tewari (4) studied the adsorption of dyes on hydrated aluminium oxide for establishing the amphoteric nature. Rup Dutta (5) studied the adsorption of congo red and fuchsine base by hydrous beryllium oxide aged for different periods.

This chapter deals with the results on the adsorption of malachite green, methylene blue, alizarin sulphonic acid and methyl orange by silicic acid, ferric oxide and alumina gels. These investigations were particularly undertaken in order to find support to our studies on the interaction of dyes with these sols described in chapters I and II. It will be interesting to add that no authentic data on the adsorption isotherms of these systems are available in the literature.

EXPERIMENTAL

1. Reagents:

Stock solutions of $1.5x10^{-4}$M concentration of alizarin sulphonic acid (sod. salt), $4.51x10^{-5}$M concentration of methyl orange (sod. salt), $3.14x10^{-5}$M concentration of methylene blue and $1.96x10^{-5}$M malachite green were prepared in double distilled water.

2. Apparatus and technique:

Bausch and Lomb 'Spectronic 20' colorimeter was used for adsorption measurements.

3. Procedure:

The three sols of silicic acid, $Al(OH)_3$ and $Fe(OH)_3$ were prepared by the method given in chapters IV and II respectively. The gels were prepared by the dialysis of above sols. In the case of silicic acid, the gel was dried (6) for four hours at 110°C. The gels of Al_2O_3 and Fe_2O_3 were dried at a temperature between 70° to 90°C. Their particle size was adjusted with the help of a sieve (B.S. 100 passing).

Sat. 4.(a) Silicic acid gel:

(i) 100 mg. of silica gel + varying amount of dye (6 c.c., 7 c.c., 8 c.c., 9 c.c., 10 c.c. of $1.5x10^{-4}$M alizarin sulphonic acid), total volume made upto 10 c.c. by the addition of double distilled water.

(ii) 100 mg. of silica gel + varying amounts of dye (1, 2, 3, 4, 5, c.cs. of $4.51x10^{-5}$M methyl orange), total volume made upto 10 c.c. by the addition of double distilled water.

(iii) 100 mg. of silica gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of $1.96x10^{-5}$M malachite green), total volume made upto 10 c.c. by the addition of double distilled water.

(iv) 100 mg.of silica gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 3.14×10^{-5} M methylene blue), total volume made up-to 10 c.c. by double distilled water.

(b) <u>Ferric Oxide gel</u>:

(i) 50 mg. of ferric oxide gel + varying amount of dye (6, 7, 8, 9, 10 c.cs of 1.5×10^{-4} M alizarin sulphonic acid), total volume made upto 10 c.c. by the addition of double distilled water.

(ii) 50 mg. of ferric oxide gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 4.51×10^{-5} M methyl orange), total volume made upto 10 c.c. by the addition of double distilled water.

(iii) 50 mg. of ferric oxide gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 3.14×10^{-5} M methylene blue), total volume made upto 10 c.c. by the addition of double distilled water.

(iv) 50 mg. of ferric oxide gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 1.96×10^{-5} M malachite green, total volume made upto 10 c.c. by the addition of double distilled water.

(c) <u>Alumina gel</u>:

(i) 100 mg. of alumina gel + varying amount of dye (6, 7, 8, 9, 10 c.cs of 1.5×10^{-4} M alizarin sulphonic acid), total volume was made upto 10 c.c. by the addition of double distilled water.

(ii) 100 mg. of alumina gel + varying amount of dye

(1, 2, 3, 4, 5 c.cs of 4.51×10^{-5}M methyl orange), total volume was made upto 10 c.c. by the addition of double distilled water.

(iii) 100 mg. of alumina gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 3.14×10^{-5}M methylene blue), total volume was made upto 10 c.c. by the addition of double distilled water.

(iv) 100 mg. of alumina gel + varying amount of dye (1, 2, 3, 4, 5 c.cs of 1.96×10^{-5}M malachite green), total volume was made upto 10 c.c. by the addition of double distilled water.

The gels after drying were presoaked in small quantity of double distilled water prior to the addition of dye solution.

Adsorption isotherms were run by making successive additions of dye stock solutions (given above). The adsorbents and dye solutions were agitated to equilibriate after each addition of dye prior to colorimetric measurements of dye solute. Total equilibrium solutions were 10 c.c. in volume. The readings were taken after sufficient time of mixing till it attains equilibrium. The concentration of the dye solute in the equilibrium solutions was measured colorimetrically. The equilibrium solutions were centrifuged in preparation for transmittance measurements. From the difference in optical density (O.D.) values the concentrations of the dye adsorbed could be determined.

TABLE No.1

O.D. of the dyes at different wavelength:

Wavelength mμ	Absorption for 4.51×10^{-5}M methyl orange	Wavelength mμ	Absorption for 1.5×10^{-4}M alizarin sulphonic acid
340	0.16	340	0.31
350	0.225	350	0.31
375	0.47	375	0.36
400	0.77	400	0.47
425	1.0	425	0.49
450	1.4	430	0.47
475	1.2	435	0.44
500	0.68	450	0.335
525	0.26	475	0.16
550	0.05	500	0.06
575	0.005	525	0.035

TABLE No.2

O.D. of methylene blue and malachite green at different wavelengths.

Wavelength mμ	Absorption for 3.14×10^{-5}M methylene blue	Wavelength mμ	Absorption for 1.96×10^{-5}M malachite green
340	0.06	340	0.03
350	0.045	350	0.03
375	0.025	375	0.07
400	0.02	400	0.17
425	0.015	425	0.20
450	0.035	450	0.055
475	0.07	475	0.02
500	0.09	500	0.05
525	0.130	525	0.11
550	0.28	550	0.28
575	0.57	575	0.52
600	1.3	600	0.86
625	1.6	625	0.88
650	1.9	650	0.255
675	0.87	675	0.045
700	0.155	700	0.01
725	0.03	725	-
750	0.01	750	-

TABLE No.3

Adsorption of alizarin sulphonic acid by silica gel:

O.D. of gel-dye and water-dye mixture at different wavelengths

Average surface area by sieve analysis = 945 Sq. cm. per gm.

Wave-length in mμ	Set No.4a(i)6		Set No. 4a(i)7		Set No.4a(i)8		Set No.4a(i)9		Set No.4a(i)10	
	O.D. gel+dye mixture	O.D. water + dye mixture	O.D. gel + dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+ dye mixture	O.D. gel+dye mixture	O.D. water+ dye mixture	O.D. gel+ dye mixture	O.D. water + dye mixture
340	0.52	0.205	0.58	0.23	0.66	0.26	0.72	0.285	0.80	0.30
350	0.39	0.19	0.44	0.22	0.50	0.245	0.54	0.27	0.60	0.29
375	0.20	0.20	0.22	0.245	0.25	0.28	0.27	0.31	0.29	0.345
400	0.145	0.27	0.16	0.32	0.18	0.37	0.20	0.405	0.21	0.46
425	0.185	0.28	0.21	0.33	0.24	0.38	0.26	0.42	0.28	0.47
450	0.28	0.195	0.32	0.23	0.36	0.265	0.40	0.29	0.435	0.325
475	0.39	0.105	0.44	0.11	0.50	0.125	0.56	0.14	0.61	0.14
500	0.47	0.06	0.54	0.055	0.62	0.055	0.70	0.06	0.75	0.045
525	0.49	0.045	0.56	0.04	0.66	0.035	0.75	0.04	0.80	0.02
550	0.44	0.035	0.50	0.03	0.59	0.025	0.67	0.025	0.73	0.01
575	0.32	0.025	0.36	0.02	0.42	0.015	0.49	0.015	0.53	0.01
600	0.195	0.015	0.225	0.01	0.265	0.01	0.31	0.01	0.335	0.005
625	0.065	-	0.07	-	0.08	-	0.095	-	0.10	-

TABLE No.4

Adsorption of methyl orange by silica gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths

Wave-length in mμ	Set No.4a(ii)1		Set No.4a(ii)2		Set No.4a(ii)3		Set No.4a(ii)4		Set No.4a(ii)5	
	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture
340	0.085	0.015	0.095	0.03	0.12	0.045	0.13	0.06	0.16	0.08
350	0.09	0.02	0.1	0.04	0.135	0.06	0.16	0.085	0.185	0.11
375	0.11	0.04	0.145	0.085	0.20	0.135	0.25	0.18	0.30	0.23
400	0.12	0.07	0.20	0.15	0.28	0.225	0.355	0.31	0.44	0.38
425	0.140	0.09	0.24	0.19	0.345	0.30	0.44	0.39	0.55	0.49
450	0.155	0.105	0.27	0.225	0.39	0.35	0.51	0.46	0.62	0.57
475	0.14	0.10	0.25	0.215	0.37	0.325	0.47	0.43	0.58	0.54
500	0.095	0.06	0.165	0.13	0.23	0.20	0.305	0.27	0.38	0.34
525	0.045	0.02	0.07	0.045	0.095	0.07	0.125	0.095	0.155	0.12
550	-	-	-	-	0.035	0.01	0.04	0.015	0.045	0.02

TABLE No:5

Adsorption of malachite green by silica gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths

Wave-length in mμ	Set No.4a(iii)1		Set No.4a(iii)2		Set No.4a(iii)3		Set No.4a(iii)4		Set No.4a(iii)5	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
575	0.02	0.02	0.045	0.04	0.035	0.055	0.03	0.09	0.045	0.12
600	0.02	0.04	0.04	0.06	0.035	0.10	0.03	0.165	0.045	0.23
625	0.02	0.04	0.04	0.065	0.030	0.11	0.025	0.18	0.040	0.24
650	0.01	0.02	0.03	0.020	0.02	0.025	0.020	0.045	0.03	0.06
675	0.01	-	0.025	-	0.015	-	0.015	0.005	0.025	0.01
700	0.005	-	0.020	-	0.015	-	0.015	-	0.025	-

TABLE No.6

Adsorption of methylene blue by silica gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths

Wave-length in mμ	Set No.4a(iv)1		Set No.4a(iv)2		Set No.4a(iv)3		Set No.4a(iv)4		Set No.4a(iv)5	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
575	0.025	0.025	0.04	0.07	0.07	0.12	0.075	0.19	0.065	0.245
600	0.025	0.06	0.045	0.16	0.075	0.25	0.075	0.38	0.065	0.48
625	0.030	0.09	0.04	0.225	0.070	0.34	0.07	0.52	0.06	0.62
650	0.025	0.14	0.035	0.33	0.065	0.51	0.065	0.75	0.055	0.89
675	0.02	0.08	0.030	0.19	0.05	0.295	0.05	0.43	0.045	0.50
700	0.01	-	0.015	0.01	0.04	0.02	0.045	0.04	0.025	0.055
725	-	-	-	-	-	-	0.03	-	-	-

TABLE No.7

Adsorption of alizarin sulphonic acid on ferric oxide gel:

Average surface area of ferric oxide gel = 990 sq.cm. per gm.

O.D. of gel-dye and water-dye mixtures at different wavelengths

Wave-length in mμ	Set No.4b(i)6		Set No.4b(i)7		Set No.4b(i)8		Set No.4b(i)9		Set No.4b(i)10	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
340	0.13	0.205	0.195	0.23	0.13	0.26	0.18	0.285	0.115	0.30
350	0.125	0.19	0.195	0.22	0.13	0.245	0.18	0.27	0.105	0.29
375	0.13	0.20	0.185	0.245	0.115	0.28	0.165	0.31	0.085	0.345
400	0.11	0.27	0.165	0.32	0.105	0.37	0.155	0.405	0.08	0.46
425	0.105	0.28	0.15	0.33	0.095	0.38	0.135	0.42	0.175	0.47
450	0.09	0.195	0.13	0.23	0.085	0.265	0.12	0.29	0.085	0.325
475	0.085	0.105	0.115	0.11	0.08	0.125	0.11	0.14	0.095	0.15
500	0.08	0.06	0.110	0.055	0.075	0.055	0.115	0.06	0.10	0.045
525	0.075	0.045	0.105	0.04	0.085	0.035	0.105	0.04	0.11	0.02
550	0.07	0.035	0.10	0.03	0.075	0.025	0.10	0.025	0.095	0.01
575	0.065	0.025	0.085	0.02	0.065	0.015	0.085	0.015	0.085	0.01
600	0.055	0.015	0.075	0.01	0.055	0.01	0.07	0.01	0.06	0.005

TABLE No.8

Adsorption of methyl orange on ferric oxide gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4b(ii)1		Set No.4b(ii)2		Set No.4b(ii)3		Set No.4b(ii)4		Set No.4b(ii)5	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
340	0.10	0.015	0.16	0.03	0.105	0.045	0.09	0.06	0.06	0.08
350	0.105	0.02	0.165	0.04	0.115	0.06	0.11	0.085	0.08	0.11
375	0.12	0.04	0.185	0.085	0.145	0.135	0.16	0.18	0.125	0.23
400	0.135	0.07	0.195	0.15	0.18	0.225	0.23	0.31	0.175	0.38
425	0.140	0.09	0.200	0.19	0.20	0.205	0.28	0.39	0.215	0.49
450	0.15	0.105	0.200	0.225	0.225	0.35	0.315	0.46	0.24	0.57
475	0.145	0.10	0.195	0.215	0.21	0.325	0.30	0.43	0.225	0.54
500	0.110	0.06	0.16	0.13	0.150	0.20	0.20	0.27	0.150	0.34
525	0.08	0.02	0.12	0.045	0.09	0.07	0.09	0.095	0.07	0.12
550	0.06	0.01	0.085	0.01	0.06	0.01	0.05	0.015	0.035	0.02

TABLE No.9

Adsorption of methylene blue on ferric oxide gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4b(iii)1		Set No.4b(iii)2		Set No.4b(iii)3		Set No.4b(iii)4		Set No.4b(iii)5	
	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture
525	-	-	0.02	0.01	0.03	0.015	0.04	0.035	0.075	0.05
550	0.005	0.01	0.03	0.025	0.055	0.05	0.08	0.085	0.13	0.115
575	0.02	0.025	0.07	0.07	0.115	0.12	0.165	0.19	0.25	0.245
600	0.03	0.06	0.135	0.16	0.215	0.25	0.32	0.38	0.475	0.48
625	0.045	0.09	0.175	0.225	0.29	0.34	0.43	0.52	0.60	0.62
650	0.06	0.14	0.20	0.33	0.385	0.51	0.54	0.75	0.87	0.89
675	0.05	0.09	0.12	0.19	0.23	0.295	0.33	0.43	0.49	0.50
700	0.01	0.03	0.015	0.01	0.025	0.02	0.04	0.04	0.075	0.055

TABLE No.10

Adsorption of malachite green on ferric oxide gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4b(iv)1		Set No.4b(iv)2		Set No.4b(iv)3		Set No.4b(iv)4		Set No.4b(iv)5	
	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture
525	0.07	-	0.075	0.005	0.085	0.01	0.095	0.015	0.095	0.02
550	0.07	0.01	0.095	0.015	0.10	0.025	0.135	0.04	0.155	0.06
575	0.075	0.02	0.12	0.04	0.13	0.055	0.19	0.09	0.24	0.12
600	0.085	0.04	0.16	0.06	0.18	0.10	0.285	0.165	0.37	0.23
625	0.080	0.04	0.165	0.065	0.185	0.11	0.30	0.18	0.38	0.24
650	0.035	0.02	0.045	0.020	0.04	0.025	0.05	0.045	0.115	0.06
675	0.02	-	0.02	-	0.015	-	0.015	0.005	0.04	0.01

TABLE No.11

Adsorption of alizarin sulphonic acid on alumina gel:

Average surface area of alumina gel = 1000 sq.cm. per gm.

O.D.(absorption) of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4c(i)7		Set No.4c(i)8		Set No.4c(i)9		Set No.4c(i)10	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
340	0.10	0.23	0.13	0.26	0.15	0.285	0.18	0.30
350	0.09	0.22	0.10	0.245	0.14	0.27	0.16	0.29
375	0.15	0.245	0.06	0.28	0.16	0.31	0.19	0.345
400	0.10	0.32	0.01	0.37	0.02	0.405	0.20	0.46
425	0.005	0.33	0.025	0.38	0.03	0.42	0.03	0.47
450	0.01	0.23	0.01	0.265	0.01	0.29	0.02	0.325
475	0.01	0.11	-	0.125	0.01	0.14	0.01	0.14

TABLE No.12

Adsorption of methyl orange on alumina gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4c(ii)1		Set No.4c(ii)2		Set No.4c(ii)3		Set No.4c(ii)4		Set No.4c(ii)5	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
340	0.005	0.015	0.03	0.03	0.05	0.045	0.07	0.06	0.075	0.08
350	0.01	0.02	0.04	0.04	0.065	0.06	0.09	0.085	0.105	0.11
375	0.035	0.04	0.08	0.085	0.130	0.135	0.185	0.18	0.22	0.23
400	0.06	0.07	0.14	0.15	0.215	0.225	0.30	0.31	0.365	0.38
425	0.08	0.09	0.18	0.19	0.28	0.30	0.385	0.39	0.47	0.49
450	0.095	0.105	0.21	0.225	0.33	0.35	0.44	0.46	0.54	0.57
475	0.090	0.10	0.20	0.215	0.31	0.325	0.42	0.43	0.52	0.54
500	0.05	0.06	0.115	0.13	0.19	0.20	0.27	0.27	0.325	0.34
525	0.01	0.02	0.04	0.045	0.065	0.07	0.10	0.095	0.12	0.12

TABLE No.13

Adsorption of methylene blue on alumina gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4c(iii)1		Set No.4c(iii)2		Set No.4c(iii)3		Set No.4c(iii)4		Set No.4c(iii)5	
	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture	O.D. gel +dye mixture	O.D. water+dye mixture
550	0.01	0.01	0.025	0.025	0.02	0.05	0.07	0.085	0.06	0.115
575	0.025	0.025	0.055	0.07	0.065	0.12	0.16	0.19	0.135	0.245
600	0.06	0.06	0.12	0.16	0.14	0.25	0.32	0.38	0.275	0.48
625	0.085	0.09	0.175	0.225	0.195	0.34	0.43	0.52	0.37	0.62
650	0.13	0.14	0.24	0.33	0.26	0.51	0.59	0.75	0.56	0.89
675	0.08	0.08	0.145	0.19	0.16	0.295	0.35	0.43	0.33	0.50
700	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.04	0.035	0.055

TABLE No.14

Adsorption of malachite green on alumina gel:

O.D. of gel-dye and water-dye mixtures at different wavelengths:

Wave-length in mμ	Set No.4c(iv)1		Set No.4c(iv)2		Set No.4c(iv)3		Set No.4c(iv)4		Set No.4c(iv)5	
	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture	O.D. gel+dye mixture	O.D. water+dye mixture
550	0.01	0.01	0.005	0.015	0.01	0.025	0.015	0.04	0.01	0.06
575	0.02	0.01	0.015	0.04	0.02	0.055	0.03	0.09	0.025	0.12
600	0.04	0.03	0.03	0.06	0.04	0.10	0.06	0.165	0.050	0.23
625	0.04	0.015	0.035	0.065	0.045	0.11	0.065	0.18	0.055	0.24
650	0.02	0.01	0.01	0.020	0.01	0.025	0.015	0.045	0.015	0.06

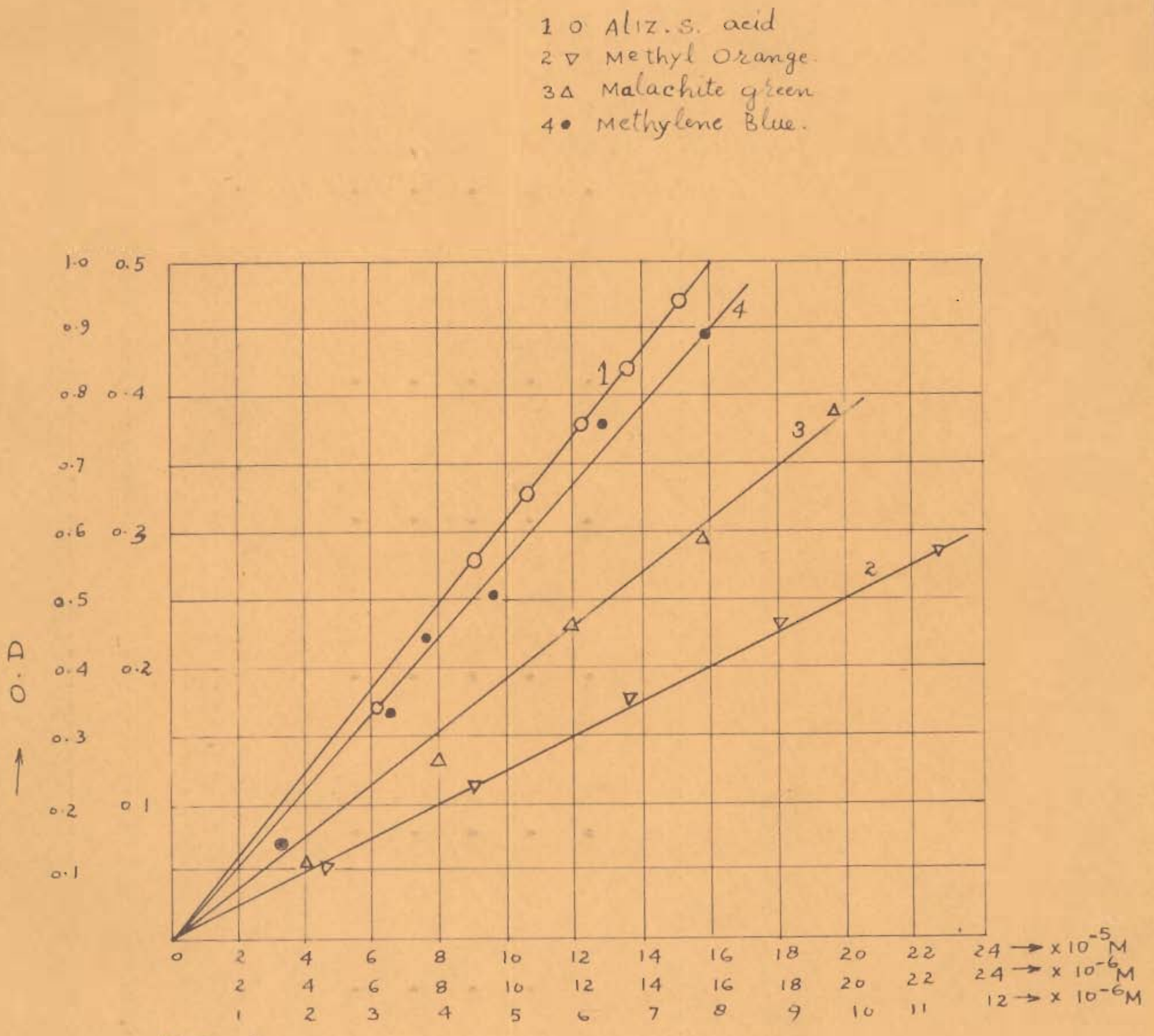

1 ○ Aliz. s. acid
2 ▽ Methyl Orange.
3 △ Malachite green
4 ● Methylene Blue.
1.0 0.5
0.9
0.8 0.4
0.7
0.6 0.3
0.5
0.4 0.2
0.3
0.2 0.1
0.1
O.D →
1
2
3
4
0 2 4 6 8 10 12 14 16 18 20 22 24 → x 10^{-5}M
2 4 6 8 10 12 14 16 18 20 22 24 → x 10^{-6}M
1 2 3 4 5 6 7 8 9 10 11 12 → x 10^{-6}M
→ CONC. OF DYE

FIG_ 41.

TABLE No.15

O.D. at different dilutions of the dyes:

Conc. of aliz.s.acid	O.D. at the maxima of aliz.s.acid	Conc. of methyl orange	O.D. at the mixima of methyl orange	Conc. of malachite green	O.D. at the maxima of malachite green	Conc. of methylene blue	O.D. at the maxima of methylene blue
6.0×10^{-5} M	0.16	4.51×10^{-6} M	0.105	1.96×10^{-6} M	0.055	3.14×10^{-6} M	0.14
7.5×10^{-5} M	0.22	9.02×10^{-6} M	0.225	3.92×10^{-6} M	0.13	6.28×10^{-6} M	0.33
9.0×10^{-5} M	0.28	13.53×10^{-6} M	0.35	5.88×10^{-6} M	0.23	9.42×10^{-6} M	0.51
10.5×10^{-5} M	0.33	18.04×10^{-6} M	0.46	7.84×10^{-6} M	0.29	12.56×10^{-6} M	0.75
12.0×10^{-5} M	0.38	22.55×10^{-6} M	0.57	9.80×10^{-6} M	0.38	15.70×10^{-6} M	0.89
	Fig.(41) curve 1		Fig.(41) curve 2		Fig.(41) curve 3		Fig.(41) curve 4

DISCUSSION

The difference in the behaviour of the acid and basic dyes towards silicic acid gel is evident from the adsorption studies.

TABLE No.16

Silica gel and alizarin sulphonic acid

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$\frac{1}{C_s}$ (M)
9.0×10^{-5} M	0.095	3.[illegible]$\times10^{-5}$ M	5.9×10^{-5} M	0.33×10^{5}	0.16×10^{5}
10.5×10^{-5} M	0.120	3.8×10^{-5} M	6.7×10^{-5} M	0.26×10^{5}	0.14×10^{5}
12.0×10^{-5} M	0.140	4.5×10^{-5} M	7.7×10^{-5} M	0.22×10^{5}	0.129×10^{5}
13.5×10^{-5} M	0.160	5.1×10^{-5} M	8.3×10^{-5} M	0.19×10^{5}	0.12×10^{5}
15.0×10^{-5} M	0.190	6.1×10^{-5} M	8.9×10^{-5} M	0.16×10^{5}	0.11×10^{5}

Fig.(42) curve (1). Fig (43) Curve 1.

TABLE No.17

Silica gel and methyl orange

Data for dye adsorbed and equilibrium concentration of dye

Initial concentration of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)
4.51×10^{-6} M	-0.05	-2.0×10^{-6} M	6.2×10^{-6} M
9.02×10^{-6} M	-0.045	-1.8×10^{-6} M	10.8×10^{-6} M
13.53×10^{-6} M	-0.04	-1.6×10^{-6} M	15.6×10^{-6} M
18.04×10^{-6} M	-0.05	-2.0×10^{-6} M	20.2×10^{-6} M
22.55×10^{-6} M	-0.05	-2.0×10^{-6} M	24.0×10^{-6} M

Fig.(42) curve (4).

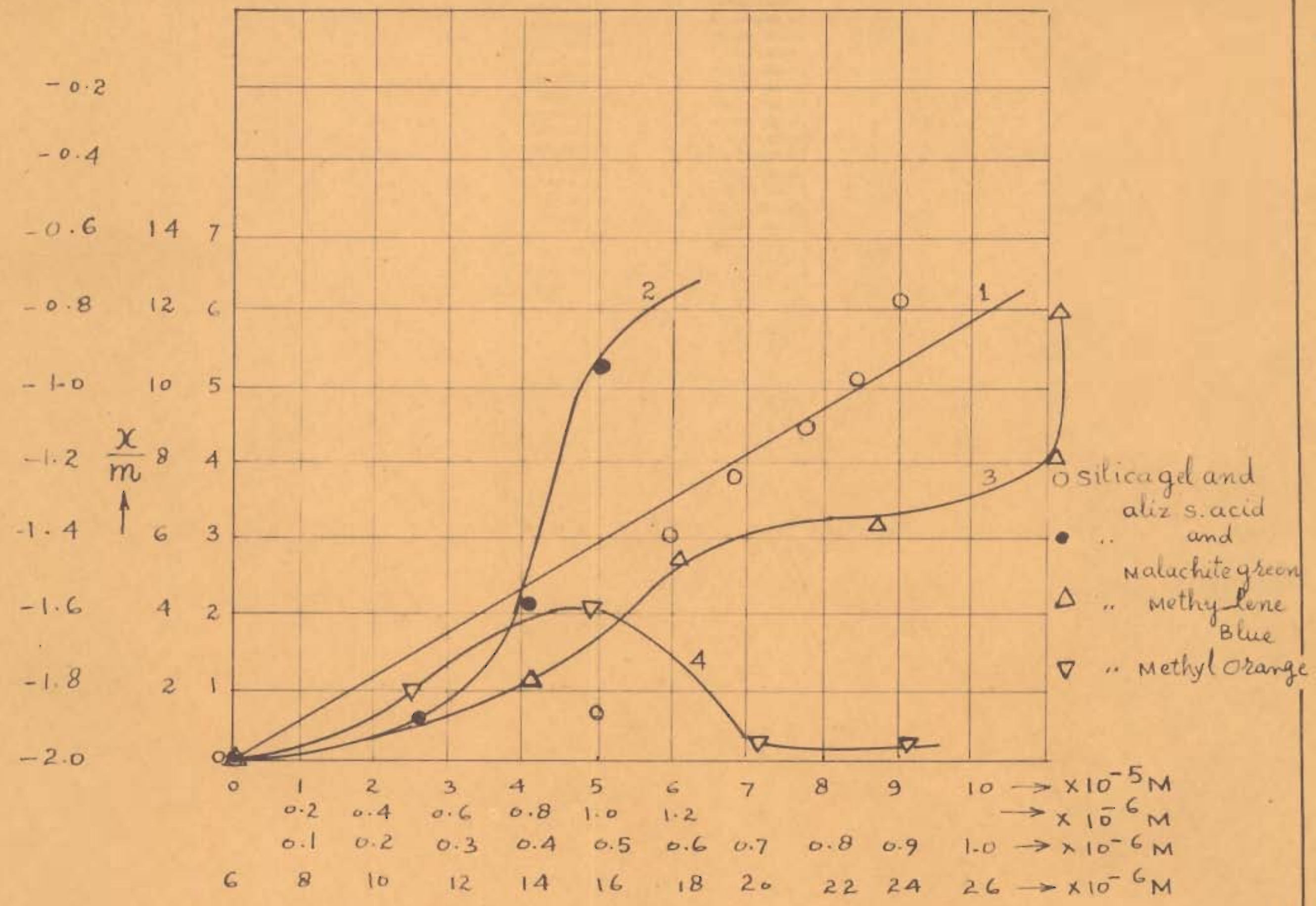


FIG- 42. → EQUILIBRIUM CONC OF DYE (C_S)

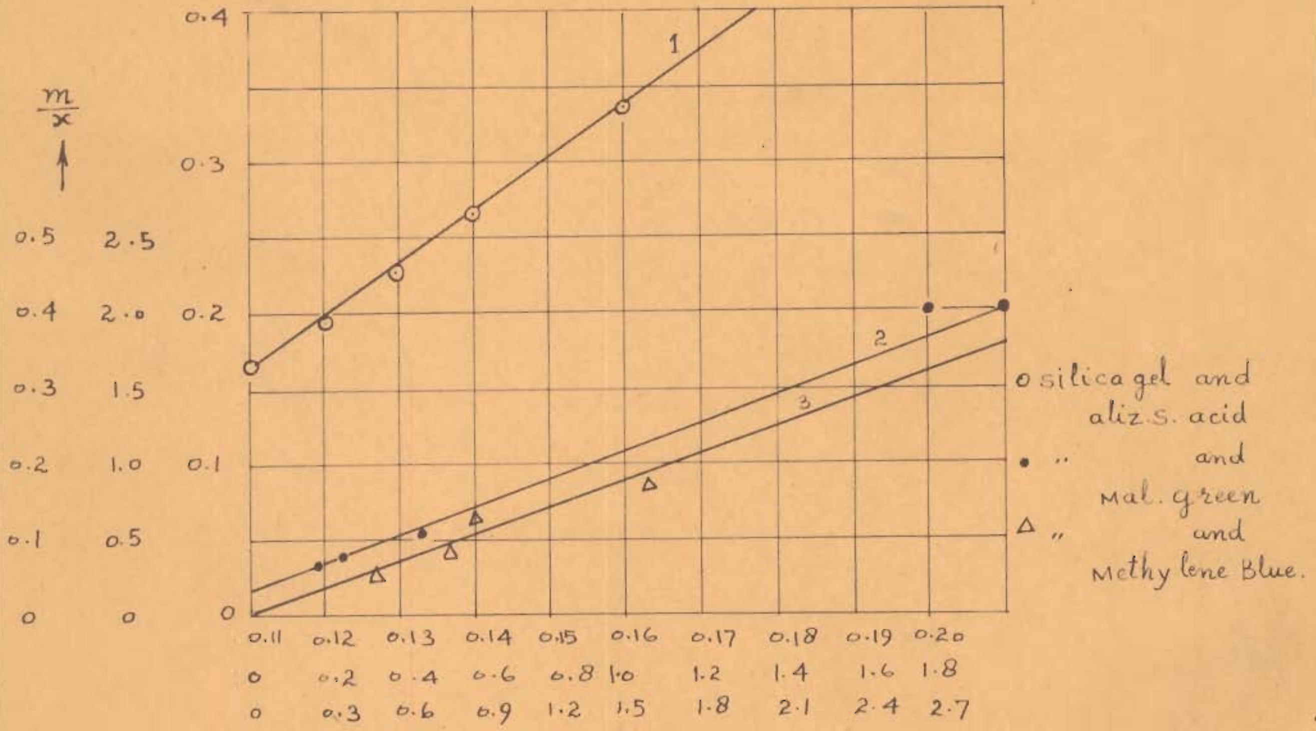


FIG - 43. → $1/c_S$

TABLE No.18

Silica gel and malachite green

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
1.96×10^{-6} M	0.020	0.50×10^{-6} M	0.50×10^{-6} M	2.0×10^{6}	2.0×10^{6}
3.92×10^{-6} M	0.025	0.55×10^{-6} M	1.0×10^{-6} M	1.8×10^{6}	0.55×10^{6}
5.88×10^{-6} M	0.080	2.10×10^{-6} M	2.0×10^{-6} M	0.47×10^{6}	0.50×10^{6}
7.84×10^{-6} M	0.155	4.05×10^{-6} M	2.65×10^{-6} M	0.24×10^{6}	0.37×10^{6}
9.80×10^{-6} M	0.200	5.25×10^{-6} M	3.0×10^{-6} M	0.19×10^{6}	0.33×10^{6}

Fig.(42) curve(2). Fig.(43). Curve (2)

TABLE No.19

Silica gel and methylene blue:

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
3.14×10^{-6} M	0.115	2.0×10^{-6} M	0.40×10^{-6} M	0.50×10^{6}	2.5×10^{6}
6.28×10^{-6} M	0.295	5.3×10^{-6} M	0.60×10^{-6} M	0.18×10^{6}	1.6×10^{6}
9.42×10^{-6} M	0.445	7.9×10^{-6} M	1.1×10^{-6} M	0.12×10^{6}	0.9×10^{6}
12.56×10^{-6} M	0.685	12.1×10^{-6} M	1.2×10^{-6} M	0.08×10^{6}	0.83×10^{6}
15.70×10^{-6} M	0.835	14.8×10^{-6} M	2.0×10^{-6} M	0.06×10^{6}	0.50×10^{6}

Fig.(42) curve(3). Fig(43) Curve(3).

A plot of equilibrium concentration of dye against amount of the dye adsorbed per 100 mg. of silica gel(x/m) are typical physical adsorption isotherms in the case of methylene blue and malachite green, the adsorption data are

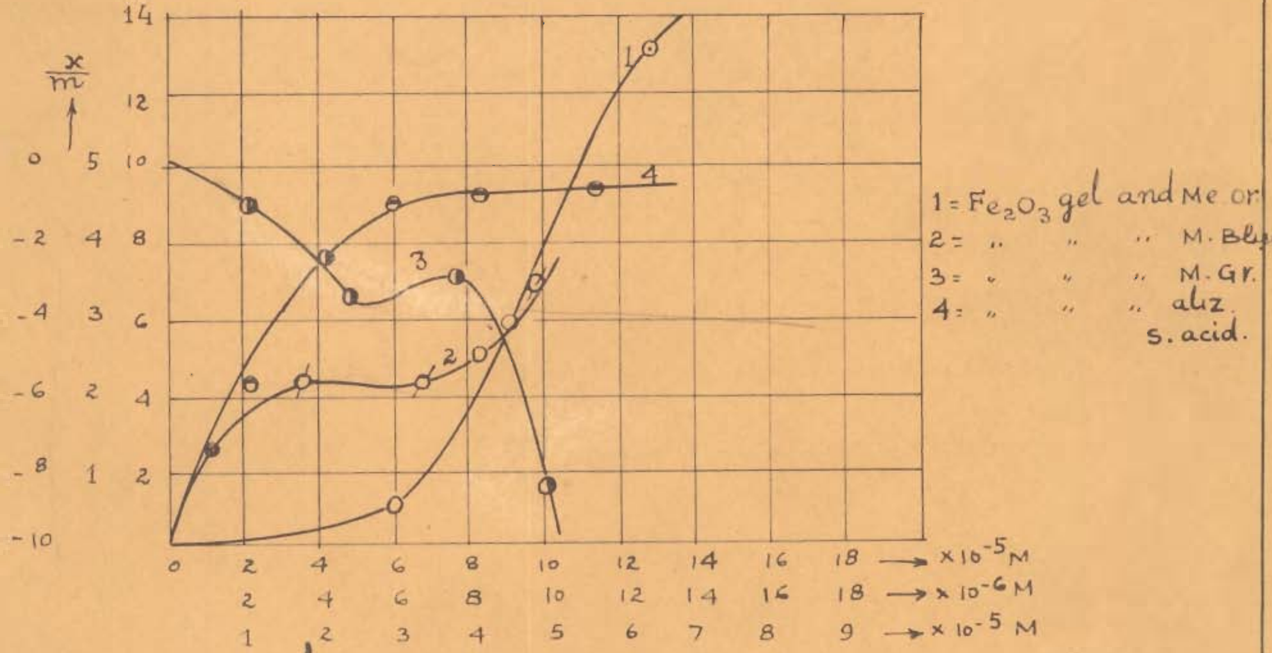


FIG. 44. → Eq. CONC. OF DYE (C_S)

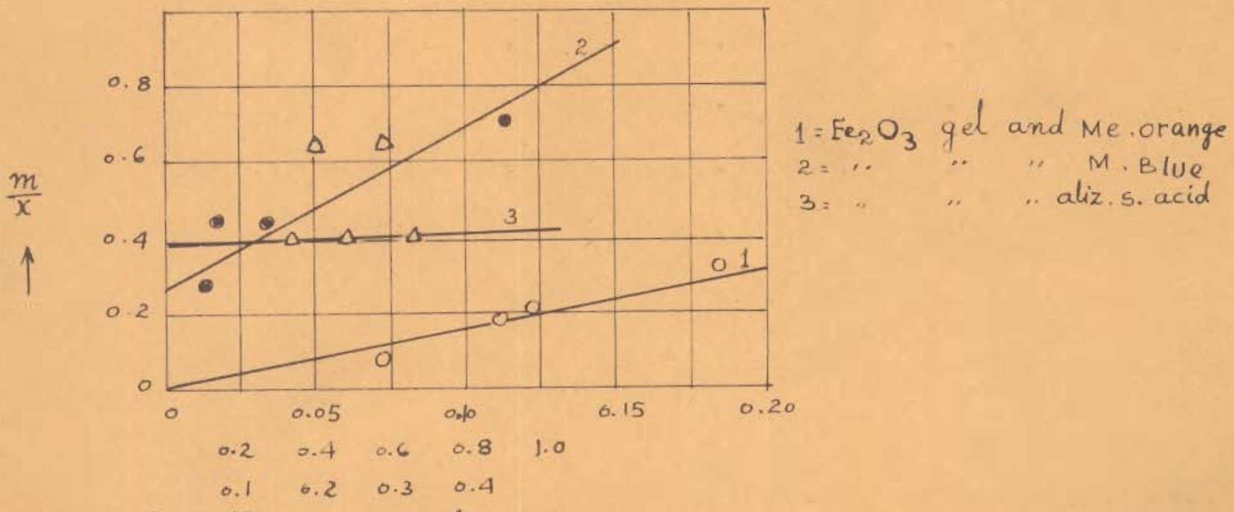


FIG-45. → $1/c_s$

seen to fit well in Langmuir adsorption equation. On the other hand methyl orange is found to be negatively adsorbed. From these observations it is evident that the thickness of the material adsorbed is only monomolecular, i.e. the material condenses only on a bare surface in the case of methylene blue, malachite green and alizarin sulphonic acid. Methyl orange is found to be negatively adsorbed by silica gel, this would involve swelling of the gel by imbibing water, consequently resulting in an increase of optical density (O.D.) values.

Ferric oxide gel:

TABLE No.20

Ferric oxide gel and alizarin sulphonic acid

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
9.0×10^{-5}M	0.175	5.6×10^{-5}M	3.4×10^{-5}M	0.17×10^{5}	0.29×10^{5}
10.5×10^{-5}M	0.180	5.8×10^{-5}M	4.8×10^{-5}M	0.17×10^{5}	0.20×10^{5}
12.0×10^{-5}M	0.285	9.1×10^{-5}M	3.0×10^{-5}M	0.10×10^{5}	0.33×10^{5}
13.5×10^{-5}M	0.285	9.1×10^{-5}M	4.1×10^{-5}M	0.10×10^{5}	0.24×10^{5}
15.0×10^{-5}M	0.375	9.4×10^{-5}M	5.6×10^{-5}M	0.10×10^{5}	0.17×10^{5}

Fig. (44) curve 4. Fig. (45) Curve (3).

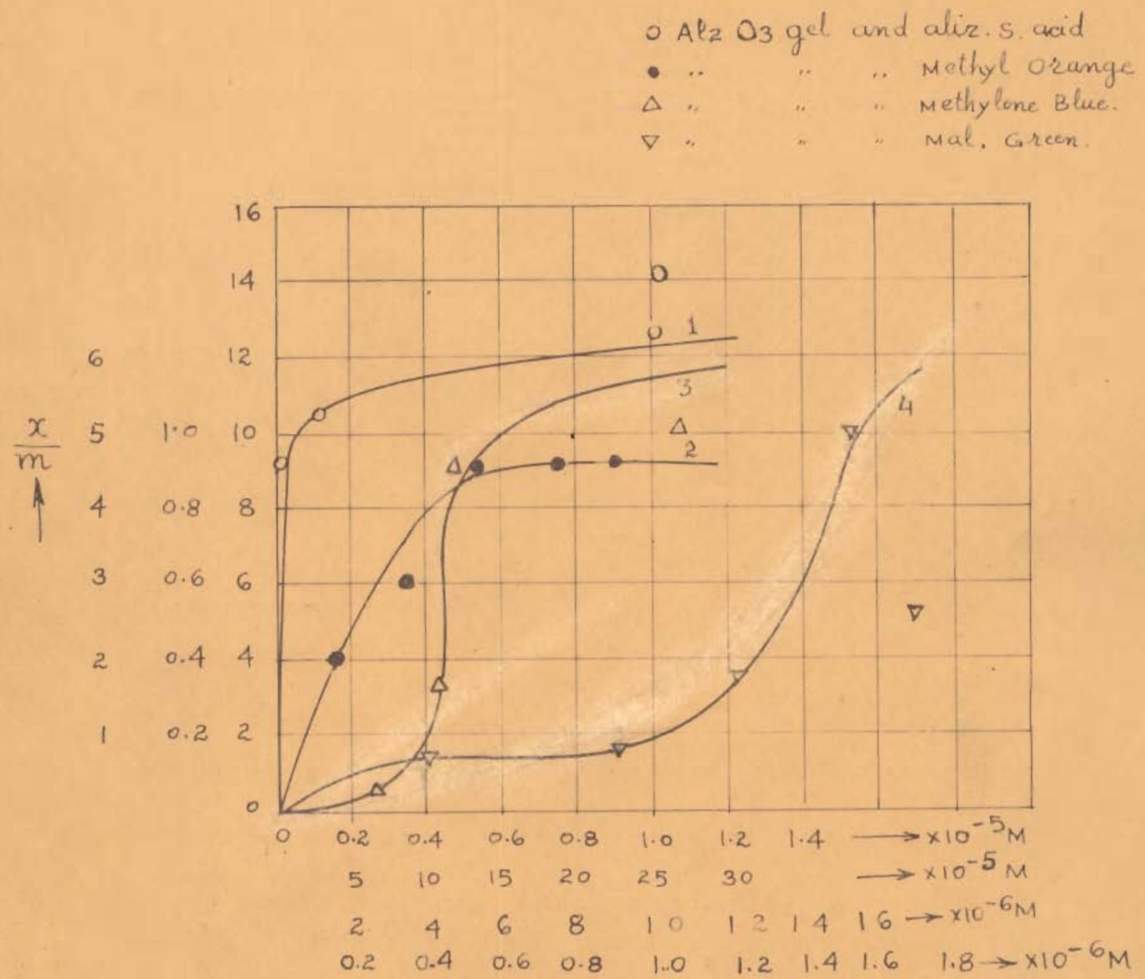


FIG- 46. → Eq. CONC. OF DYE (C_S)

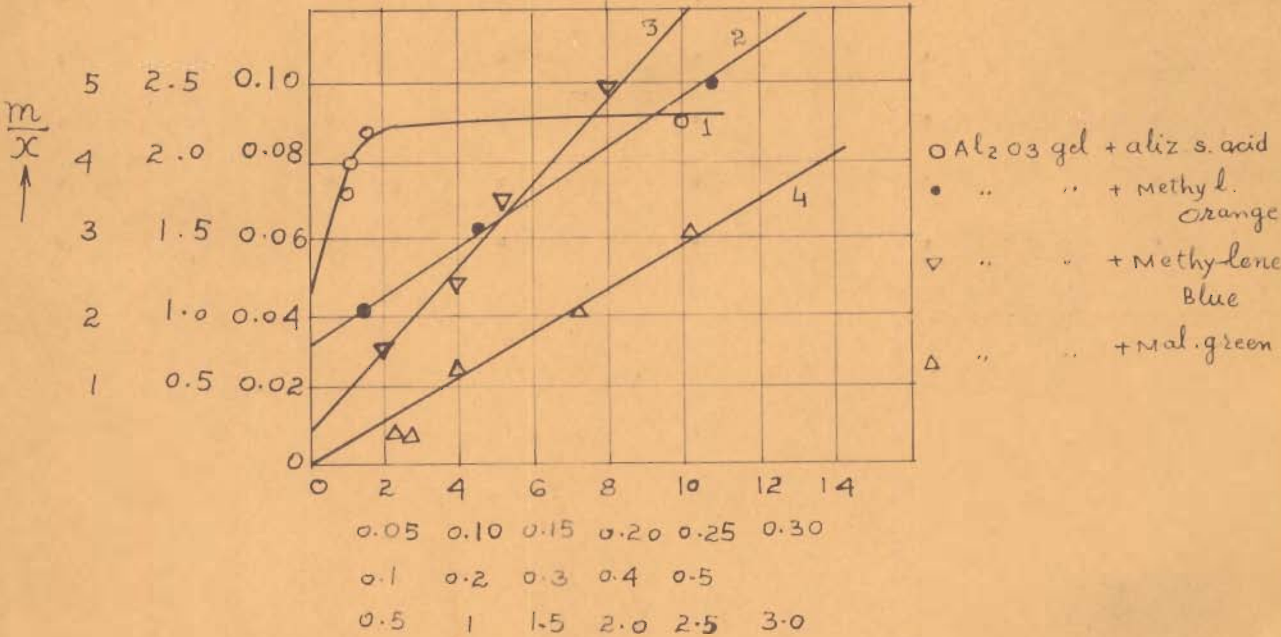


FIG- 47. → $1/C_S$

TABLE No.21

Ferric oxide gel and methyl orange

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye(C_s)	m/x (M)	$1/C_s$ (M)
$9.02x10^{-6}$ M	0.025	$1.0x10^{-6}$ M	$6.0x10^{-6}$ M	$1.0x10^{6}$	$0.16x10^{6}$
$13.53x10^{-6}$ M	0.125	$5.0x10^{-6}$ M	$8.2x10^{-6}$ M	$0.2x10^{6}$	$0.12x10^{6}$
$18.04x10^{-6}$ M	0.145	$5.8x10^{-6}$ M	$9.0x10^{-6}$ M	$0.17x10^{6}$	$0.11x10^{6}$
$22.55x10^{-6}$ M	0.33	$13.2x10^{-6}$ M	$12.6x10^{-6}$ M	$0.07x10^{6}$	$0.07x10^{6}$

Fig.(44) curve 1 Fig (45) Curve 1

TABLE No.22

Ferric oxide gel and methylene blue

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye(C_s)	m/x (M)	$1/C_s$ (M)
$3.14x10^{-6}$ M	0.08	$1.4x10^{-6}$ M	$1.1x10^{-6}$ M	$0.70x10^{6}$	$0.90x10^{6}$
$6.28x10^{-6}$ M	0.13	$2.3x10^{-6}$ M	$3.6x10^{-6}$ M	$0.43x10^{6}$	$0.27x10^{6}$
$9.42x10^{-6}$ M	0.125	$2.2x10^{-6}$ M	$6.8x10^{-6}$ M	$0.45x10^{6}$	$0.14x10^{6}$
$12.56x10^{-6}$ M	0.210	$3.7x10^{-6}$ M	$9.6x10^{-6}$ M	$0.27x10^{6}$	$0.10x10^{6}$
$15.70x10^{-6}$ M	0.02	$0.40x10^{-6}$ M	$15.6x10^{-6}$ M	-	-

Fig.(44) curve 2. Fig (45) Curve 2.

TABLE No.23

Ferric oxide gel and malachite green

Data for the dye adsorbed and equilibrium concentration of dye.

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)
1.96×10^{-6} M	-0.04	-1.1×10^{-6} M	2.1×10^{-6} M
3.92×10^{-6} M	-0.10	-2.6×10^{-6} M	4.2×10^{-6} M
5.88×10^{-6} M	-0.137	-3.6×10^{-6} M	4.8×10^{-6} M
7.84×10^{-6} M	-0.109	-2.9×10^{-6} M	7.6×10^{-6} M
9.80×10^{-6} M	-0.325	-8.5×10^{-6} M	9.9×10^{-6} M

Fig.(44) curve 3.

In the case of alizarin sulphonic acid the adsorption data do not fit well either in Langmuir or Freundlich adsorption isotherm showing the possibility of chemisorption or interstial adsorption. In the case of methyl orange and methylene blue the data fit in well in Langmuir isotherm. On the other hand malachite green is negatively adsorbed on the gel.

Aluminium oxide gel

TABLE No.24

Aluminium oxide gel and alizarin sulphonic acid

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye(C_s)	m/x (M)	$1/C_s$ (M)
10.5×10^{-5} M	0.325	10.4×10^{-5} M	0.1×10^{-5} M	0.09×10^{5}	10.0×10^{5}
12.0×10^{-5} M	0.355	11.4×10^{-5} M	0.8×10^{-5} M	0.087×10^{5}	1.2×10^{5}
13.5×10^{-5} M	0.390	12.5×10^{-5} M	1.0×10^{-5} M	0.080×10^{5}	1.0×10^{5}
15.0×10^{-5} M	0.440	14.1×10^{-5} M	1.2×10^{-5} M	0.070×10^{5}	0.83×10^{5}

Fig.(46) curve 1. Fig (47) Curve 1.

TABLE No.25

Aluminium oxide gel and methyl orange

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
4.5×10^{-6} M	0.01	0.4×10^{-6} M	3.8×10^{-6} M	2.5×10^{6}	0.26×10^{6}
9.02×10^{-6} M	0,015	0.6×10^{-6} M	8.4×10^{-6} M	1.6×10^{6}	0.11×10^{6}
13.53×10^{-6} M	0.02	0.9×10^{-6} M	13.0×10^{-6} M	1.1×10^{6}	0.07×10^{6}
18.00×10^{-6} M	0.02	0.9×10^{-6} M	18.0×10^{-6} M	1.1×10^{6}	0.05×10^{6}
22.55×10^{-6} M	0.03	1.0×10^{-6} M	21.5×10^{-6} M	1.0×10^{6}	0.04×10^{6}

Fig.(46) curve 2. Fig(47) Curve 2.

TABLE No.26

Aluminium oxide gel and methylene blue

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
3.14×10^{-6} M	0.01	0.2×10^{-6} M	2.5×10^{-6} M	5.0×10^{6}	0.40×10^{6}
6.28×10^{-6} M	0.09	1.6×10^{-6} M	4.3×10^{-6} M	0.62×10^{6}	0.23×10^{6}
9.42×10^{-6} M	0.25	4.5×10^{-6} M	4.6×10^{-6} M	0.22×10^{6}	0.21×10^{6}
12.56×10^{-6} M	0.16	2.8×10^{-6} M	9.8×10^{-6} M	0.35×10^{6}	0.10×10^{6}
15.70×10^{-6} M	0.34	5.9×10^{-6} M	10.2×10^{-6} M	0.16×10^{6}	0.09×10^{6}

Fig.(46) curve 3 Fig (47) Curve 3.

TABLE No.27

Aluminium oxide gel and malachite green

Data for dye adsorbed and equilibrium concentration of dye

Initial conc. of dye	Difference of O.D.	Dye adsorbed (x/m)	Equilibrium conc. of dye (C_s)	m/x (M)	$1/C_s$ (M)
3.92×10^{-6} M	0.030	0.75×10^{-6} M	0.90×10^{-6} M	1.30×10^{6}	1.10×10^{6}
5.88×10^{-6} M	0.065	1.70×10^{-6} M	1.20×10^{-6} M	0.58×10^{6}	0.80×10^{6}
7.84×10^{-6} M	0.115	3.0×10^{-6} M	1.70×10^{-6} M	0.33×10^{6}	0.58×10^{6}
9.80×10^{-6} M	0.185	4.85×10^{-6} M	1.90×10^{-6} M	0.20×10^{6}	0.55×10^{6}

Fig.(46) curve 4. Fig (47) Curve (4).

In the case of alizarin sulphonic acid physical adsorption isotherms were obtained although it was difficult to fit in the data in either Langmuir or the classical adsorption equation. Instead the curves were similar to the isotherms for vapour adsorption on colloids. The extent of adsorption in this case probably is more closely related to their chemical nature than to their molecular size or molecular weight. The nature of the curves in the case of methyl orange, methylene blue and malachite green are different and the adsorption data are found to seen fit in well in Langmuir adsorption equation. A perusal of the data (tables 24, 25, 26 and 27) show that the gel shows great adsorption capacity for alizarin sulphonic acid and methylene blue while this tendency is quite small for methyl orange and malachite green. Although adsorption is possible in all the cases but it is only with the acid dye (alizarin sulphonic acid) that it shows greater adsorption.

SOL-GEL TRANSFORMATION OF SILICIC ACID SOL IN PRESENCE OF DYES

Silicon dioxide, comprising the bulk (60%) of the earth crust, forms the basis of world's Oldest civilization as is evident from the existence of thousand years old glass and ceramic industries and relatively recent use of colloidal silicates in the production of excellent ceramics, the drilling of oil wells, the manufacture of catalysts for the petroleum industry and industrial products like building materials. Inspite of its abundent use in the primitive civilization and man's age-long interest in its manifold uses, the chemistry of this compound, especially when in solution remained obscure for a very long time.

Most of the changes that silica undergoes in nature involve interaction with water. The outstanding characteristics of silica water system is the formation of colloidal solutions. Klemm (1) has shown that solubility of amorphons silica in the form of silica gel increases rapidly as the pH rises above 8 or 9. The subject of soluble silicates with emphasis on the state of polymerisation has been comprehensively reviewed by Vail (2) in a two volume monograph that deals with both the practical and theoritical aspects of the soluble silicate.

Treadwell and Wieland (3) have advanced the theory of polymerisation of silicic acid, taking into consideration the co-ordination requirements as a distinguishing feature between the chemistry of carbon and that of silicon.

W.A. Weyl (4) has revived and clarified Treadwell and Wieland's hypothesis that silica may have a co-ordination number of six with respect to oxygen in the form of hydroxy group. Weyl Visualized that the process of polymerisation of $Si(OH)_4$ involves the sharing of OH^- between different silicon atoms leading to the formation of polymeric units in which each Si^{4+} is surrounded octahedrally by six OH^- ions. Formation of chain like molecules in this manner according to Weyl leads to a second process which involves a condensation with the polymer, so that adjoining silicon ions become linked together directly by oxygen ions, while water is eliminated.

Weyl's theory concerns the mechanism of siloxane bond formation but does not permit prediction of the nature of the polymers which are formed. It is known that in the presence of small amounts of alkali, silicic acid may polymerise to form stable dispersion of colloidal particles, which in acid solution give silica gel. Carman (5) has presented a more detailed picture of the structure of colloidal silica. He first visualizes a large mass of pure silica, consisting of a three dimensional network of SiO_4 tetrahedra and conforming in composition to SiO_2 by linking every oxygen to two silicon atoms. The surface of silicon atoms will strive to complete tetrahedral coordination, and in contact with moisture, this will be accomplished by the formation of OH groups on the surface of silica. It is visualized that two hydrogen ions are held equally by the two negatively charged oxygen ions and they are held firmly, giving hydroxyl groups. The surface of a colloidal silica particle is so large that the hydration is measureable, and one may speak of colloidal hydrated silica. Carman goes on to point out that as a result, silica is capable of every "degree of hydration" depending purely upon particle size and ranging from H_4SiO_4 to colloidal silica to large crystals or amorphous masses of anhydrous silica.

Kruyt and Postma (6) pointed out that there existed two groups of silicic acid sols. The first group has a pH 4.5 or less, and the viscosity of sol increases with time, and the other groups of pure silica sols having a pH of 7 or higher are relatively stable. The viscosity in the latter either remains the same or decreases with time. The difference in behaviour is explained as follows: The more alkali sols bear a negative charge and are thereby stabilized. However, the addition of soluble salts lower the charge of the particles and causes gelation or precipitation. On the acid side, where there is essentially no charge aggregation or flocculation occurs, an increase in viscosity and eventually gelation results.

The formation of colour lakes by the interaction of dyes with metal hydrous oxide has been extensively investigated although a precise knowledge of the various factors effecting it are still unknown. Another important aspect connected with the interaction of dyes with sols is the reaction with silicic acid sol. Studies in this direction have been less extensive and need a more critical and comprehensive treatment. It was therefore considered desirable to study the sol-gel transformation of silicic acid with typical anionic and cationic dyes.

The work described in this chapter deals with the results on the variations of viscosity, pH and conductance during the gelation of silicic acid in presence of acid and basic dyes.

EXPERIMENTAL

Preparation of solutions:

(a) The B.D.H and Merck product of dyes, alizarin sulphonic acid (sod. salt), methyl orange (sod. salt), methylene blue (cl^-) and malachite green (cl^-) were dissolved in double distilled water.

(b) Preparation of silicic acid sol:

Silicic acid sol (7) was prepared by diluting 40 cc of concentrated hydrochloric acid with 125 cc of double distilled water. 75 cc of sodium silicate solution (sp.gr. 1.16) was added to the dilute acid with constant stirring. The mixture was dialysed till the pH of the sol reaches to 1.5. The silica content was determined gravimetrically by evaporating 5 cc sol in a weighed crucible to dryness and then igniting until the weight was constant. The silica content was fixed at 51.0 gms. per litre by dilution.

Time of setting of gel

The time of gelation with dialysis was determined by Fleming's method (8). Mixtures of silicic acid sol and dyes were taken in different dialysing bags. The time of setting was taken to be one when the fluid ceased to flow on inverting the test tubes containing the gelation mixture.

Viscosity measurements

The viscosity of various gelation mixtures was determined by Scarpa's method (9) modified by Farrow (10) and improved by Prasad, Mehta and Desai (11) at a constant temperature of 30 ± 0.1°C. The viscometer used for the present studies was Ostwald viscometer B.S.S type. The formula used takes into account times t_1 and t_2 required for filling and emptying the bulbs under a definite pressure, V be the volume of the bulb, R the radius of the capillary and L is the length

$$\eta = \frac{\pi P R^4}{8LV} \cdot \frac{t_1 x t_2}{t_1 + t_2} = \text{constt.} \ \frac{t_1 x t_2}{t_1 + t_2}$$

if the same temperature and pressure were employed. The value of the constant for a particular viscometer was determined by measuring t_1 and t_2 for a liquid of known viscosity (benzene). Once, the value of constant is known, the viscosity for the sol-dye mixture can be determined.

pH measurements

The variation in hydrogen ion concentration during sol-gel transformation of the various mixtures of sol and dyes was determined with the help of Cambridge bench pH meter.

Conductivity measurements

The conductivity measurements were carried out during the sol-gel transformation of the various mixtures by using T.W.T. conductivity bridge.

20 cc of silicic acid (ph = 1.5) was taken in each set of experiments (SiO_2 = 5.1 gm per 100 ml). Varying amount of dyes were mixed. The total volume in each set was kept equal to 30 cc. The mixture of each set was taken in parchment paper bags of the same size and variations in

viscosity, pH and conductance measured with time of dialysis.

The following sets of dye-sol mixtures were investigated:

Set No. 1.

Silicic acid sol (51.0 gms./litre) + methyl orange (2.0×10^{-2}M) mixtures. Each mixture contains 20 cc of the sol and varying amounts (0 cc, 2 cc, 6 cc, 8 cc, 10 cc) of the dye. Total volume made upto 30 cc by double distilled water.

Set No. 2.

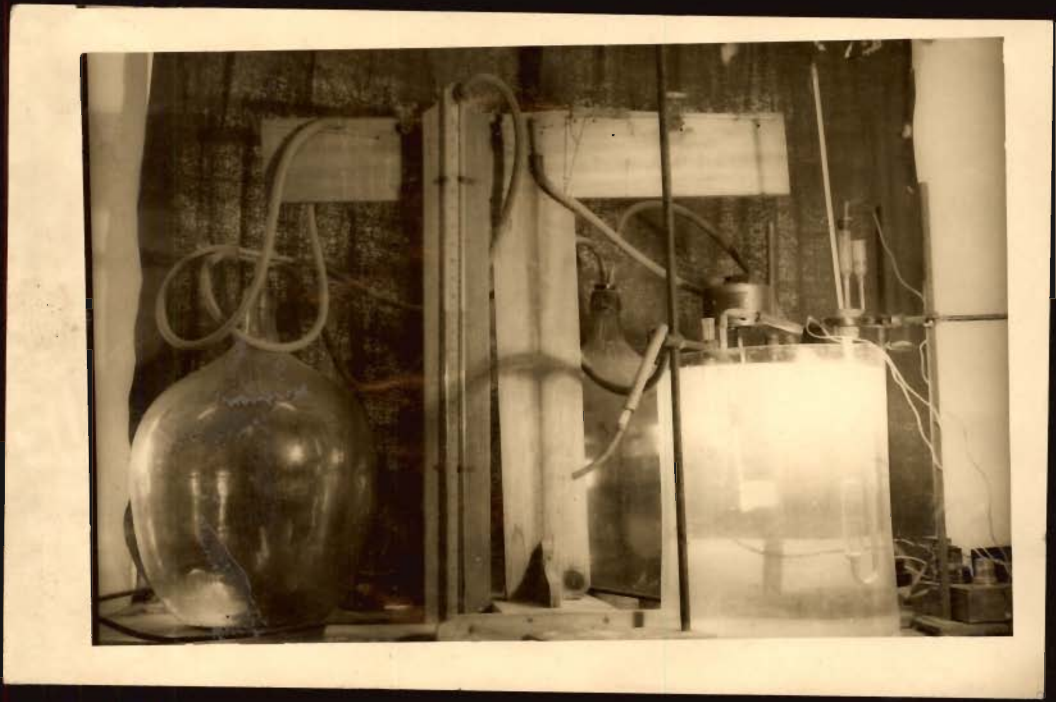
Silicic acid sol (51.0 gms./litre) + alizarin sulphonic acid (2.0×10^{-2}M) mixtures. Each mixture contains 20 cc of the sol and varying amounts (0 cc, 2 cc, 4 cc, 6 cc, 8 cc, 10 cc) of the dye. Total volume made upto 30 cc by double distilled water.

Set No. 3.

Silicic acid sol (51.0 gms./litre) + methylene blue (2.0×10^{-2}M) mixtures. Each mixture contains 20 cc of the sol and varying amounts (0 cc, 2 cc, 4 cc, 6cc, 8 cc, 10 cc) of the dye. Total volume made upto 30 cc by double distilled water.

Set No. 4.

Silicic acid sol (51.0 gms./litre) + malachite green (2.0×10^{-2}M) mixtures. Each mixture contains 20 cc of the sol and varying amounts (0 cc, 2 cc, 4 cc, 6 cc, 8 cc, 10 cc) of the dye. Total volume made upto 30 cc by double distilled water.



VISCOSITY APPARATUS

Initial pHs of sol and dyes are 2.6, 6.10 (methyl orange), 2.32 (aliz. s. acid), 3.48 (methylene blue), 2.36 (malachite green) respectively.

For measuring the variations in viscosity at different dilutions of the dye solutions, the following set no. 5 was investigated.

Set No. 5.

0 cc, 2 cc, 6 cc, 8 cc, 10 cc of methyl orange (2.0×10^{-2}M). Total volume made upto 30 cc by double distilled water.

0 cc, 2 cc, 4 cc, 6 cc, 8 cc, 10 cc of alizarin sulphonic acid (2.0×10^{-2}M). Total volume made upto 30 cc by double distilled water.

0 cc, 2 cc, 4 cc, 6 cc, 8 cc, 10 cc of methylene blue (2.0×10^{-2}M). Total volume made upto 30 cc by double distilled water.

0 cc, 2 cc, 4 cc, 6 cc, 8 cc, 10 cc of malachite green (2.0×10^{-2}M). Total volume made upto 30 cc by double distilled water.

Set No.1

Table No.1

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of methyl orange.

Tempt. = $30^{o} \pm 0.1^{o}C$, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			6 c.c. of the dye		
	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)
0	1.213	2.68	2.10×10^{-2}	1.273	2.79	1.95×10^{-2}	1.287	3.0	2.06×10^{-2}
60	1.260	3.20	1.65×10^{-2}	1.327	3.15	1.65×10^{-2}	1.340	3.33	1.50×10^{-2}
120	1.334	3.66	1.15×10^{-2}	1.416	3.56	1.22×10^{-2}	1.445	3.94	1.08×10^{-2}
150	1.526	4.06	1.10×10^{-2}	1.609	3.92	1.15×10^{-2}	1.783	4.05	1.00×10^{-2}
180	2.315	4.38	1.00×10^{-2}	2.096	4.14	1.05×10^{-2}	2.279	4.05	0.89×10^{-2}
240	-	-	-	3.783	4.11	0.85×10^{-2}	3.667	4.06	0.75×10^{-2}
	Fig.(49) curve 1			Fig.(49) curve 2			Fig.(49) curve 4		

Time of dialysis (mts)	8 c.c. of the dye			10 c.c. of the dye		
0	1.302	3.12	2.00×10^{-2}	1.341	3.22	1.82×10^{-2}
60	1.397	3.45	1.54×10^{-2}	1.472	3.50	1.60×10^{-2}
120	1.681	4.14	1.02×10^{-2}	2.090	4.10	1.16×10^{-2}
150	2.085	4.10	0.90×10^{-2}	3.212	4.03	1.02×10^{-2}
180	2.580	4.13	0.80×10^{-2}	3.703	4.18	0.68×10^{-2}
240	4.258	4.18	0.60×10^{-2}	14.47	4.11	0.72×10^{-2}
	Fig.(49) curve 5			Fig.(49) curve 6		

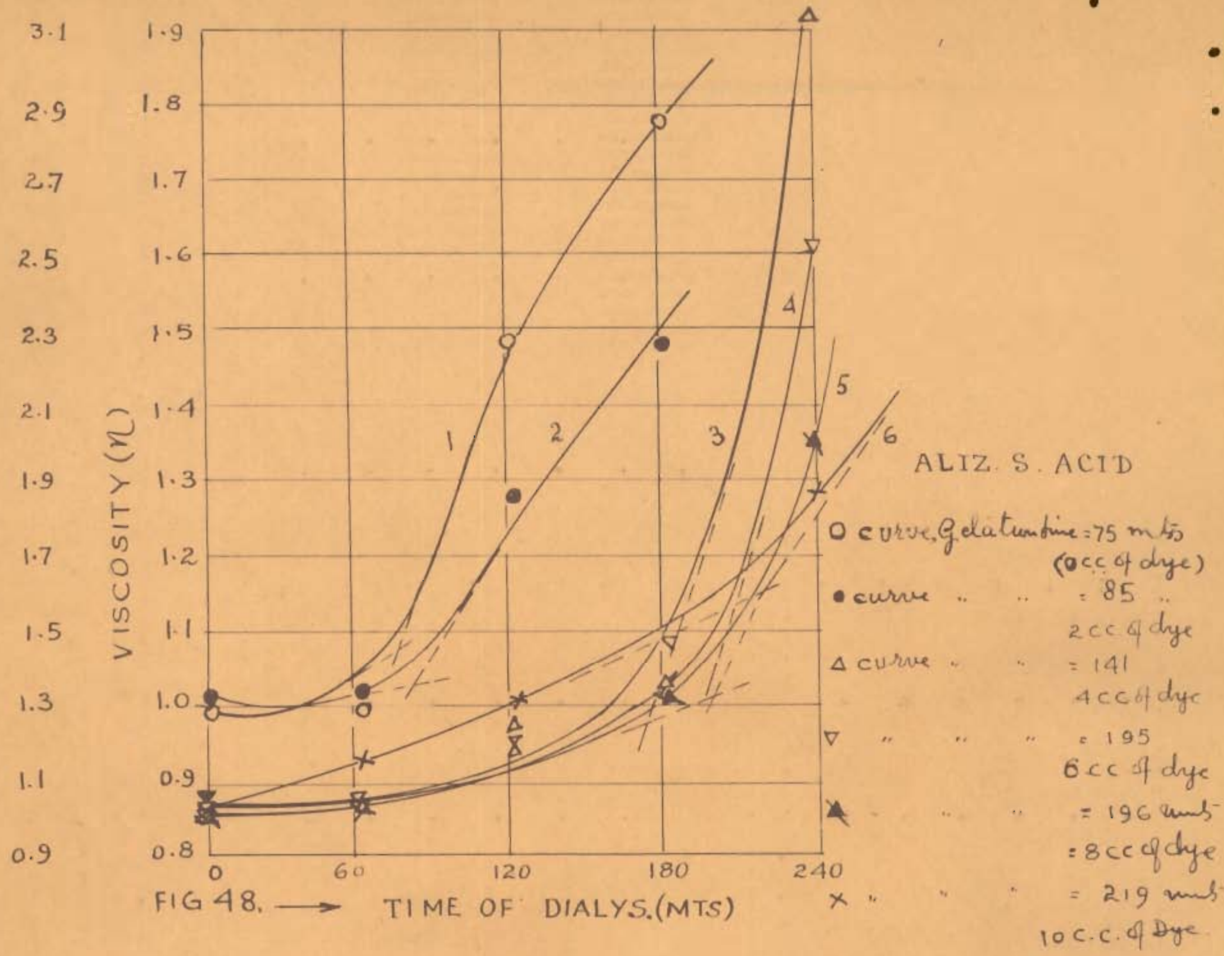


FIG 48. → TIME OF DIALYS. (MTS)

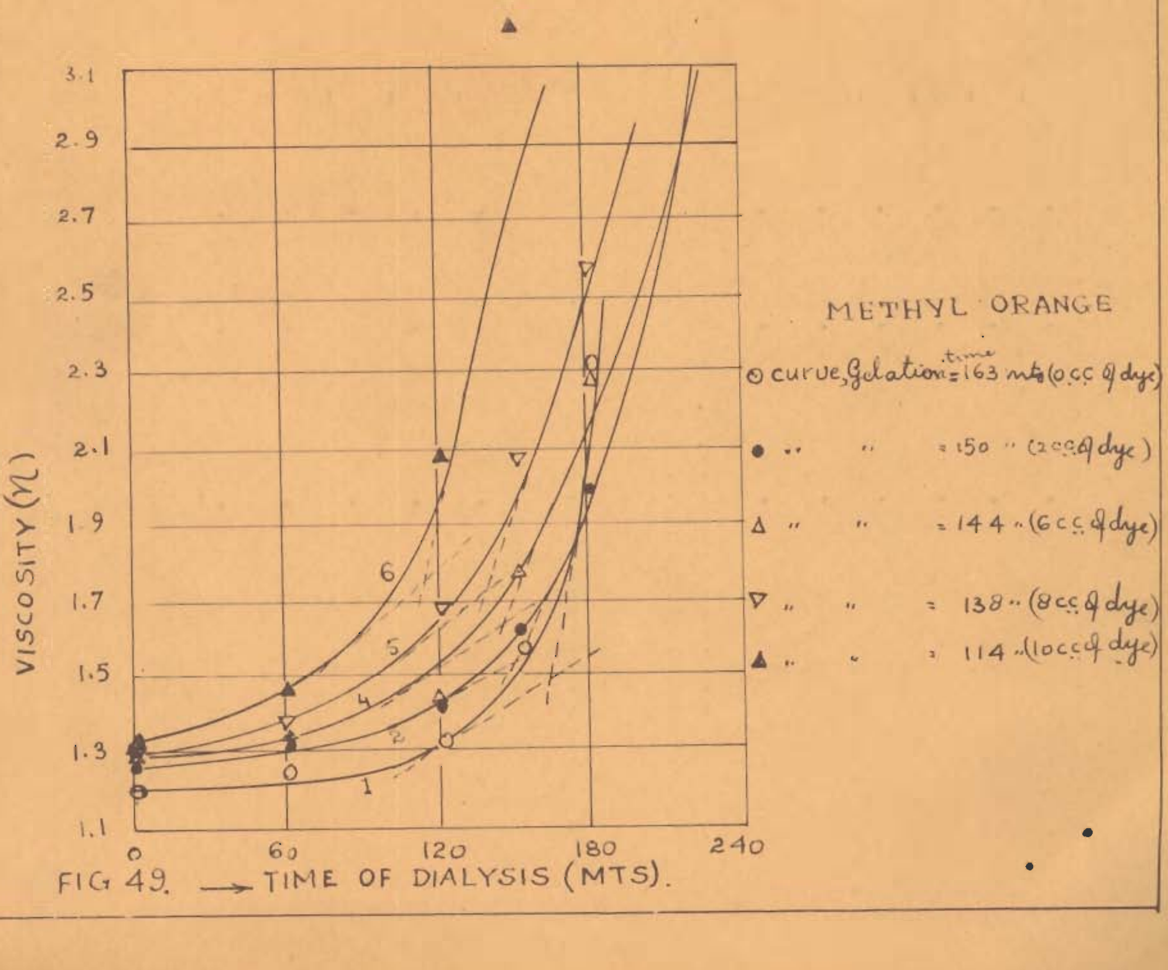


FIG 49. → TIME OF DIALYSIS (MTS).

Set No.2

Table No.2

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of alizarin sulphonic acid.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			4 c.c. of the dye		
	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)
0	0.9940	2.62	2.15×10^{-2}	1.003	2.52	2.22×10^{-2}	1.002	2.46	2.20×10^{-2}
60	1.001	3.13	1.55×10^{-2}	1.014	3.07	1.68×10^{-2}	1.016	3.04	1.72×10^{-2}
120	1.483	3.98	1.00×10^{-2}	1.275	3.75	1.14×10^{-2}	1.185	3.62	1.12×10^{-2}
150	1.526	4.00	0.92×10^{-2}	1.320	3.90	0.90×10^{-2}	1.200	3.92	1.00×10^{-2}
180	1.773	4.60	0.82×10^{-2}	1.407	4.40	0.80×10^{-2}	1.311	4.14	0.90×10^{-2}
240	-	-	-	-	-	-	3.119	4.65	0.72×10^{-2}
	Fig.(48) curve 1			Fig.(48) curve 2			Fig.(48) curve 3		

Time of dialysis (mts)	6 c.c. of the dye			8 c.c. of the dye			10 c.c. of the dye		
0	1.002	2.42	2.40×10^{-2}	1.013	2.38	2.45×10^{-2}	1.016	2.36	2.53×10^{-2}
60	1.017	3.00	1.78×10^{-2}	1.019	2.99	1.79×10^{-2}	1.148	2.99	1.75×10^{-2}
120	1.184	3.54	1.20×10^{-2}	1.228	3.53	1.18×10^{-2}	1.310	3.53	1.15×10^{-2}
150	1.210	3.85	1.10×10^{-2}	1.300	3.80	1.00×10^{-2}	1.350	3.90	1.00×10^{-2}
180	1.311	4.04	0.98×10^{-2}	1.331	4.02	0.95×10^{-2}	1.463	4.08	0.90×10^{-2}
240	2.504	4.65	0.72×10^{-2}	1.990	4.51	0.70×10^{-2}	1.855	4.40	0.72×10^{-2}
	Fig.(48) curve 4			Fig.(48) curve 5			Fig.(48) curve 6		

Set No.3

Table No.3

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of methylene blue.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			4 c.c. of the dye		
	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)
0	1.008	2.49	2.30×10^{-2}	1.010	2.48	2.35×10^{-2}	1.021	2.47	2.36×10^{-2}
30	1.004	3.04	1.70×10^{-2}	1.030	3.06	1.75×10^{-2}	1.048	2.97	1.80×10^{-2}
60	1.024	3.20	1.40×10^{-2}	1.037	3.17	1.45×10^{-2}	1.070	3.10	1.55×10^{-2}
90	1.033	3.46	1.15×10^{-2}	1.060	3.41	1.22×10^{-2}	1.105	3.28	1.35×10^{-2}
120	1.066	3.88	0.95×10^{-2}	1.118	3.76	1.08×10^{-2}	1.158	3.56	1.15×10^{-2}
	Fig.(50) curve 1			Fig.(50) curve 2			Fig.(50) curve 3		

	6 c.c. of the dye			8 c.c. of the dye			10 c.c. of the dye		
0	1.037	2.46	2.38×10^{-2}	1.058	2.46	2.39×10^{-2}	1.113	2.46	2.40×10^{-2}
30	1.069	2.98	1.85×10^{-2}	1.155	3.02	1.70×10^{-2}	1.203	2.96	1.88×10^{-2}
60	1.113	3.09	1.54×10^{-2}	1.192	3.18	1.45×10^{-2}	1.368	3.11	1.52×10^{-2}
90	1.137	3.29	1.30×10^{-2}	1.237	3.53	1.05×10^{-2}	1.480	3.34	1.36×10^{-2}
120	1.208	3.59	1.10×10^{-2}	1.548	4.03	0.90×10^{-2}	1.851	3.72	1.04×10^{-2}
	Fig.(50) curve 4			Fig.(50) curve 5			Fig.(50) curve 6		

Set No.2 **Table No.2**

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of alizarin sulphonic acid.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			4 c.c. of the dye		
	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)
0	0.9940	2.62	2.15×10^{-2}	1.003	2.52	2.22×10^{-2}	1.002	2.46	2.20×10^{-2}
60	1.001	3.13	1.55×10^{-2}	1.014	3.07	1.68×10^{-2}	1.016	3.04	1.72×10^{-2}
120	1.483	3.98	1.00×10^{-2}	1.275	3.75	1.14×10^{-2}	1.185	3.62	1.12×10^{-2}
150	1.526	4.00	0.92×10^{-2}	1.320	3.90	0.90×10^{-2}	1.200	3.92	1.00×10^{-2}
180	1.773	4.60	0.82×10^{-2}	1.407	4.40	0.80×10^{-2}	1.311	4.14	0.90×10^{-2}
240	-	-	-	-	-	-	3.119	4.65	0.72×10^{-2}
	Fig.(48) curve 1			Fig.(48) curve 2			Fig.(48) curve 3		

	6 c.c. of the dye			8 c.c. of the dye			10 c.c. of the dye		
0	1.002	2.42	2.40×10^{-2}	1.013	2.38	2.45×10^{-2}	1.016	2.36	2.53×10^{-2}
60	1.017	3.00	1.78×10^{-2}	1.019	2.99	1.79×10^{-2}	1.148	2.99	1.75×10^{-2}
120	1.184	3.54	1.20×10^{-2}	1.228	3.53	1.18×10^{-2}	1.310	3.53	1.15×10^{-2}
150	1.210	3.85	1.10×10^{-2}	1.300	3.80	1.00×10^{-2}	1.350	3.90	1.00×10^{-2}
180	1.311	4.04	0.98×10^{-2}	1.331	4.02	0.95×10^{-2}	1.463	4.08	0.90×10^{-2}
240	2.504	4.65	0.72×10^{-2}	1.990	4.51	0.70×10^{-2}	1.855	4.40	0.72×10^{-2}
	Fig.(48) curve 4			Fig.(48) curve 5			Fig.(48) curve 6		

Set No.3

Table No.3

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of methylene blue.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			4 c.c. of the dye		
	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)
0	1.008	2.49	2.30×10^{-2}	1.010	2.48	2.35×10^{-2}	1.021	2.47	2.36×10^{-2}
30	1.004	3.04	1.70×10^{-2}	1.030	3.06	1.75×10^{-2}	1.048	2.97	1.80×10^{-2}
60	1.024	3.20	1.40×10^{-2}	1.037	3.17	1.45×10^{-2}	1.070	3.10	1.55×10^{-2}
90	1.033	3.46	1.15×10^{-2}	1.060	3.41	1.22×10^{-2}	1.105	3.28	1.35×10^{-2}
120	1.066	3.88	0.95×10^{-2}	1.118	3.76	1.08×10^{-2}	1.158	3.56	1.15×10^{-2}
	Fig.(50) curve 1			Fig.(50) curve 2			Fig.(50) curve 3		
	6 c.c. of the dye			8 c.c. of the dye			10 c.c. of the dye		
0	1.037	2.46	2.38×10^{-2}	1.058	2.46	2.39×10^{-2}	1.113	2.46	2.40×10^{-2}
30	1.069	2.98	1.85×10^{-2}	1.155	3.02	1.70×10^{-2}	1.203	2.96	1.88×10^{-2}
60	1.113	3.09	1.54×10^{-2}	1.192	3.18	1.45×10^{-2}	1.368	3.11	1.52×10^{-2}
90	1.137	3.29	1.30×10^{-2}	1.237	3.53	1.05×10^{-2}	1.480	3.34	1.36×10^{-2}
120	1.208	3.59	1.10×10^{-2}	1.548	4.03	0.90×10^{-2}	1.851	3.72	1.04×10^{-2}
	Fig.(50) curve 4			Fig.(50) curve 5			Fig.(50) curve 6		

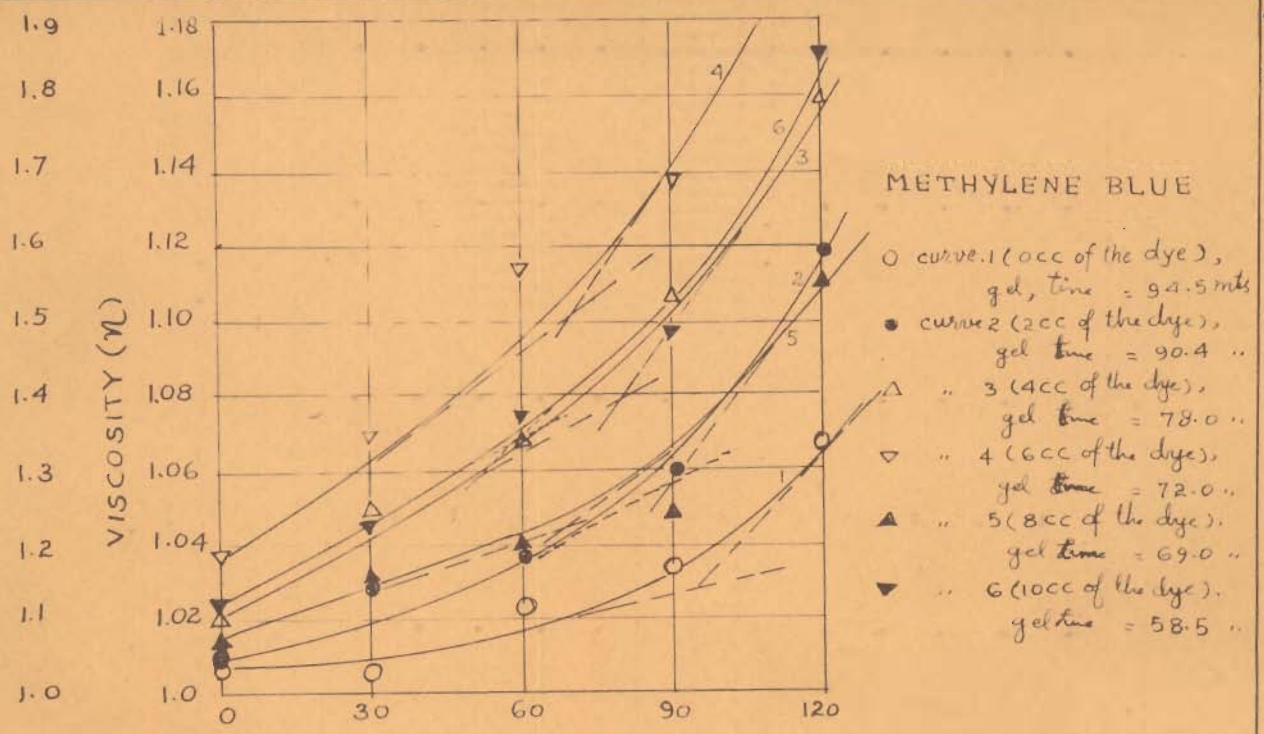


FIG 50. → TIME OF DIALYSIS (MTS)

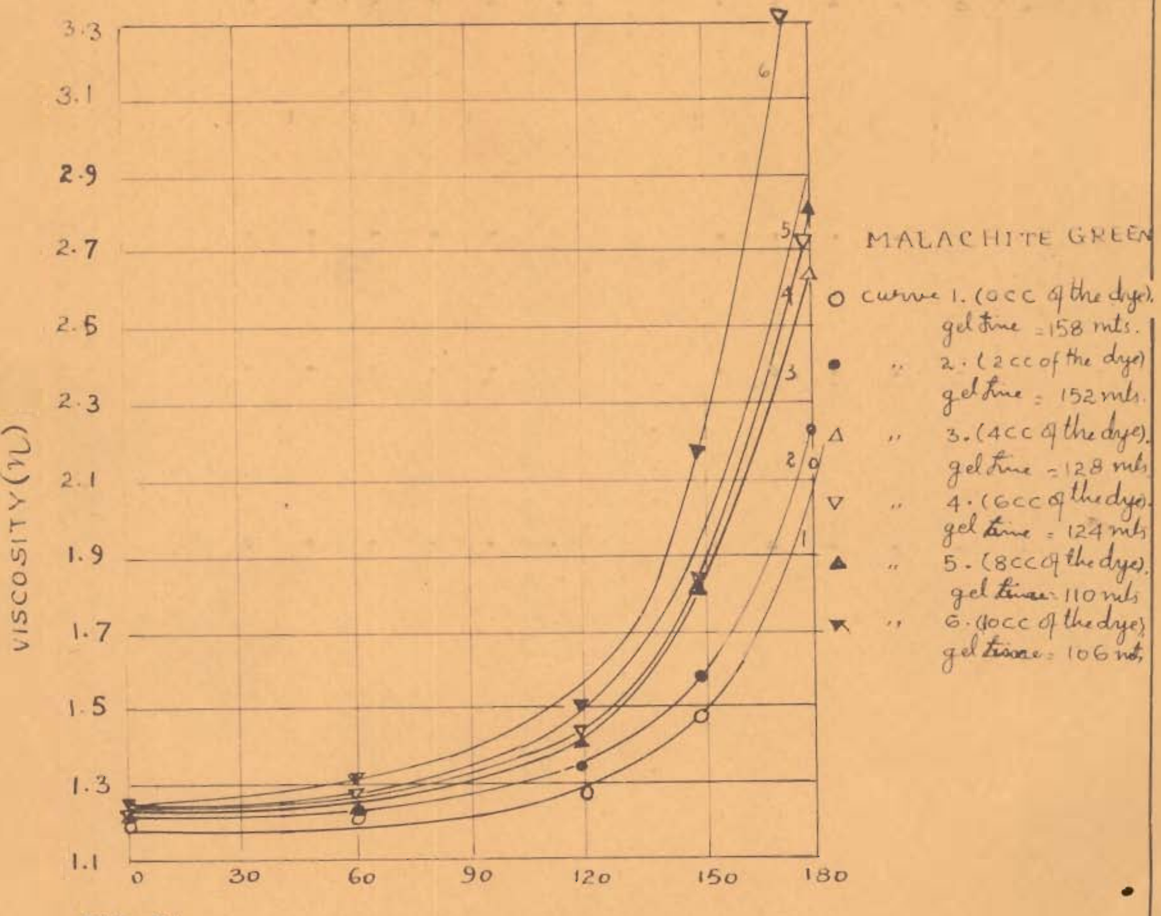


FIG-51. → TIME OF DIALYSIS (MTS)

Set No.4

Table No.4

Variations in viscosity, pH and conductivity with dialysis of silicic acid sol in presence of malachite green.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts)	0 c.c. of the dye			2 c.c. of the dye			4 c.c. of the dye		
	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise	pH	Conductance (mhos)
0	1.199	2.53	2.15x10^{-2}	1.210	2.40	2.25x10^{-2}	1.212	2.32	2.30x10^{-2}
60	1.208	3.39	1.60x10^{-2}	1.232	3.46	1.66x10^{-2}	1.239	3.42	1.70x10^{-2}
120	1.276	3.74	1.06x10^{-2}	1.335	3.84	1.15x10^{-2}	1.405	3.93	1.18x10^{-2}
150	1.469	4.04	0.90x10^{-2}	1.564	3.88	0.95x10^{-2}	1.794	3.86	1.02x10^{-2}
180	2.136	4.52	0.74x10^{-2}	2.225	4.24	0.85x10^{-2}	2.629	4.06	0.88x10^{-2}
	Fig.(51) curve 1			(Fig.(51) curve 2			Fig.(51) curve 3		

	6 c.c. of the dye			8 c.c. of the dye			10 c.c. of the dye		
0	1.218	2.29	2.35x10^{-2}	1.223	2.27	2.35x10^{-2}	1.232	2.25	2.36x10^{-2}
60	1.251	3.40	1.65x10^{-2}	1.277	3.28	1.72x10^{-2}	1.285	3.18	1.75x10^{-2}
120	1.429	3.75	1.10x10^{-2}	1.406	3.77	1.12x10^{-2}	1.508	3.65	1.20x10^{-2}
150	1.816	3.76	0.92x10^{-2}	1.805	3.72	0.95x10^{-2}	2.171	3.67	1.05x10^{-2}
180	2.420	4.02	0.78x10^{-2}	2.808	4.00	0.78x10^{-2}	4.889	3.99	0.88x10^{-2}
	Fig.(51) curve 4			Fig.(51) curve 5			Fig.(51) curve 6		

Set No.5

Table No.5

Variations in viscosity with increasing concentration of methyl orange, alizarin sulphonic acid, methylene blue and malachite green.

Tempt. = 30° ± 0.1°C, P = 35.2 cms. of water

Dyes	0 c.c. of the dye	2 c.c. of the dye	4 c.c. of the dye	6 c.c. of the dye	8 c.c. of the dye	10 cc of the dye	
	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity centipoise)	
methyl orange	0.8007	0.8217	0.8230	0.8241	0.8243	0.8258	Fig (56) curve 1.
alizarin sulphonic acid	0.8007	0.8237	0.8237	0.8239	0.8241	0.8249	Fig (56) curve 2
methylene blue	0.8007	0.8245	0.8245	0.8247	0.8249	0.8250	Fig (56) curve 3
malachite green	0.8007	0.8224	0.8224	0.8250	0.8254	0.8271	Fig (56) curve 4

DISCUSSION

Before discussing the experimental results on the gelation time of silicic acid sol as influenced by the presence of dyes, it is worthwhile to consider the behaviour of the pure sol when converted into a gel by prolonged dialysis. A plot of time of dialysis against viscosity would reveal that after a certain stage of dialysis there is an abrupt increase in viscosity. It is at this stage that optimum conditions necessary for the conversion of the sol into a gel are realised. The time after which this change takes place may be termed as gelation time (12,13), which is quite distinct from the time of setting which is ordinarily taken as the time required for any gel forming mixture to set into a gel. A perusal of the data (Table 6) would reveal that the time of setting become minimum only when the sol has been dialysed sufficiently to cross the limit pertaining to gelation time.

Table No.6

Time of setting and gelation time for a dialysed silica sol of pH 1.5.

Time of dialysis (mts)	Sol 1.		Sol II		Sol III		Sol IV		Gelation time from curves between time of dialysis & viscosity
	Setting time by Fleming's method	Viscosity (centipoise)	Setting time by Fleming's method	Viscosity (centi-poise)	Setting time by Fleming's method	Viscosity (centi-poise)	Setting time by Fleming's method	Viscosity (centi-poise)	
0	60 hrs.	1.213	63 hrs.	0.9940	62 hrs.	1.008	61 hrs.	1.199	Sol 1-163 m
60	12 "	1.260	15 "	1.001	14 "	1.024	11 "	1.208	Sol.II-75mt
120	6 "	1.334	4 "	1.483	4 "	1.066	7 "	1.276	Sol.III-95 mts.
150	3 "	1.526	3 "	1.526	-	-	4 "	1.469	Sol.IV-158 mts.
180	1 "	2.315	1.5"	1.773	-	-	1 "	2.136	

Undoubtedly rise in viscosity of colloidal systems may be explained in the light of factors, viz., solvation, electroviscous effect, aggregation of particles etc. in the case of pure sois, a forthright explaination is difficult to give for complex systems comprising of mixtures of a sol and a foreign substance (electrolyte or non-electrolyte) or two different sols. In such cases due consideration has to be given to structural changes accompanying the interaction of the different chemical entities present. It would be highly interesting if investigations on such complex colloidal systems can be carried out by the simple techniques of viscometry and the results are explained interms of what we have designated as gelation time.

The data on the viscosities of sol-dye mixtures may be studied from two angles.

1. Variations in viscosity with progressive dialysis in presence of a fixed amount of dye, when abrupt change in viscosity takes place.

2. Change in viscosity with the addition of gradually increasing amount of the dye for a dialysed sol.

Although a continuous increase in viscosity with dialysis is observed in all cases, the extent to which this change takes place is dependent on the nature of the dye employed. Thus for a fixed concentration of the dye, viz., 4.0 mM/litre of the dye the extent of variations in different cases are as shown in the following table.

Table No.7

Variations in viscosity with dialysis of silica-dye sol mixtures

Time of dialysis (mts.)	Viscosity pure sol (centipoise Sol.I	Viscosity sol+ methyl orange (centipoise)	Viscosity pure sol (centipoise Sol.II	Viscosity sol+ alizarin sulphonic acid (centipoise)	Viscosity pure sol (centipoise Sol.III.	Viscosity sol+methylene blue (centipoise)	Viscosity pure sol (centipoise Sol.IV (	Viscosity sol + Malachite green (centipoise).
0	1.213	1.287	0.9940	1.002	1.008	1.037	1.199	1.218
60	1.260	1.340	1.001	1.017	1.024	1.113	1.208	1.251
120	1.334	1.445	1.483	1.184	1.066	1.208	1.276	1.429
150	1.526	1.783	1.526	1.210	-	-	1.469	1.816
180	2.315	2.279	1.773	1.311	-	-	2.136	2.420

From the above it is evident that the overall increase in viscosity is less in the case of acid-dye sol mixtures than in the pure sols. The overall increase being methyl orange (77%), alizarin sulphonic acid (31%) as against 90% and 78% of the pure sols respectively. With the basic dyes the results are, however, quite different, Here the overall increase in viscosity is larger (16.5% for methylene blue and 98.6% for malachite green) as against 5.7% and 78% of pure sols respectively.

The large increase in viscosity of the pure sol can be explained simply in terms of hydration or solvation although electroviscous effects may also be operative but to a lesser extent in view of the almost uncharged nature of the silica particles (14,15) in a sol prepared at pH 1.5. The difference in the relative variations in viscosity with dialysis between the pure sol and sol-dye mixture would, however, not be explained simply in terms of hydration or solvation but in terms of the colloid-chemical behaviour of the new aggregates formed by the interaction of the dye with the silica particles. In this context the results on the change in viscosity and pH with concentration after a fixed period of dialysis are worth considering.

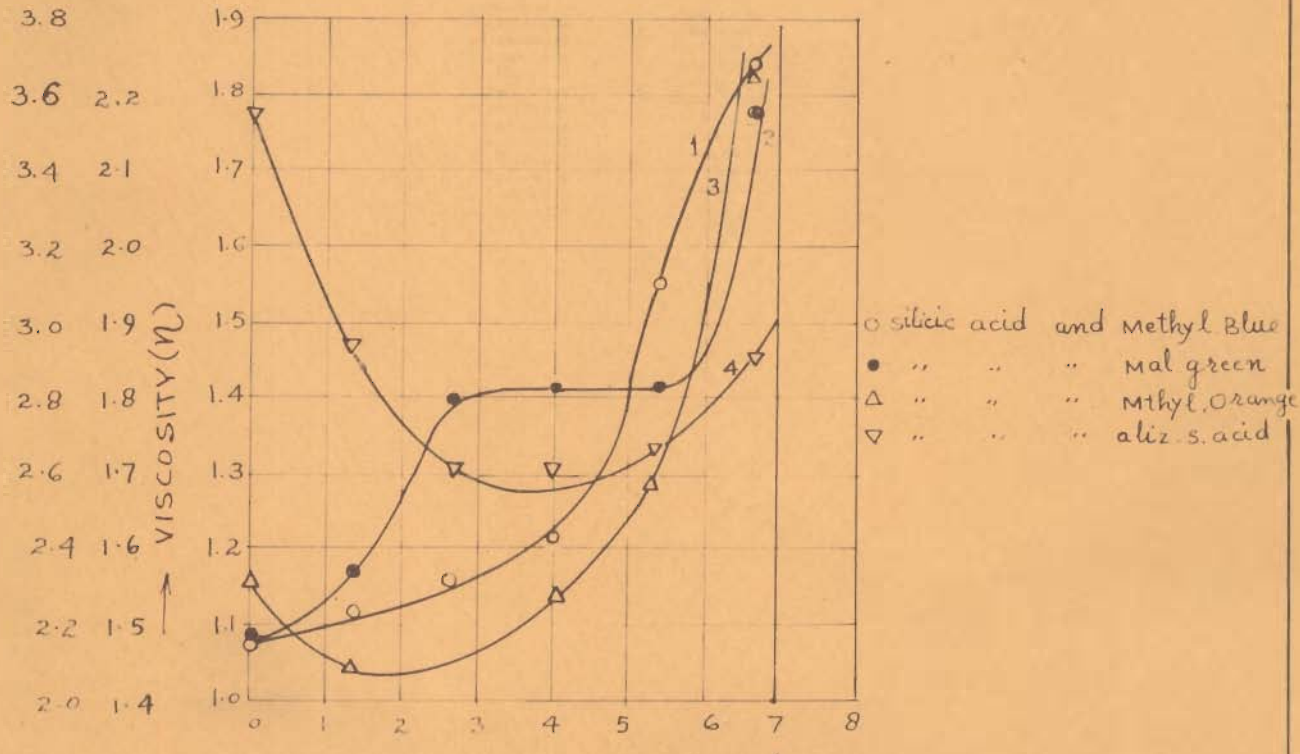


FIG-52. → CONC. OF DYE (mM/LITRE)

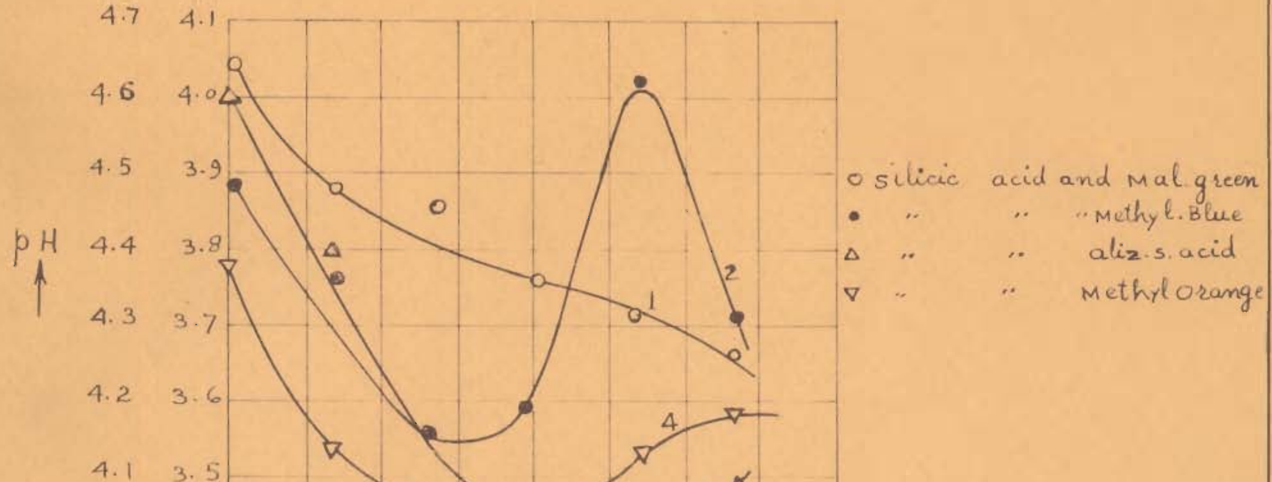


FIG-53. → CONC. OF DYE (mM/LITRE)

Table No.8

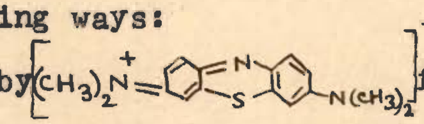
Variation in viscosity and pH of a dialysed silica sol in presence of increasing amount of the dye.

Conc. of dye m.M/lit.	Viscosity silicic acid + methylene blue mixture (centipoise)	pH silicic acid + methylene blue mixture	Viscosity silicic acid + malachite green mixture (centipoise	pH silicic acid + malachite green mixture	Viscosity silicic acid + methyl orange (centipoise)	pH silicic acid + methyl orange	Viscosity silicic acid + aliz.s. acid mixture (centipoise)	pH silicic acid + aliz.s. acid mixture
0	1.066	3.88	1.469	4.04	2.315	4.38	1.773	4.60
1.33	1.118	3.76	1.564	3.88	2.096	4.14	1.407	4.40
2.66	1.158	3.56	1.794	3.86	-	-	1.311	4.14
4.00	1.208	3.59	1.816	3.76	2.279	4.05	1.311	4.04
5.33	1.548	4.03	1.805	3.72	2.580	4.13	1.331	4.02
6.66	1.851	3.72	2.171	3.67	3.703	4.18	1.463	4.08
	Fig (52) Curve 1.	Fig (53) Curve 2.	Fig (52) Curve 2	Fig (53) Curve 1	Fig (52) Curve 3	Fig (53) Curve 4	Fig (52) Curve 4	Fig (53) Curve 3.

A plot of concentration of dye against viscosity would reveal that the viscosity increases with increase in concentration of the dye both in the case of methylene blue and malachite green although the nature of curves is slightly different in both the cases (Fig.52). With acid dyes the behaviour is altogether different, the concentration-viscosity curves showing a decrease over a long concentration range followed by a slight increase in the case of alizarin sulphonic acid and marked increase in the case of methyl orange (Fig.52).

Another factor worth taking into account while explaining the gelation tendency of silicic acid in presence of dyes is the structure of the dyes and the molecular rearrangements they may undergo in the different pH ranges. Since the silicic acid sol has a fairly low pH, the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

Since the existence of uncharged silica particles in the sol may be attributed to the strong adsorption of counter H^+ and subsequent appearence of OH groups on the surface of silica micelle, Adsorption of methylene blue would take place in the following ways:

Replacement of H^+ ions by  followed by its subsequent adsorption. Since such big cation cannot enter into the electronic structure of $\bar{O}$ ion, addition of methylene blue would not form a definite compound or group with the cation of the dye, and, therefore the possibility of chemical adsorption is very little. Physical adsorption can, therefore, be expected. Our results on the decrease in

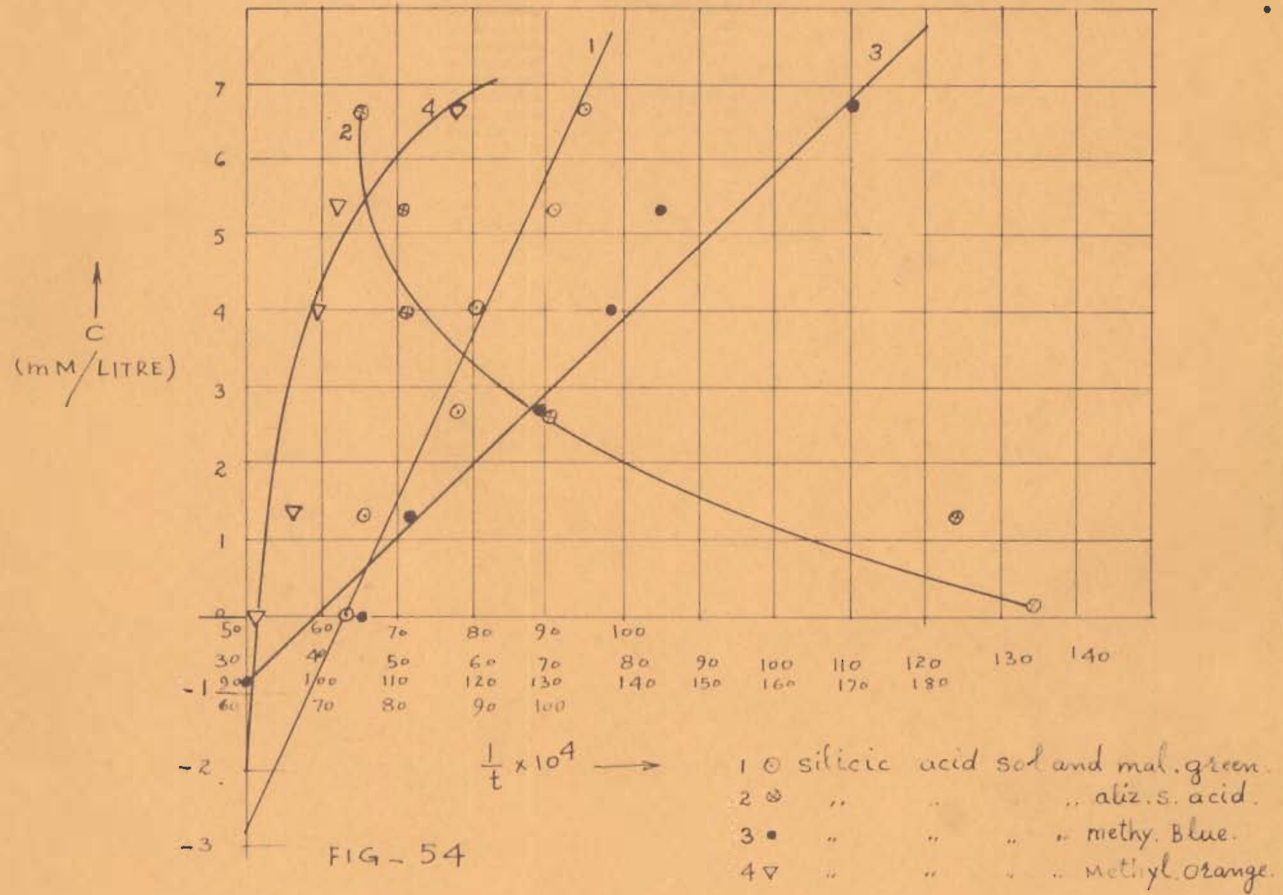

C (mM/LITRE)
7
6
5
4
3
2
1
0
-1
-2
-3
1
2
3
4
50 60 70 80 90 100
30 40 50 60 70 80 90 100 110 120 130 140
90 100 110 120 130 140 150 160 170 180
60 70 80 90 100
$\frac{1}{t} \times 10^4$ →
1 ⊙ silicic acid sol and mal. green.
2 ⊗ ,, ,, ,, aliz. s. acid.
3 ● ,, ,, ,, methy. Blue.
4 ▽ ,, ,, ,, Methyl. Orange.

FIG_54

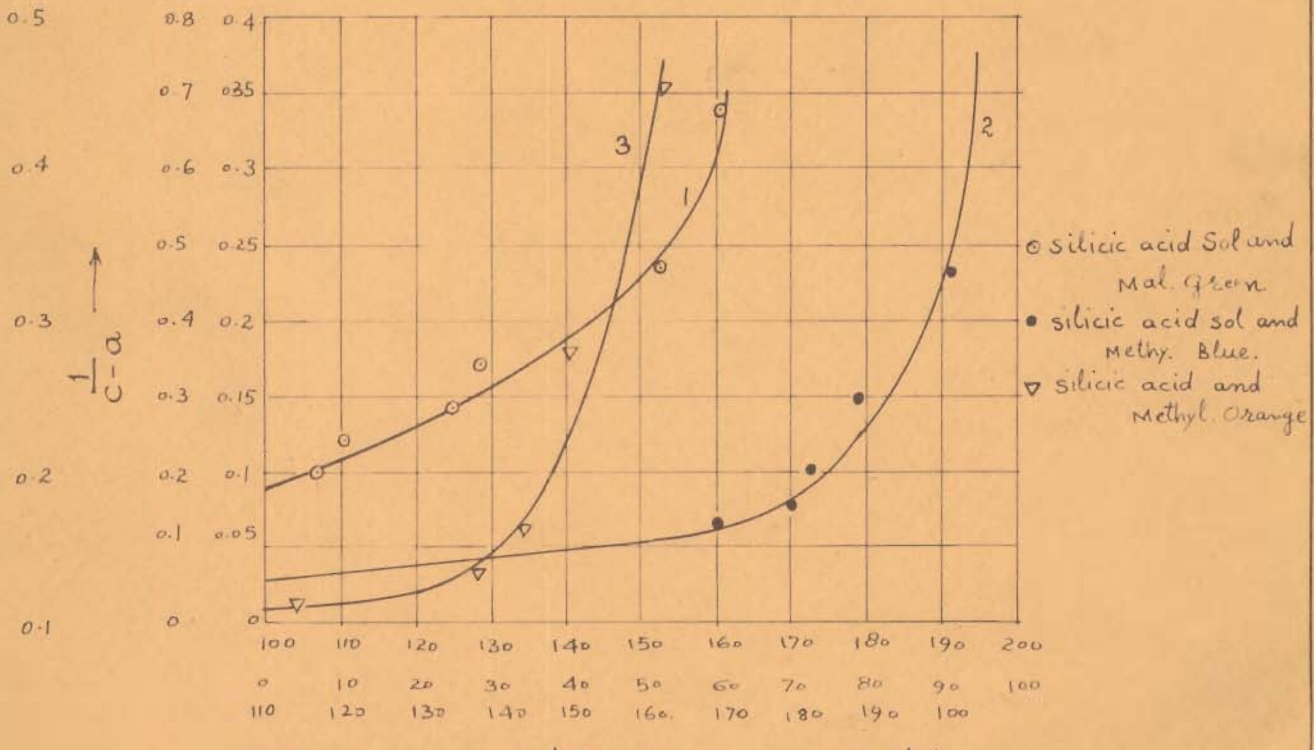

0.5 0.4 0.3 0.2 0.1
0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
0.4 0.35 0.3 0.25 0.2 0.15 0.1 0.05 0
$\frac{1}{C-a}$
1
2
3
100 110 120 130 140 150 160 170 180 190 200
0 10 20 30 40 50 60 70 80 90 100
110 120 130 140 150 160 170 180 190 100
⊙ silicic acid Sol and Mal. Green
● silicic acid sol and Methy. Blue.
▽ silicic acid and Methyl. Orange
→ t (GELATION TIME IN mts).

FIG - 55

pH and physical adsorption Chapter III. support this mechanism. The hydration accompanying the adsorption of basic dye seems to be connected with the gradual increase in aggregation upto a critical size. When hydration is maximum a sudden increase in viscosity leads one to believe that after the critical size has been attained the gel formation starts (Fig.52). Another factor which should not, however, be lost sight of is the possible combination between the sulphur of the dye and the OH of the silanol group of silicic acid.

Preliminary experiments have shown that methylene blue does not change its colour either in the acid or basic medium. The addition of sol, however, brings about a slight deepening of the colour which may be due to the chemical interaction between S of the dye and OH of the silanol group. The results on the variation in pH with addition of methylene blue also support this view (Fig.53). It appears that upto a certain concentration the adsorption phenomenon is operative resulting in the release of H^+ ions but afterwards chemical combination takes place resulting in irregular variations in pH. The behaviour with malachite green can also be explained on similar lines except for the fact that there is nothing inherent in the structure of the molecule which may point towards some sort of chemical interaction between the dye and the active sites of the silicic acid sol.

Another aspect from which the gelation can be studied is that of controlled coagulation of silic acid by the addition of dye. On plotting 'C' (Concentration of dye) and 1/t and 1/c-a and t (time of gelation), typical curves are obtained for Bhattacharya's equation (16) for coagulation of hydrophobic sols by electrolytes. These curves, however, differ significantly from the usual ones in one respect, that is, the value of a (critical stability concentration) comes out to be negative (Fig.54). Although the negative values of the constants a (c.s.c.) has no real significance they point towards the fact that in highly hydrated system like that of silicic acid gelation would not necessarily take place through controlled coagulation. However, controlled coagulation may become operative in presence of foreign substances. It is for this reason that silicic acid sol undergoes gelation in a shorter time in presence of basic dyes for equally dialysed samples. Since both the sol and the dye do not come out of the dialysing bag during dialysis an inter-relationship between the time of gelation and concentration of dye for dialysed samples is justifiable.

Alizarin sulphonic acid is well known for its tendency to form colour lakes with metal hydrous oxide sols through exchange adsorption. This behaviour would not be exhibited by silicic acid in view of the nonexistence of counter ions in its double layer. The only possible way in which alizarin sulphonic acid can influence the gelation of silicic acid can, therefore, be through compound formation. Since a change in the original colour of the dye from light yellow to violet is observed on the addition of the sol after prolonged dialysis, there is a great possibility of the combination between the silanol and the phenolic group, resulting in a rearrangement involving quinonoid structure.

The decrease in viscosity with concentration (curve 4 Fig.52) as well as marked variation in pH (curve 3 Fig.53) support this view point. It appears that behaviour of the acid dyes is different from that of the basic dyes and the possibility of realising gelation through controlled coagulation is very remote. Here aggregation is very difficult to achieve. The rate of gelation is very slow and gelation can only set in when the critical size-hydration limit is reached. The initial decrease in viscosity may be attributed to the peptisation of the sol by the small amounts of the dye. However, with increase in concentration of the dye the hydration tendency increases resulting in a large increase of viscosity. Such a behaviour is quite likely since together with hydration, orientation of the methyl orange to the quinonoid structure is also likely takes place. The initial decrease of viscosity may be attributed to chemical changes accompanying dye-sol interaction where as purely adsorption effects seems to be operative in the higher concentration range. It is for this reason that the decrease in pH with concentration is not so marked as in the case of alizarin sulphonic acid (Fig.53 curve3). An appreciable decrease in pH is observed only in the later stages. The data on the variations in conductance (tables, 1,2,3,4 page 150-153) with progressive dialysis fail to provide either any information regarding the difference in behaviour of the different dyes towards silicic acid sol or the influence of the dyes on the gelation process. The only little information obtained is that conductivity falls off rapidly as the sol changes into the gel and this effect is more marked with the basic dyes. The entrenchment of the liquid by the gel structure make the ions less mobile with the result that the conductivity decreases. Once the gel structure sets in, the conductance values acquire almost a constant value.

SOL-GEL TRANSFORMATION OF FERRIC HYDROXIDE AND ALUMINIUM HYDROXIDE SOLS IN PRESENCE OF ACID AND BASIC DYES

Investigations on the sol-gel transformation of inorganic gel forming systems containing dyes have not so far been studied. The few references available in the existing literature (1-4) do not deal with this aspect of the problem but describe the influence of dyes on the stability on hydrophobic sols. Since hydrous oxide sols are widely employed as mordants, a study of their gelation in presence of acid and basic dyes was considered worth attempting. In this chapter the results of the studies on the interaction of alizarin sulphonic acid, methyl orange, malachite green and methylene blue dyes with ferric oxide and aluminium oxide sols have been discussed.

EXPERIMENTAL

Preparation of solutions:

(a) Stock solutions of the concentrations 2.0×10^{-2} M of dyes (B.D.H or Merck product) alizarin sulphonic acid (sod. salt), methyl orange (sod.salt), methylene blue (cl^{-}) and malachite green (cl^{-}) were prepared in double distilled water.

(b) Preparation of ferric hydroxide sol:

Although a number of methods have been suggested by Pean deSt. Gilles, Giolitti and Graham for the preparation of ferric hydroxide sol, the method recommended by Graham was employed for the preparation of the positively charged ferric hydroxide sol. The ferric oxide content was determined gravimetrically. The pH of the sol was adjusted to 3.76 by dialysing the sol in a parchment bag.

(c) Preparation of aluminium hydroxide sol:

Vide chapter II page 76. Here pH was adjusted to 3.70.

Apparatus and technique:

Time of setting of gel: The time of gelation with dialysis was determined by Fleming's method as given in chapter IV.

Viscosity, pH and conductivity measurements:

These measurements were carried out as given in chapter IV.

Cataphoretic measurements:

Cataphoretic measurements were carried out under constant voltage in the same manner as given in chapter II.

Ferric hydroxide sol:

40 c.c. of ferric hydroxide sol was taken in each set of experiments (Fe_2O_3 = 2.49 gms per 100 ml). Varying amount of dyes were mixed. The total volume in each set was kept equal to 60 c.c. The mixture of each set was taken in parchment paper bags of the same size and variations in viscosity, pH, ζ-potential and conductance measured with time of dialysis.

The following sets of dye-sol mixtures were investigated.

Set No.1 :

Ferric oxide sol (24.9 gms per litre) + alizarin sulphonic acid (2.0×10^{-2}M) mixtures. Each mixture contains 40 c.c. of the sol and varying amounts (0 c.c., 1 c.c., 2 c.c. 2.5 c.c., 3.0 c.c., 3.5 c.c.) of the dye. Total volume was made upto 60 c.c. by double distilled water.

Set No.2

Ferric oxide sol (24.9 gms per litre) + methyl orange (2.0×10^{-2}M) mixtures. Each mixture contains 40 c.c. of the sol and varying amounts (0 c.c., 2 c.c., 3 c.c., 4 c.c.) of the dye. Total volume was made upto 60 c.c. by double distilled water.

Set No.3:

Ferric oxide sol (24.9 gms per litre) + methylene blue (2.0×10^{-2}M) mixtures. Each mixture contains 40 c.c. of the sol and varying amounts (0 c.c., 5 c.c., 6 c.c., 7 c.c) of the dye. Total volume was made upto 60 c.c. by double distilled water.

Set No.4:

Ferric oxide sol (24.9 gms per litre) + malachite green (2.0×10^{-2}M) mixtures. Each mixture contains 40 c.c. of the sol and varying amounts (0 c.c., 5 c.c., 6 c.c., 7 c.c.) of the dye. Total volume was made upto 60 c.c. by double distilled water.

Initial pH's of sol and dyes are 3.76, 2.32 (alizarin sulphonic acid), 6.10 (methyl orange), 3.48 (methylene blue), 2.36 (malachite green) respectively.

For measuring the variations in viscosity at different dilutions of the dye solutions, the following set No.5 was investigated.

Set No.5:

1 c.c., 2 c.c., 2.5 c.c., 3 c.c., 3.5 c.c. of alizarin s. acid (2.0×10^{-2}M). Total volume was made upto 60 c.c by double distilled water.

2 c.c., 3 c.c., 4 c.c. of methyl orange (2.0×10^{-2}M)

total volume was made upto 60 c.c. by double distilled water.

5 c.c., 6 c.c., 7 c.c. of methylene blue (2.0×10^{-2}M). Total volume was made upto 60 c.c. by double distilled water.

5 c.c., 6 c.c., 7 c.c. of malachite green (2.0×10^{-2}M). Total volume was made upto 60 c.c. by double distilled water.

Aluminium hydroxide sol:

20 c.c. of aluminium hydroxide (1.0 gms per 100 ml Al_2O_3) was taken in each set of experiments. Varying amounts of dyes were mixed. The total volume in each set was kept equal to 30 c.c. The mixture of each set was taken in parchment paper bags of the same size and variations in viscosity, pH and conductivity measured with time of dialysis.

The following sets of mixtures were used for gelation measurements.

Set No.6:

Alumina sol (10 gms per litre) + alizarin sulphonic acid (2.0×10^{-2}M) mixtures. Each mixture contains 20 c.c. of the sol and varying amounts (0 c.c., 0.5 c.c., 1,0 c.c., 1.5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

Set No.7:

Alumina sol (10 gms per litre) + methyl orange (2.0×10^{-2}M) mixtures. Each mixture contains 20 c.c. of the sol and varying amounts (0.5 c.c., 1.0 c.c., 1.5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

Set No.8:

Alumina sol (10 gms per litre) + methylene blue (2.0×10^{-2}M) mixtures. Each mixture contains 20 c.c. of the sol and varying amounts (0.5 c.c., 1.0 c.c., 1.5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

Set No.9:

Alumina sol (10 gms per litre) + malachite green (2.0×10^{-2}M) mixtures. Each mixture contains 20 c.c. of the sol and varying amounts (0.5 c.c., 1.0 c.c., 1.5 c.c.) of the dye. Total volume was made upto 30 c.c. by double distilled water.

Initial pH's of sol and dyes are 3.70, 2.32 (alizarin sulphonic acid), 6.10(methyl orange), 3.48 (methylene blue), 2.36 (malachite green) respectively.

For measuring the variations in viscosity at different dilutions of the dye solutions, the following set was used.

Set No.10:

0.5 c.c., 1.0 c.c., 1.5 c.c. (concentration = 2.0×10^{-2}M) of each dye. Total volume was made upto 30 c.c. by double distilled water.

TABLE No.1

Set No.1

Variations in viscosity, pH, ζ-potential and conductivity with dialysis of ferric oxide sol in presence of alizarin sulphonic acid.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water.

Time of dialysis (mts.)	0 c.c. of the dye				1.0 c.c. of the dye				2.0 c.c. of the dye			
	Viscosity (centi-poise)	pH	ζ-potential (volt)	Conductance (mhos)	Viscosity (centi-poise)	pH	ζ-potential (volt)	Conductance (mhos)	Viscosity (centi-poise)	pH	ζ-potential (volt)	Conductance (mhos)
0	0.9260	3.78	5.074×10^{-8}	0.80×10^{-3}	0.9408	3.99	9.02×10^{-8}	1.20×10^{-3}	0.9389	4.06	7.71×10^{-8}	1.5×10^{-3}
480	0.9311	4.30	3.825×10^{-8}	0.76×10^{-3}	0.9461	4.19	9.07×10^{-8}	1.05×10^{-3}	0.9466	4.21	7.78×10^{-8}	1.22×10
1080	0.9426	4.84	2.583×10^{-8}	0.60×10^{-3}	0.9479	4.70	7.78×10^{-8}	0.59×10^{-3}	0.9501	4.68	7.80×10^{-8}	0.71×10
1740	0.9590	5.07	2.124×10^{-8}	0.53×10^{-3}	0.9583	4.91	3.94×10^{-8}	0.48×10^{-3}	0.9607	4.93	5.26×10^{-8}	0.52×10^{-3}
2640	1.023	5.28	2.002×10^{-8}	0.40×10^{-3}	0.9886	5.34	2.31×10^{-8}	0.25×10^{-3}	0.9913	5.32	5.09×10^{-8}	0.35×10^{-3}

	2.5 c.c. of the dye				3.0 c.c. of the dye				3.5 c.c. of the dye			
0	0.9434	4.06	6.462×10^{-8}	1.60×10^{-3}	0.9499	4.08	5.205×10^{-8}	1.78×10^{-3}	0.9596	4.08	3.94×10^{-8}	1.92×10^{-3}
480	0.9521	4.22	6.519×10^{-8}	1.29×10^{-3}	0.9570	4.23	5.243×10^{-8}	1.32×10^{-3}	0.9763	4.24	4.01×10^{-8}	1.38×10^{-3}
1080	0.9583	4.65	7.189×10^{-8}	0.71×10^{-3}	0.9665	4.73	6.200×10^{-8}	0.68×10^{-3}	0.9949	4.69	5.45×10^{-8}	0.74×10^{-3}
1740	0.9709	4.82	5.990×10^{-8}	0.56×10^{-3}	1.002	4.85	5.489×10^{-8}	0.52×10^{-3}	1.031	4.85	6.88×10^{-8}	0.55×10^{-3}
2640	0.9945	5.20	5.811×10^{-8}	0.36×10^{-3}	1.180	5.36	5.362×10^{-8}	0.42×10^{-3}	1.068	5.26	6.24×10^{-8}	0.44×10^{-3}

TABLE No.2

Set No.2

Variations in viscosity, pH, ζ-potential and conductivity with dialysis of ferric oxide sol in presence of methyl orange.

Tempt. = $30^{\circ}C \pm 0.1^{\circ}C$, P = 35.2 cms. of water

Time of dialysis (mts.)	0 c.c. of the dye				2 c.c. of the dye			
	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)
0	0.9260	3.78	5.074×10^{-8}	0.80×10^{-3}	0.9298	3.82	3.821×10^{-8}	0.85×10^{-3}
480	0.9311	4.30	3.825×10^{-8}	0.76×10^{-3}	0.9363	4.34	2.565×10^{-8}	0.78×10^{-3}
1080	0.9426	4.84	2.583×10^{-8}	0.60×10^{-3}	0.9530	4.88	2.611×10^{-8}	0.60×10^{-3}
1740	0.9590	5.07	2.124×10^{-8}	0.53×10^{-3}	0.9716	5.14	2.900×10^{-8}	0.53×10^{-3}
2640	1.023	5.28	2.002×10^{-8}	0.40×10^{-3}	1.171	5.34	8.021×10^{-8}	0.40×10^{-3}

	3 c.c. of the dye				4 c.c. of the dye			
0	0.9389	3.84	2.572×10^{-8}	0.92×10^{-3}	0.9515	3.85	1.303×10^{-8}	0.95×10^{-3}
480	0.9389	4.31	2.572×10^{-8}	0.85×10^{-3}	0.9581	4.17	1.312×10^{-8}	0.98×10^{-3}
1080	0.9535	4.77	2.612×10^{-8}	0.65×10^{-3}	0.9736	4.63	1.334×10^{-8}	0.84×10^{-3}
1740	0.9738	5.10	4.200×10^{-8}	0.56×10^{-3}	0.9926	5.01	2.100×10^{-8}	0.80×10^{-3}
2640	1.023	5.28	7.004×10^{-8}	0.45×10^{-3}	1.073	5.23	4.410×10^{-8}	0.56×10^{-3}

TABLE No.3

Set No.3

Variations in viscosity, pH, ζ-potential and conductivity with dialysis of ferric oxide sol in presence of methylene blue.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts.)	0 c.c. of the dye				5 c.c. of the dye			
	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)
0	0.9260	3.78	5.074×10^{-8}	0.80×10^{-3}	0.9255	3.81	3.803×10^{-8}	1.08×10^{-3}
480	0.9311	4.30	3.825×10^{-8}	0.76×10^{-3}	0.9274	4.32	3.812×10^{-8}	0.78×10^{-3}
1080	0.9426	4.84	2.583×10^{-8}	0.60×10^{-3}	0.9353	4.86	3.843×10^{-8}	0.55×10^{-3}
1740	0.9590	5.07	2.124×10^{-8}	0.53×10^{-3}	0.9605	5.14	6.50×10^{-8}	0.48×10^{-3}
2640	1.023	5.28	2.002×10^{-8}	0.40×10^{-3}	1.039	5.28	9.96×10^{-8}	0.35×10^{-3}

	6 c.c. of the dye				7 c.c. of the dye			
0	0.9241	3.84	2.531×10^{-8}	1.15×10^{-3}	0.9237	3.85	1.266×10^{-8}	1.21×10^{-3}
480	0.9315	4.25	3.827×10^{-8}	0.86×10^{-3}	0.9274	4.25	2.541×10^{-8}	0.87×10^{-3}
1080	0.9371	4.80	3.850×10^{-8}	0.60×10^{-3}	0.9361	4.74	3.847×10^{-8}	0.65×10^{-3}
1740	0.9625	5.00	6.850×10^{-8}	0.55×10^{-3}	0.9696	4.95	3.990×10^{-8}	0.56×10^{-3}
2640	1.002	5.18	8.233×10^{-8}	0.44×10^{-3}	0.9954	5.15	4.091×10^{-8}	0.44×10^{-3}

TABLE No.4

Set No.4

Variations in viscosity, pH, ζ-potential and conductivity with dialysis of ferric oxide sol in presence of malachite green

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts.)	0 c.c. of the dye				5 c.c. of the dye			
	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)	Viscosity (centipoise)	pH	ζ-potential (volt)	Conductance (mhos)
0	0.9260	3.78	5.074×10^{-8}	0.80×10^{-3}	0.9350	3.62	1.280×10^{-8}	1.020×10^{-3}
480	0.9311	4.30	3.825×10^{-8}	0.76×10^{-3}	0.9281	4.34	2.542×10^{-8}	0.78×10^{-3}
1080	0.9426	4.84	2.583×10^{-8}	0.60×10^{-3}	0.9426	4.98	2.583×10^{-8}	0.55×10^{-3}
1740	0.9590	5.07	2.124×10^{-8}	0.53×10^{-3}	0.9729	5.14	2.750×10^{-8}	0.49×10^{-3}
2640	1.023	5.28	2.002×10^{-8}	0.40×10^{-3}	1.025	5.31	5.034×10^{-8}	0.35×10^{-3}

	6 c.c. of the dye				7 c.c. of the dye			
0	0.9322	3.60	2.554×10^{-8}	1.09×10^{-3}	0.9410	3.56	1.276×10^{-8}	1.12×10^{-3}
480	0.9281	4.38	2.542×10^{-8}	0.79×10^{-3}	0.9490	4.21	1.273×10^{-8}	0.82×10^{-3}
1080	0.9521	4.98	2.608×10^{-8}	0.57×10^{-3}	0.9499	4.94	2.602×10^{-8}	0.60×10^{-3}
1740	0.9721	5.02	2.900×10^{-8}	0.52×10^{-3}	0.9618	4.98	2.710×10^{-8}	0.52×10^{-3}
2640	1.064	5.25	4.373×10^{-8}	0.41×10^{-3}	1.030	5.18	2.821×10^{-8}	0.41×10^{-3}

STABILITY CURVES

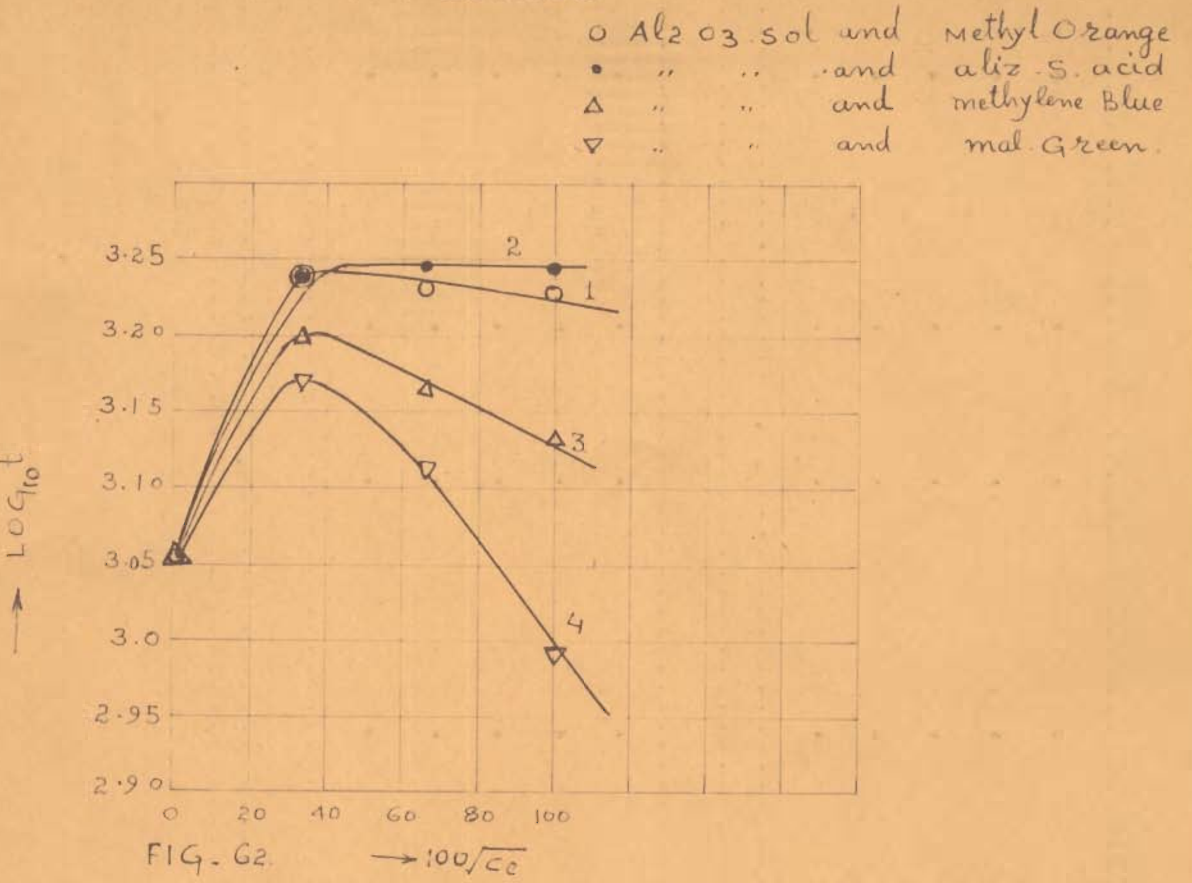


FIG. 62

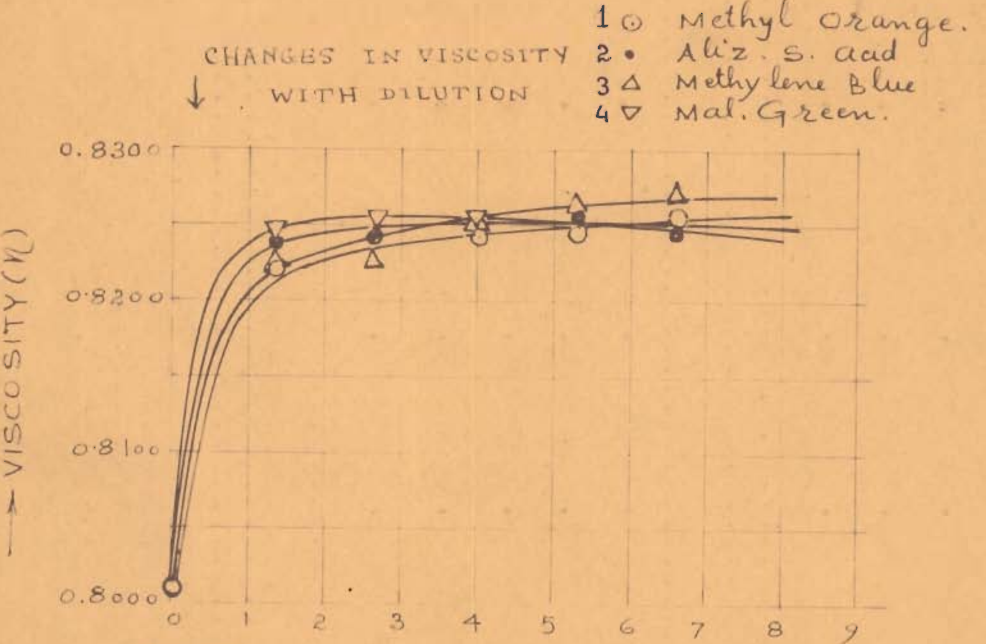


FIG56. → CONC. OF DYE (mM/LITRE)

TABLE No.5

Set No.5

Variations in viscosity of alizarin sulphonic acid, methyl orange, methylene blue and malachite green with increasing concentration of these dyes.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Dyes	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	
alizarin sulphonic acid(1,2,2.5,3,3.5 ccs.)	0.8230	0.8237	0.8237	0.8237	0.8237	Fig.(63) curve(3)
methyl orange (2,3,4 ccs.)	0.8217	0.8217	0.8217	-	-	Fig.(63) curve(4)
methylene blue (5,6,7 ccs.)	0.8243	0.8245	0.8245	-	-	Fig.(63) curve(2)
malachite green (5,6,7 ccs.)	0.8243	0.8250	0.8254	-	-	Fig.(63) curve(1)

Aluminium hydroxide sol:

TABLE No.6

Set No.6

Variations in viscosity, pH and conductivity with dialysis of aluminium hydroxide sol in presence of alizarin sulphonic acid.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts.)	0 c.c. of the dye			0.5 c.c. of the dye			1.0 c.c. of the dye			1.5 c.c. of the dye		
	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)
0	1.081	3.76	5.48×10^{-3}	1.090	3.74	5.56×10^{-3}	1.353	3.60	6.02×10^{-3}	2.300	3.47	5.92×10^{-3}
255	1.055	4.08	2.90×10^{-3}	1.069	4.00	3.23×10^{-3}	1.172	3.88	4.20×10^{-3}	1.643	3.80	4.30×10^{-3}
735	1.063	4.24	1.91×10^{-3}	1.059	4.34	1.43×10^{-3}	1.115	4.27	1.88×10^{-3}	1.557	4.17	2.30×10^{-3}
1300	1.074	4.38	0.58×10^{-3}	1.053	4.33	0.85×10^{-3}	1.095	4.25	1.14×10^{-3}	1.474	4.14	1.45×10^{-3}
1575	1.091	5.40	0.28×10^{-3}	1.046	4.69	0.38×10^{-3}	1.091	4.55	0.49×10^{-3}	1.472	4.37	0.69×10^{-3}
1800	1.130	-	-	1.051	5.40	0.28×10^{-3}	1.143	5.39	0.29×10^{-3}	1.498	4.70	0.35×10^{-3}

TABLE No.7

Set No.7

Variations in viscosity, pH and conductivity with dialysis of aluminium hydroxide sol in presence of methyl orange.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Time of dialysis (mts.)	0.5 c.c. of the dye			1.0 c.c. of the dye			1.5 c.c. of the dye		
	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)	Viscosity (centi-poise)	pH	Conductance (mhos)
0	1.291	3.80	5.77×10^{-3}	2.318	3.84	5.88×10^{-3}	2.120	3.86	5.82×10^{-3}
255	1.228	4.02	3.64×10^{-3}	1.602	3.98	4.05×10^{-3}	1.549	3.99	4.00×10^{-3}
735	1.160	4.18	1.85×10^{-3}	1.364	4.15	2.14×10^{-3}	1.320	4.16	2.06×10^{-3}
1300	1.150	4.21	1.20×10^{-3}	1.227	4.21	1.20×10^{-3}	1.255	4.23	1.08×10^{-3}
1575	1.119	4.47	0.60×10^{-3}	1.171	4.52	0.50×10^{-3}	1.177	4.57	0.44×10^{-3}
1800	1.132	4.60	0.45×10^{-3}	1.179	4.70	0.35×10^{-3}	1.200	4.76	0.31×10^{-3}

TABLE No.8

Set No.8

Variations in viscosity, pH and conductivity with dialysis of aluminium hydroxide sol in presence of methylene blue.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms, of water

Time of dialysis (mts.)	0.5 c.c. of the dye			1.0 c.c. of the dye			1.5 c.c. of the dye		
	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)
0	1.082	3.82	5.40×10^{-3}	1.078	3.82	5.58×10^{-3}	1.080	3.82	5.66×10^{-3}
255	1.042	4.04	2.90×10^{-3}	1.074	4.04	3.10×10^{-3}	1.076	4.01	3.35×10^{-3}
735	1.037	4.36	1.49×10^{-3}	1.081	4.36	1.55×10^{-3}	1.073	4.36	1.75×10^{-3}
1300	1.034	4.34	0.93×10^{-3}	1.081	4.33	0.97×10^{-3}	1.060	4.27	1.19×10^{-3}
1575	1.037	4.72	0.42×10^{-3}	1.096	4.71	0.45×10^{-3}	1.078	4.60	0.56×10^{-3}
1800	1.056	4.80	0.30×10^{-3}	1.100	4.78	0.33×10^{-3}	1.081	4.71	0.42×10^{-3}

TABLE No.9

Set No.9

Variations in viscosity, pH and conductivity with dialysis of aluminium hydroxide sol in presence of malachite green.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms, of water

Time of dialysis (mts.)	0.5 c.c. of the dye			1.0 c.c. of the dye			1.5 c.c. of the dye		
	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)	Viscosity (centipoise)	pH	Conductance (mhos)
0	1.079	3.67	5.35×10^{-3}	1.109	3.51	5.50×10^{-3}	1.093	3.33	5.62×10^{-3}
255	1.062	4.02	3.05×10^{-3}	1.069	3.98	3.02×10^{-3}	1.069	3.99	2.68×10^{-3}
735	1.044	4.36	1.41×10^{-3}	1.059	4.35	1.43×10^{-3}	1.060	4.40	1.08×10^{-3}
1300	1.046	4.34	0.85×10^{-3}	1.047	4.32	0.90×10^{-3}	1.074	4.47	0.56×10^{-3}
1575	1.057	4.76	0.40×10^{-3}	1.059	4.74	0.42×10^{-3}	1.131	4.84	0.22×10^{-3}
1800	1.077	5.38	0.28×10^{-3}	1.059	4.80	0.30×10^{-3}	-	-	-

CHANGES IN VISCOSITY OF DYES WITH DILUTION

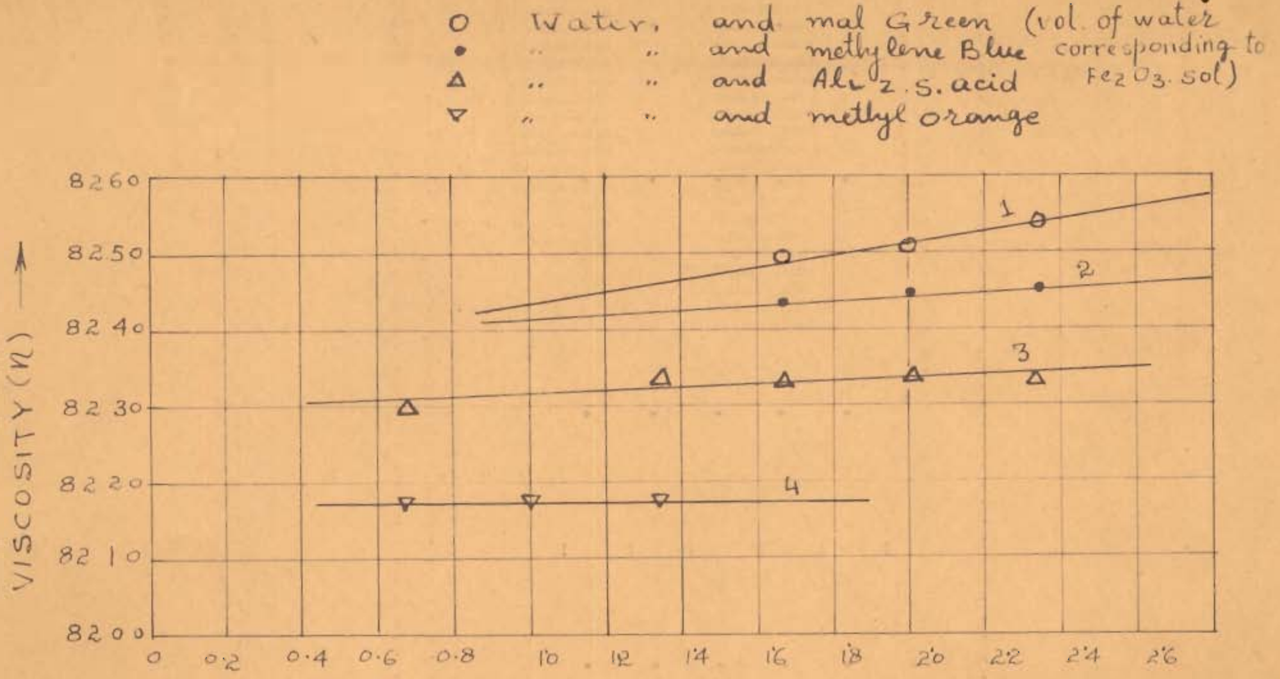


FIG-63. → CONC. of DYE (mM/LITRE)

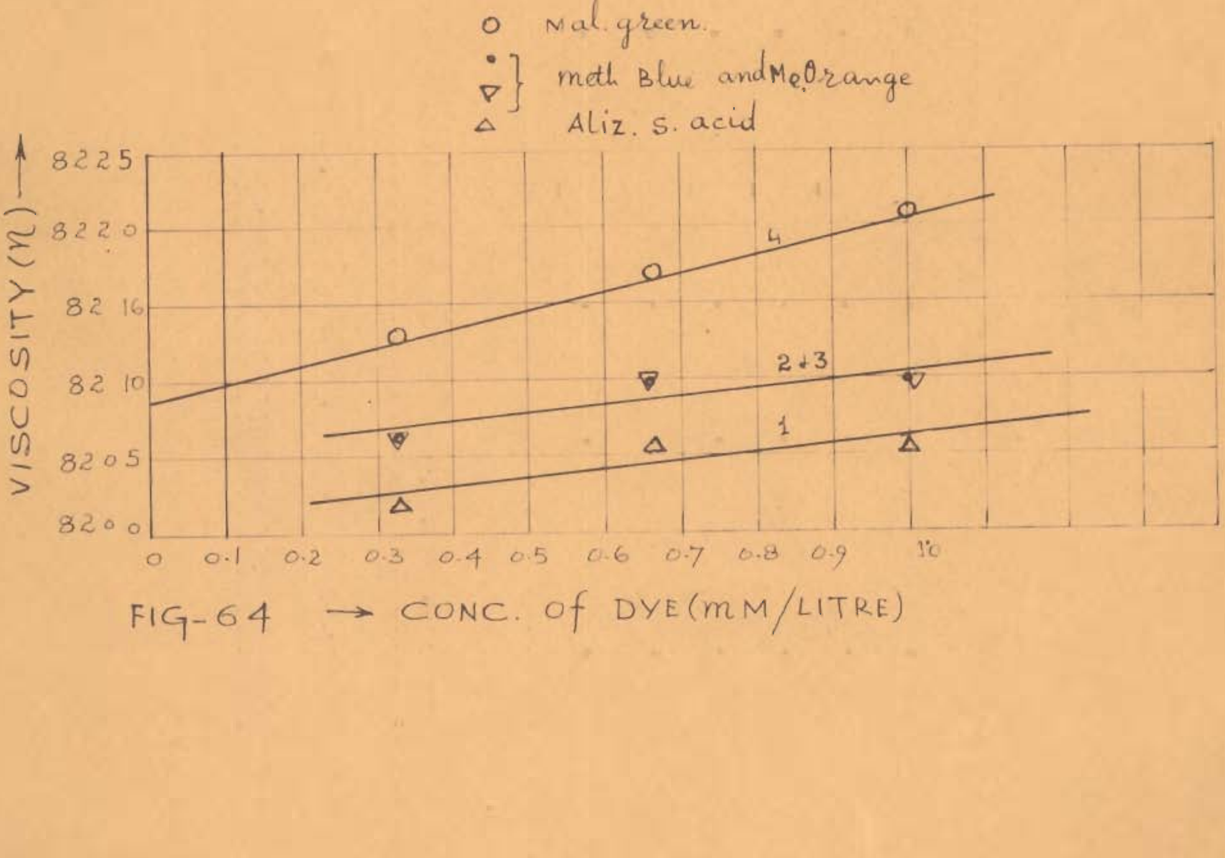


FIG-64 → CONC. of DYE (mM/LITRE)

TABLE No.10

Set No.10

Variations in viscosity with increasing concentration of alizarin sulphonic acid, methyl orange, methylene blue and malachite green.

Tempt. = 30°C ± 0.1°C, P = 35.2 cms. of water

Dyes	0.5 c.c. of the dye	1.0 c.c. of the dye	1.5 c.c. of the dye	
	Viscosity(centipoise)	Viscosity (centipoise)	Viscosity (centipoise)	
alizarin sulphonic acid	0.8202	0.8206	0.8206	Fig.(64) curve(1)
methyl orange	0.8206	0.8210	0.8210	Fig.(64) Cruve(2)
methylene blue	0.8206	0.8210	0.8210	Fig.(64) curve(3)
malachite green	0.8213	0.8217	0.8221	Fig.(64) curve(4)

VARIATIONS IN ζ-POTENTIAL

○ Aliz. S. acid and Fe_2O_3 sol.
● Methyl orange and " ".
▽ Meth. Blue and " ".
△ Mal. Green and " ".

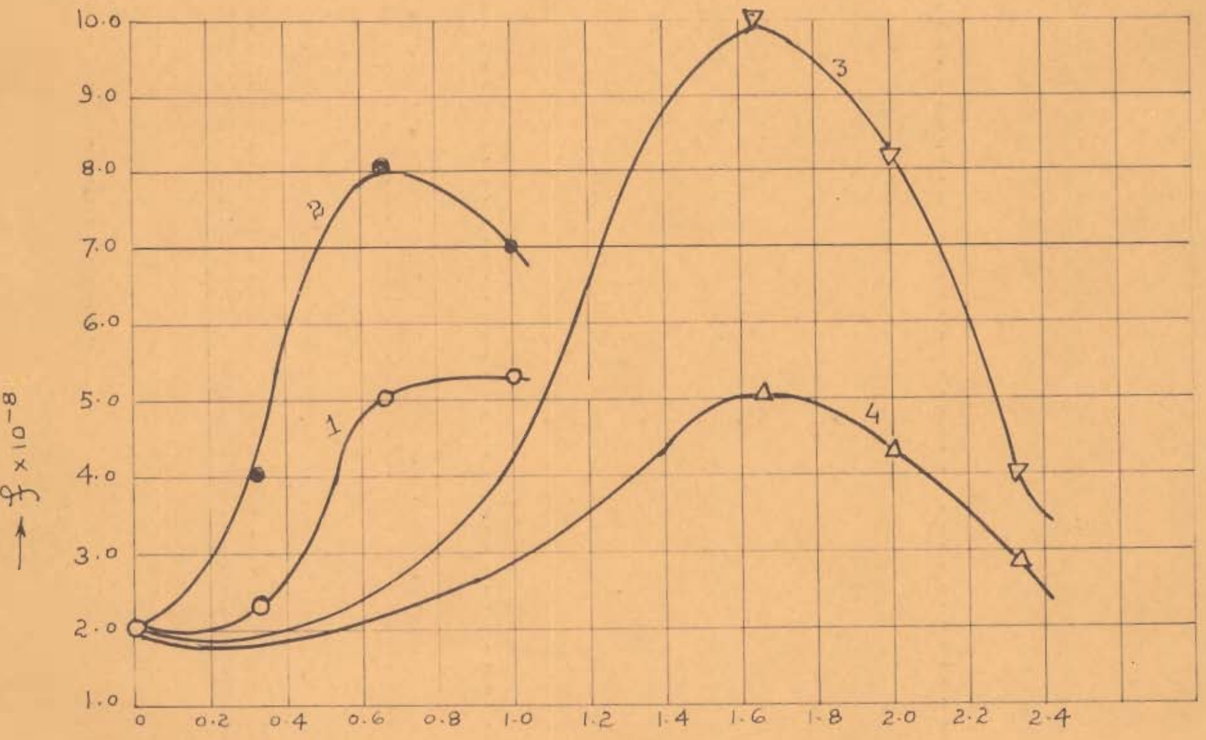


FIG-57.

DISCUSSION

Ferric oxide sol:

Before discussing the experimental results on the sol-gel transformation of ferric hydroxide sol as influenced by the presence of dyes, it is worthwhile to consider the behaviour of the pure sol when converted into a gel by prolonged dialysis. A plot of time of dialysis against viscosity would reveal that after a certain stage of dialysis there is an abrupt increase in viscosity. It is at this stage that conditions necessary for the conversion of the sol into a gel are realized. The time after which this change takes place may be termed as gelation time which is quite distinct from the time of setting which is ordinarily taken as the time required for any gel forming mixture to set into a gel. A perusal of the data (table no.11) would reveal that the time of setting becomes minimum (10 hours) only when the sol has been dialysed beyond the gelation time.

TABLE No.11

Time of setting and gelation time for dialysed Fe_2O_3 sol

Time of dialysis (mts.)	Time of setting by Fleming's method	Viscosity (centipoise)	Gelation time from curve between time of dialysis and viscosity
0	-	0.9260	
480	-	0.9311	
1080	-	0.9426	1740 mts.
1740	24 hours	0.9590	
2640	10 hours	1.023	

Fig (68) Curve 1

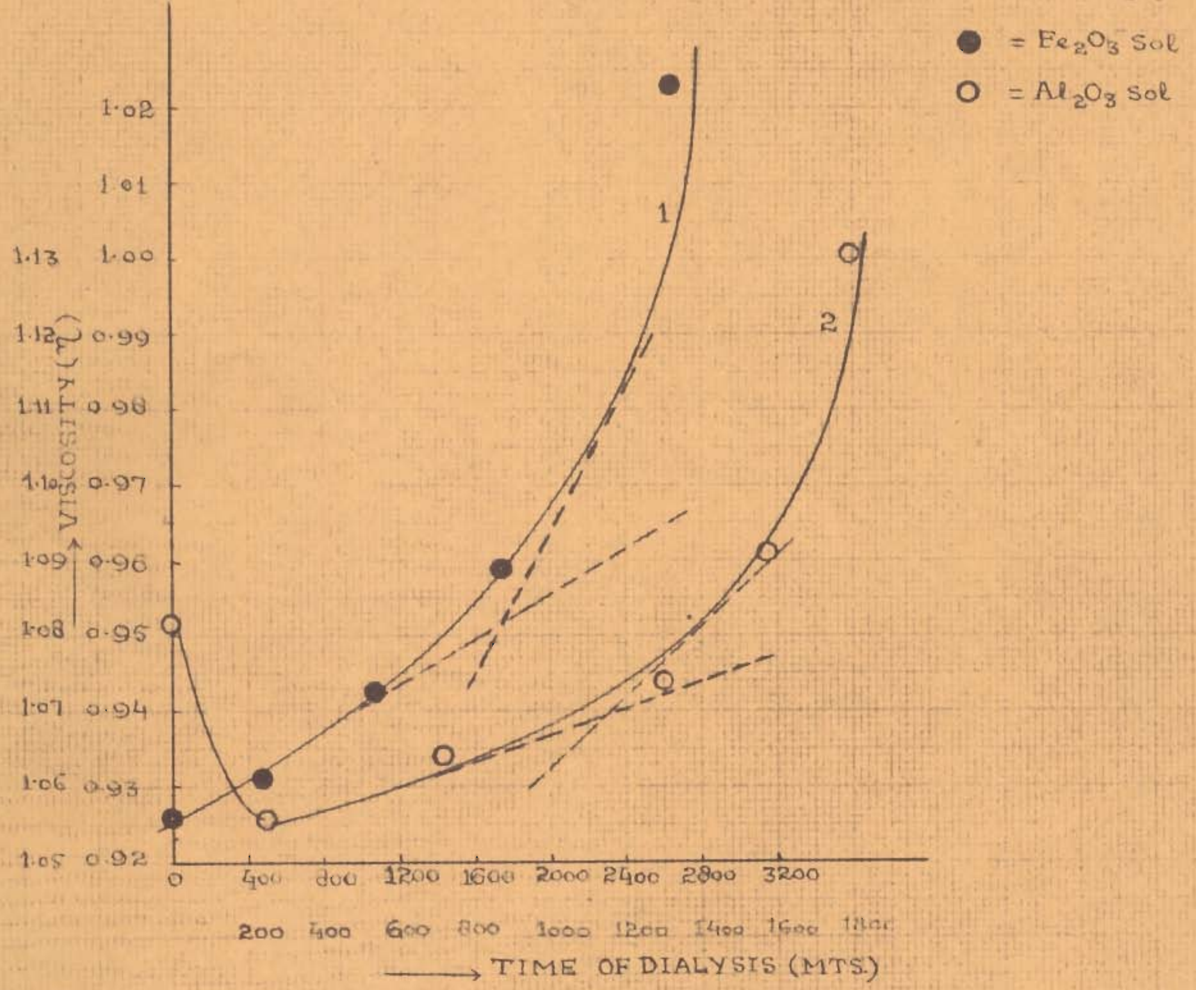


FIG. NO. 68

CHANGES IN VISCOSITY WITH DIALYSIS OF Fe_2O_3 AND Al_2O_3 SOLS.

Undoubtedly variations in viscosity of colloidal systems may be explained in the light of factors, viz; solvation, electroviscous effect, adhesion of particles etc. in the case of pure sols, a forthright explanation is difficult to give for complex systems comprising of mixtures of a sol and a foreign substance (electrolyte or non-electrolyte) or two different sols. In such cases due consideration has to be given to structural changes accompanying the interaction of the different chemical entities present therein. As will be seen from the discussion given below that simple techniques like viscosity, pH and electrophoresis can be employed to elucidate a few aspects of the problem.

The data on the viscosities of sol-dye mixtures may be considered from two angles.

(i) Variations in viscosity with progressive dialysis in presence of a fixed amount of dye, when abrupt change in viscosity takes place.

(ii) Change in viscosity with the addition of gradually increasing amount of the dye for a dialysed sol.

Although a continuous increase in viscosity with dialysis is observed in all cases, the extent to which this change takes place is dependent on the nature of the dye employed. Thus for a fixed concentration of the acid dye, viz; 1.0 mM/litre and 2.33 mM/litre of the basic dyes (higher concentration of the basic dyes had to be used for the positively charged ferric oxide sol) the extent of variations in different cases are as shown in the following table.

TABLE No.12

Variations in viscosity and ζ-potential with dialysis of ferric oxide-dye sol mixture.

Time of dialysis (mts.)	Viscosity (pure sol) centipoise	ζ-potential pure sol (volts)	Viscosity sol + methyl orange centi-poise)	ζ-potential sol+methyl orange (volts)	Viscosity sol + aliz. s.acid (centi poise)	ζ-potential sol + aliz. s. acid (volts.)	Viscosity sol + methylene blue (centi poise)	ζ-potential sol + methylene blue (volts)	Viscosity sol + malachite green (centi poise)	ζ-potential sol+ malachite green (volts)
0	0.9260	5.074×10^{-8}	0.9389	2.572×10^{-8}	0.9499	5.205×10^{-8}	0.9237	1.266×10^{-8}	0.9410	1.276×10^{-8}
480	0.9311	3.825×10^{-8}	0.9389	2.572×10^{-8}	0.9570	5.243×10^{-8}	0.9274	2.541×10^{-8}	0.9490	1.273×10^{-8}
1080	0.9426	2.583×10^{-8}	0.9535	2.612×10^{-8}	0.9665	6.200×10^{-8}	0.9361	3.847×10^{-8}	0.9499	2.602×10^{-8}
1740	0.9590	2.124×10^{-8}	0.9738	4.200×10^{-8}	1.002	5.489×10^{-8}	0.9696	3.99×10^{-8}	0.9618	2.71×10^{-8}
2640	1.023	2.002×10^{-8}	1.023	7.004×10^{-8}	1.180	5.362×10^{-8}	0.9954	4.091×10^{-8}	1.030	2.821×10^{-8}

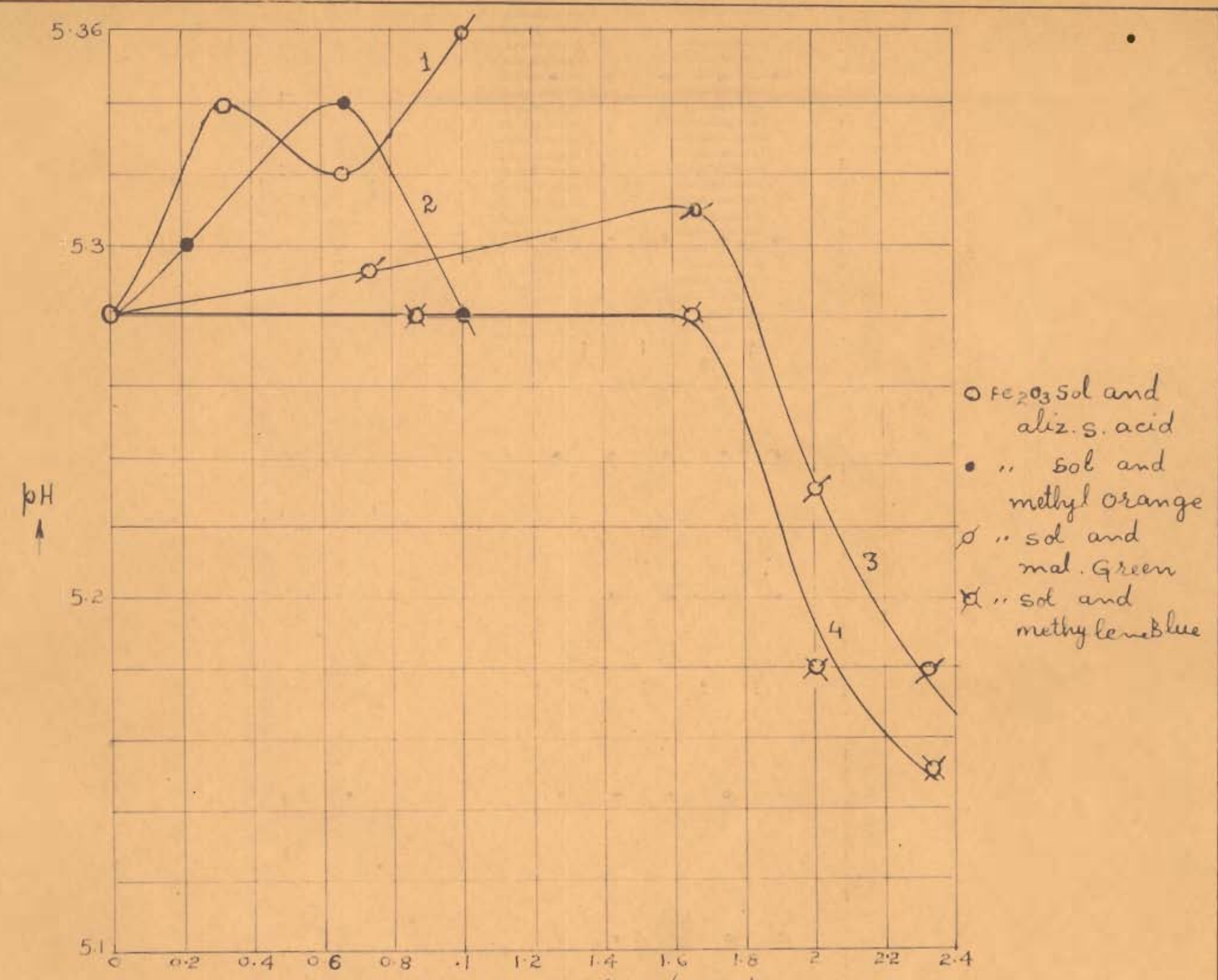


FIG-58. → CONC. OF DYE (mM/LITRE)

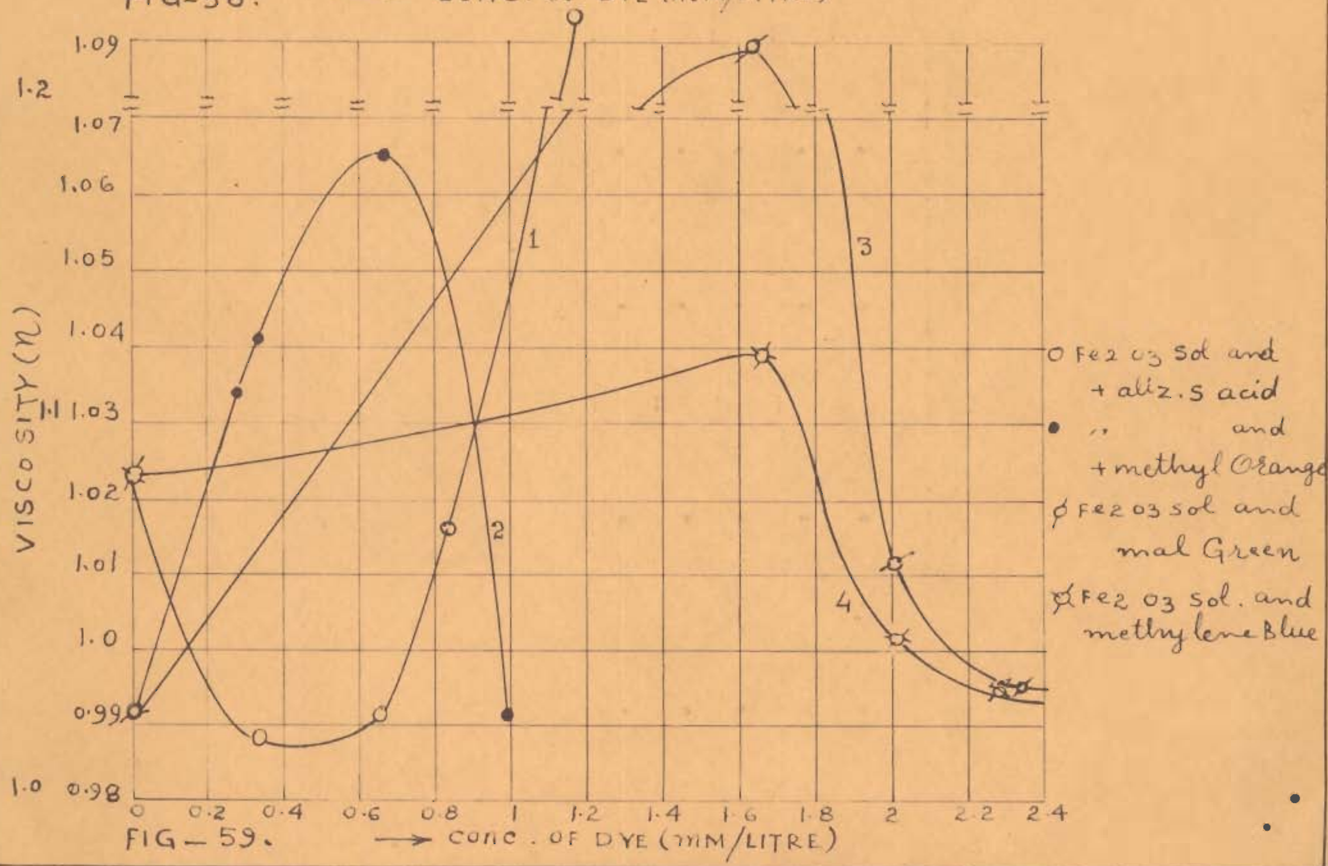


FIG — 59. → CONC. OF DYE (mM/LITRE)

From the above it is evident that in the case of pure sol the extent of increase in viscosity for a period of dialysis larger than the gelation time, say, 2640 mts. is 10.4%, the extent of increase in viscosity in the case of methyl orange and alizarin sulphonic acid (anionic dyes) is 8.9% and 25% respectively. With basic dyes e.g. methylene blue and malachite green the extent of increase in viscosity is 7.7% and 8.7% respectively. From these results it is evident that in presence of small amount of the alizarin sulphonic acid out of the four dyes brings about appreciable increase in viscosity.

Cataphoretic studies under similar conditions show that in the case of pure sol the extent of decrease in ζ-potential is 62.4%, the extent of increase in ζ-potential in the case of methyl orange, alizarin sulphonic acid, methylene blue and malachite green is 63.2%, 2.9%, 69.0% and 45.2% respectively.

The increase in viscosity and decrease in ζ-potential in the case of pure sol can be explained simply interms of hydration or solvation although electroviscous effects may also be operative. With progressive dialysis the stabilizing ions necessary to keep the sol stable are removed which result in the increase in viscosity and decrease in ζ-potential. According to Kruyt and Brigg(5) the ζ-potential is related to the stability of the system.

In the case of complex systems the only effective way of having such an increase in viscosity and ζ-potential with small amount of suspended material (2.49% Fe_2O_3) can, therefore, be explained interms of the aggregates formed by the inter-action of dyes with sol. For ascertaining this the results

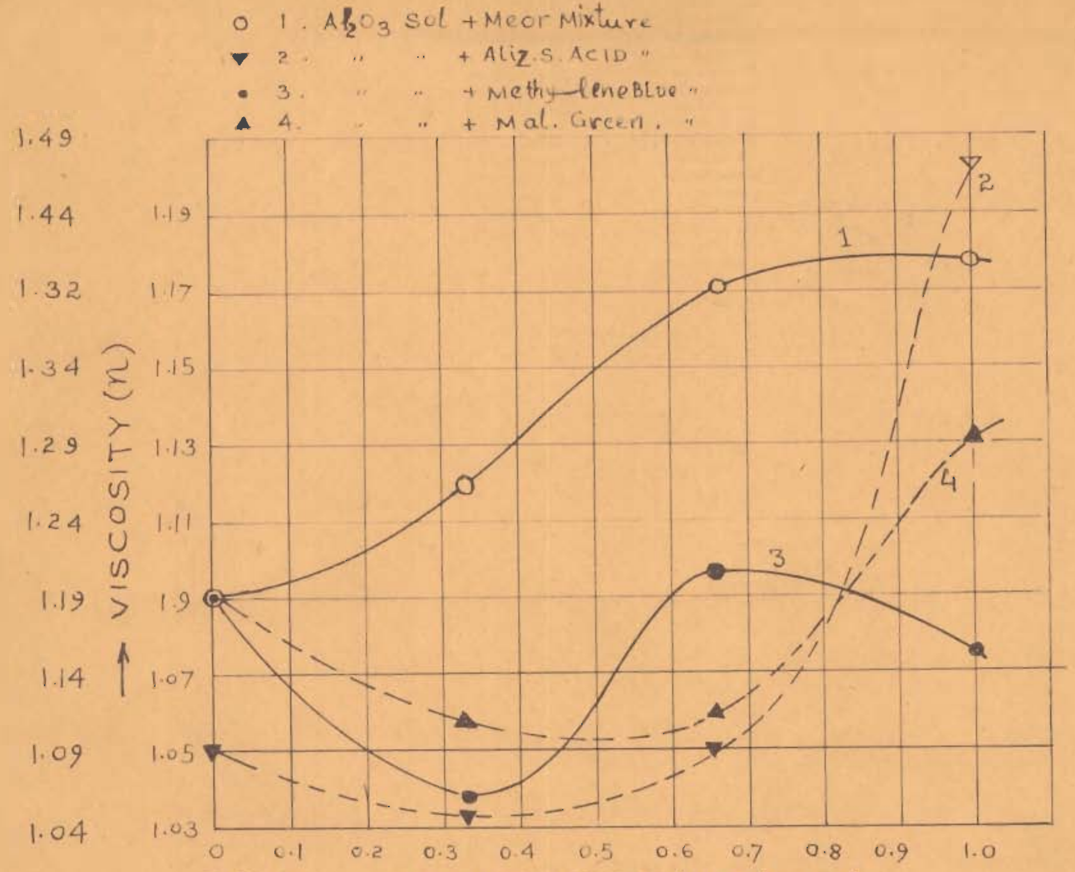


FIG. 60 → CONC. OF DYE (mM/LITRE)

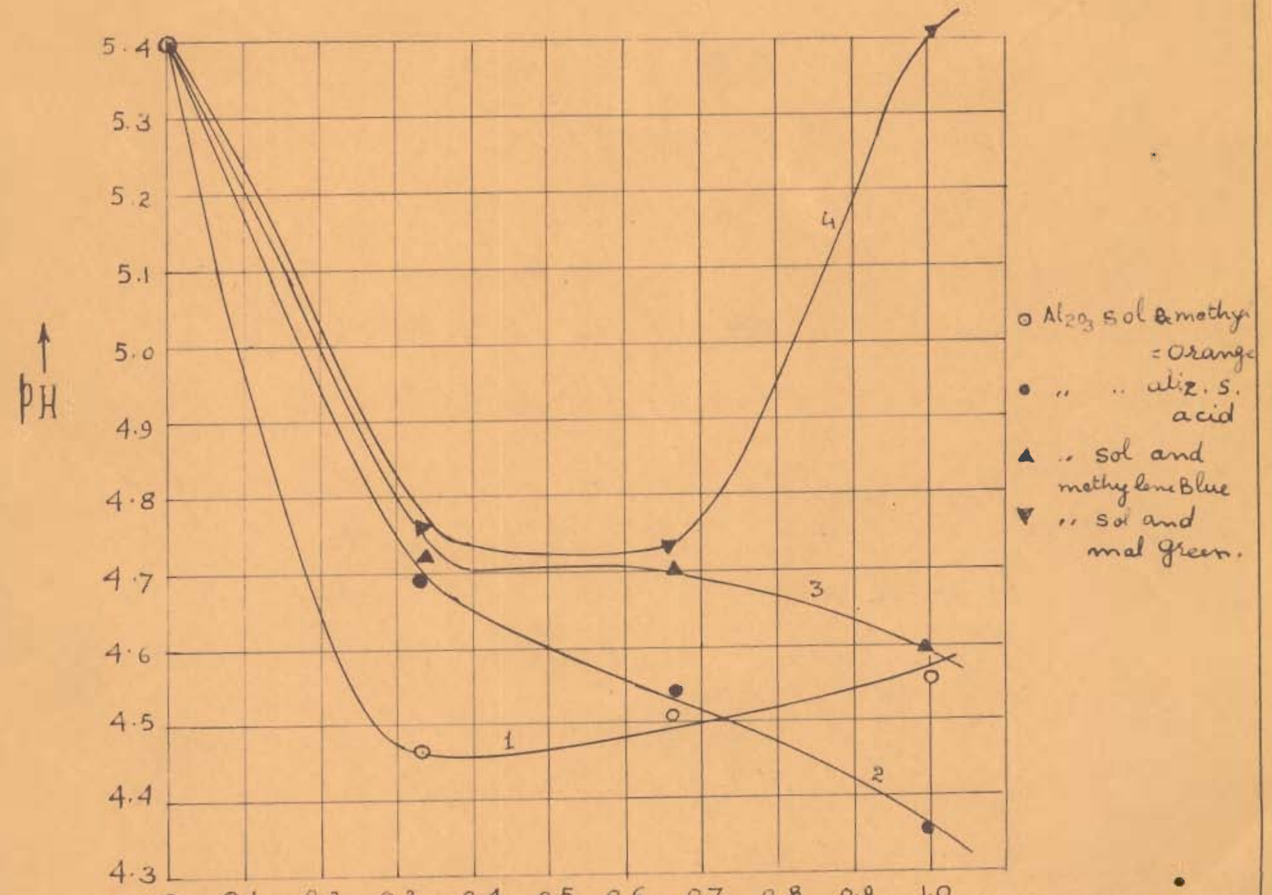


FIG_61 → CONC. OF DYE (mM/LITRE)

on the change in viscosity and ζ-potential with concentration after a fixed period of dialysis are worth considering.

TABLE No.13

Variations in viscosity, pH and ζ-potential with dialysis of ferric oxide sol-dye (anionic) mixture.

Conc. of dye mM/ litre	Viscosity sol+aliz.s. acid mixture (centi-poise)	ζ-potential sol+aliz.s. acid mixture (volts)	pH sol+ aliz. s. acid mixture	Viscosity sol+methyl orange mixture (centipoise)	ζ-potential sol+methyl orange mixture (volts)	pH sol + methyl orange mixture
0	1.023	2.002×10^{-8}	5.28	1.023	2.002×10^{-8}	5.28
0.33	0.9886	2.311×10^{-8}	5.34	-	-	-
0.66	0.9913	5.092×10^{-8}	5.32	1.171	8.021×10^{-8}	5.34
1.00	1.180	5.362×10^{-8}	5.36	1.023	7.004×10^{-8}	5.28
	Fig.(59) curve 1	Fig.(57) curve 1	Fig.(58) curve 1	Fig.(59) curve 2	Fig.(57) curve 2	Fig.(58) curve 2

TABLE No.14

Variations in viscosity, pH and ζ-potential with dialysis of ferric oxide sol-dye (cationic) mixture.

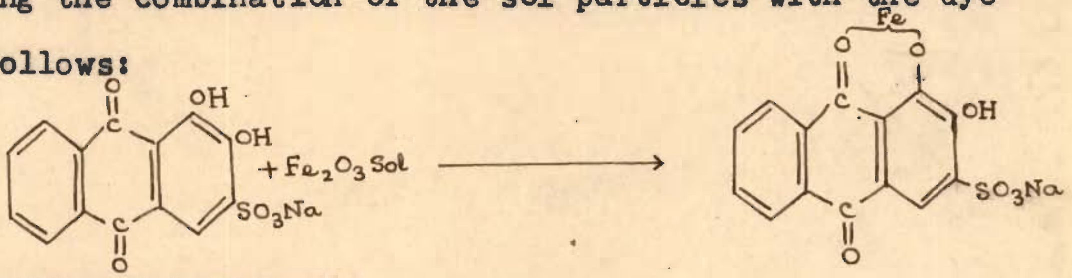
Conc. of dye mM/ litre	Viscosity sol+methylene blue mixture (centi-poise)	ζ-potential sol+ methylene blue mixture (volts)	pH sol + methylene blue mixture	Viscosity sol+ malachite green mixture (centi poise)	ζ-potential sol+malachite green mixture (volts)	pH sol+malachite green mixture
0	1.023	2.002×10^{-8}	5.28	1.023	2.002×10^{-8}	5.28
1.66	1.039	9.96×10^{-8}	5.28	1.025	5.034×10^{-8}	5.31
2.00	1.002	8.233×10^{-8}	5.18	1.064	4.373×10^{-8}	5.25
2.33	0.9954	4.091×10^{-8}	5.15	1.030	2.821×10^{-8}	5.18
	Fig.(59) curve 4	Fig.(57) curve 3	Fig.(58) curve 4	Fig.(59) curve 3	Fig.(57) curve 4	Fig.(58) curve 3

A plot of concentration of dye against viscosity would reveal that the viscosity of the dialysed sols vary slightly from the viscosity of the original sol. This behaviour is observed even in the case of alizarin sulphonic acid. In the light of these observations it may be argued that the gelation of ferric oxide sol is not dependent on the concentration of the dye present. In the case of alizarin sulphonic acid the presence of even a small amount of the dye was quite enough to make it more viscous on dialysis than the untreated sol. The variations in ζ-potential also support the fact that the gelation tendency of the sol cannot be enhanced merely by increasing the amount of the dye. On the other hand the sol after attaining on dialysis optimum condition for gelation gets more peptized on the addition of the dye . The fact that the dialysed sample of ferric oxide remains unattacked by the dye is also supported by the fact that no appreciable change in pH takes place on the gradual addition of the dye. It means that adsorption of the dyes on the ferric oxide gel does not take place otherwise it would have resulted in the release of H^+ from the inner part of the sol and consequent decrease in pH.

Another factor worth taking into account while explaining the gelation tendency of ferric oxide sol in presence of dyes is the structure of the dyes and the molecular rearrangements they may undergo in the different pH ranges. Since the ferric oxide sol has a fairly low pH (3.76), the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

Preliminary experiments have shown that methylene blue does not change its colour either in the acid or basic medium. The addition of the undialysed sol, however, brings about a deepening of the colour resulting into bluish pink colour which may be due to the adsorption of cationic part on the sol particles. Similar behaviour with malachite green is observed but here the changes in colour are observed only after keeping the sol-dye mixture for some time. With alizarin sulphonic acid the colour of the sol changes from light yellow to blood red and deep red in the case of methyl orange.

Alizarin sulphonic acid is well known for its tendency to form colour lakes with metal hydrous oxide sols through exchange adsorption. The only possible way in which alizarin sulphonic acid can influence the gelation of Fe_2O_3 can therefore, be through compound formation. Since a change in the original colour of the dye from light yellow to blood red takes place on the addition of the sol, it appears that a mechanism involving the combination of the sol particles with the dye is as follows:



alizarin sulphonic acid

Aluminium hydroxide sol:

Gelation of aluminium hydroxide sol:

Before discussing the experimental results on the sol-gel transformation of aluminium hydroxide sol as influenced by the presence of dyes, it is worthwhile to consider the behaviour of pure sol when converted into a gel by prolonged dialysis. A plot of time of dialysis against viscosity would reveal that after a certain stage of dialysis there is an abrupt increase in viscosity. This means that with progressive dialysis optimum conditions necessary to bring about gelation are realized and that the time after which an abrupt increase in viscosity takes place may conveniently be termed as gelation time (6,7) as quite distinct from the time of setting of a gel forming mixture.

A perusal of the data (table 15) would show that although the time of setting is different for samples subjected to dialysis for different time intervals (being minimum 4.5 hours when dialysed for 30 hours), the time required for the mixture to attain optimum condition for gelation has only one value.

TABLE No.15

Time of setting and gelation time for dialysed alumina sol of pH = 3.7

Time of dialysis	Time of setting by Fleming's method	Viscosity (centi-poise)	Gelation time as determined from the abrupt rise in viscosity
0	-	1.081	18.8 hrs.(1130 mts.)
4.25 hrs.(255 mts.)	-	1.055	
12.25 hrs(735 mts.)	-	1.063	
22.5 hrs.(1300 mts)	24 hours	1.074	
26.2 hrs.(1575 mts)	20 hours	1.091	
30.0 hrs.(1800 mts)	4.5 hours	1.13	

Fig (68) Curve 2

Undoubtedly the abrupt rise in viscosity of colloidal systems may be explained in the light of factors, viz., solvation, electroviscous effect, adhesion of particles etc. in the case of pure sols, a forthright explanation is difficult to give for complex systems comprising of mixtures of a sol and a foreign substance (electrolyte or non-electrolyte) or two different sols. In such cases due consideration has to be given to structural changes accompanying the interaction of the different chemical entities involved besides the factors enumerated above.

Gelation of alumina sol+dye mixtures:

With acid or anionic dyes the viscosity of the mixture decreases first and then increases near gelation time while with basic or cationic dyes the behaviour is quite different, the viscosity slightly decreases and then increases abruptly. These data may be discussed from the following two different angles.

(i) Variations in viscosity with progressive dialysis in presence of a fixed amount of dye (ii) Change in viscosity on addition of gradually increasing amount of the dye to a sol dialysed for a fixed period of time. In (i) a continuous decrease in viscosity with dialysis is observed with acid dyes, the extent to which this change takes place being dependent on the nature of the dye employed. Thus in presence of a fixed concentration of the dye, viz; 1.0mM/litre the following variations are observed.

TABLE No.16

Variations in viscosity with dialysis of Al_2O_3-dye sol mixture containing 1.0 mM/litre of the dye.

Time of dialysis (mts.)	Viscosity pure sol (centipoise)	Viscosity sol+methyl orange centipoise)	Viscosity sol+aliz. s.acid centipoise	Viscosity sol+methylene blue (centipoise)	Viscosity sol+malachite green (centipoise)
0	1.081	2.120	2.300	1.080	1.093
255	1.055	1.549	1.643	1.076	1.069
735	1.063	1.320	1.557	1.073	1.060
1300	1.074	1.255	1.474	1.060	1.074
1575	1.091	1.177	1.472	1.078	1.131
1800	1.130	1.200	1.498	1.081	-

On considering the viscosity data for samples dialysed for a period greater than the time of gelation of the pure sol (say 30 hours) it will be seen that there is a considerable decrease in viscosity, 42.5% and 36.0% in the case of methyl orange and alizarin sulphonic acid respectively, in the case of anionic dyes as against an overall increase of 0.92% in the case of pure sol. With the basic dyes the results are different. The viscosity changes are very little and only a slight increase in viscosity is observed (0.18% for methylene blue and 3.4% for malachite green).

The decrease in viscosity even on prolonged dialysis may be explained interms of peptisation. The dye used may prevent agglomeration by the adsorption of anionic part of the dye on the sol particles which may keep the sol in the stable state and not allow it to undergo gelation. These data find support in the work of Ghosh and coworkers(8) who observed that hydrous oxides, especially of the amphoteric type, develope a large adsorption capacity for anions. The results on the changes in viscosity and pH with varying concentration of the dye after a fixed period of dialysis are worth considering.

TABLE No.17

Variations in viscosity and pH of a dialysed alumina sol containing varying amounts of the dyes.

onc. of ye mM/ itre	Viscosity sol+methyl orange mixture (centi-poise)	pH sol+ methyl orange mix-ture	Visco-sity sol+ aliz. s.acid mixture (centi-poise)	pH sol+ aliz. s.acid mix-ture	Visco-sity sol+ methy-lene blue mixture (centi-poise)	pH sol+ methy-lene blue mixture	Viscosity sol+ malachite green mixture (centi-poise)	pH sol+ malachite green mixture
0	1.091	5.40	1.091	5.40	1.091	5.40	1.091	5.40
0.33	1.119	4.47	1.046	4.69	1.037	4.72	1.057	4.76
0.66	1.171	4.52	1.091	4.55	1.096	4.71	1.059	4.74
1.00	1.177	4.57	1.472	4.37	1.078	4.60	1.131	4.84
	Fig.(60)	Fig.(61)	Fig(60)	Fig.(61)	Fig(60)	Fig(61)	Fig.(60)	Fig.(61)

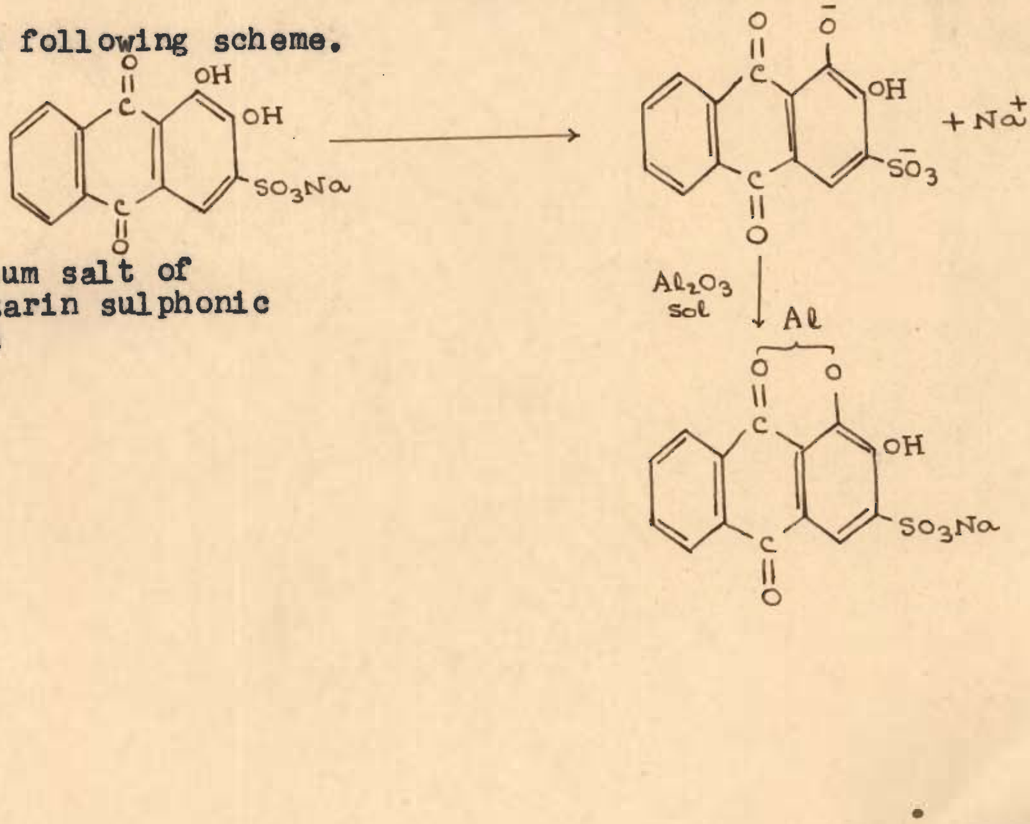
A plot of concentration of dye against viscosity would show that the viscosity increases with increase in concentration of the dye both in the case of methyl orange and alizarin sulphonic acid although the nature of curves is slightly different in both the cases (figs.60, Curve 1,2. respectively), the viscosity slightly decreases in the initial stages. With basic dyes the behaviour is altogether different, the concentration viscosity curve shows a decrease over a long concentration range followed by an abrupt increase in the case of malachite green while there is an initial increase followed by a decrease in the case of methylene blue. The difference in the nature of the products obtained with basic and acid dyes is also evident from the stability curves (the plots of stability and $\sqrt{c_e}$ where c_e is concentration of the dye), the stability of the sol increases slightly and then decreases rapidly in the case of basic dyes. But in the case of acid dyes the changes are not marked (fig.62 curve 1,2.).

Another factor worth taking into account while explaining the gelation tendency of alumina in presence of dyes is the structure of the dyes and the molecular rearrangements they may undergo in the different pH ranges. Since the alumina sol has a fairly low pH, the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

Preliminary experiments have shown that methylene blue does not change its colour either in acid or basic medium. The addition of sol, however, brings about a slight fading of the colour indicating the possibility of adsorption. The results on the variation in pH with addition of methylene blue support this view (fig 61, curve 3).The behaviour with malachite green can be explained on similar lines except for the fact that there is nothing inherent in the structure of the molecule which may point towards some sort of interaction between the dye and sol.

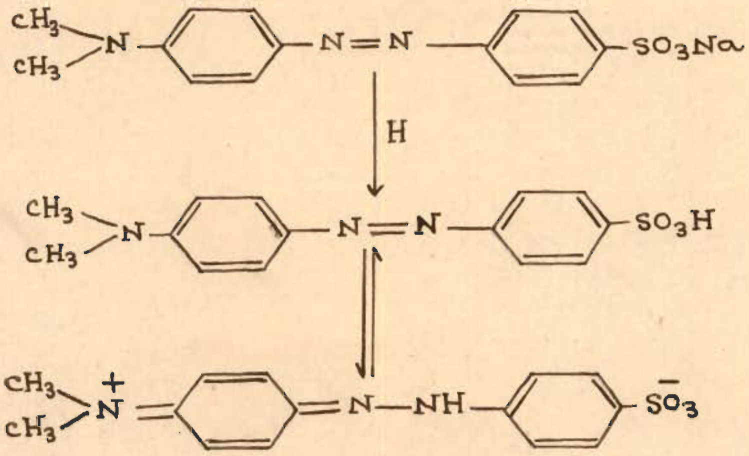
With acid dyes lake formation takes place. The alizarin lakes of the hydrous oxides are ordinarily formed by an exchange adsorption process in which the relatively strongly adsorbed alizarate ion displaces a more weakly adsorbed ion, such as chloride from the hydrous oxide. According to the view of Morgan the alizarin lakes are definite chelate metallic compounds. It is not known to what extent the above described phenomenon is connected with the lake formation process can be accounted for on the chelate compound theory.

The various changes taking place can be represented by the following scheme.



sodium salt of alizarin sulphonic acid

methyl orange:



The data on the variations in conductance with progressive dialysis fail to provide either any information regarding the difference in the behaviour of the different dyes towards ferric hydroxide and aluminium hydroxide sols or the influence of the dyes on the gelation process. The only little information obtained is that conductivity falls of rapidly as the sol changes into the gel.

The data on viscosity with increasing concentration of dyes (table no.5,10) taken for investigations reveal that viscosity remains almost constant and the appreciable variations in sol-dye mixtures (kept for four hours before starting the dialysis experiments) are due to the interaction of sols with dyes.

APPENDIX

The results reported here deal with our studies on the coagulation, ionic antagonism and acclimatisation of zinc, manganese and nickel ferrocyanides.

EXPERIMENTAL

Reagents:

1. Potassium ferrocyanide was dissolved in double distilled water and strength estimated by titrating against standard potassium permanganate solution (1). Requisite amounts of nickel sulphate, manganese chloride and zinc sulphate were dissolved in double distilled water and strengths determined gravimetrically. Electrolytes used were A.R. quality and the solutions were made in double distilled water.

2. Preparation of metal ferrocyanide sols:- The sols were prepared by the method of double decomposition. The amounts of metal salt and potassium ferrocyanide required to precipitate 2.5 gms. of the metal ferrocyanide were calculated from the following stoichiometric equations:

$$MSo_4 + K_4Fe(CN)_6 = K_2MFe(CN)_6 + K_2So_4$$

and $$MCl_2 + K_4Fe(CN)_6 = K_2MFe(CN)_6 + 2KCl$$

Calculated amounts of the reactants were mixed: 1 equivalent of salt: 5/4 equivalents of $K_4Fe(CN)_6$. The sol could only be obtained when the salt solution was gradually added to diluted $K_4Fe(CN)_6$ solution with constant stirring. Sols of the following maximum concentration could be obtained.

Nickel ferrocyanide sol = 2.5 gms per litre

Manganese ferrocyanide sol = 2.5 gms per litre

Zinc ferrocyanide sol = 2.5 gms per litre

__Time of slow coagulation:__- 5 c.c. of each sol was taken in steam dried pyrex test tubes and varying amount of electrolytes (KCl, HCl, $BaCl_2$, $AlCl_3$) and the total volume was made upto 10 c.c. by the addition of double distilled water. The concentrations of the various electrolytes in the sols were so adjusted that the minimum time of coagulation was near about 30 minutes in each case. Sols of concentrations A, A/2 were used and the time at which the sol particles left the surface of the sol was taken as the time of coagulation.

__Acclimatisation:__ The tables given below gives the volume of each electrolyte required to coagulate 5 c.c. of the Ni, Mn and Zn ferrocyanide sols in one hour and also the volume of each electrolyte which shows the maximum acclimatisation effect when a small quantity of the electrolyte is in contact with 5 c.c. of the sol for 15 minutes.

__Table No.1__

Strength of nickel ferrocyanide sol A = 2.5 gms per litre

Vol. of the sol + electrolyte + water = 10 c.c.

Temperature = 31 ± 0.1°C

Sol. A	Electrolyte	Volume of the electrolyte	Precipitation conc. in gms. equivalent per litre	Volume which gave maximum acclimatisation effect.	Maximum acclimatisation in gms equivalent per litre.
	2N NaCl	0.8 c.c.	0.16	0.08 c.c.	0.016
	N/2 KCl	1.5 c.c.	0.075	0.15 c.c.	0.0075
	N/5 HCl	1.7 c.c.	0.034	0.06 c.c.	0.0012
	N/100 $BaCl_2$	1.4 c.c.	0.0014	-	-
	N/50 $CaCl_2$	1.4 c.c.	0.0028	0.07 c.c.	0.00014
Sol.A/2					
	2N NaCl	0.4 c.c.	0.08	0.05 c.c.	0.01
	N/2 KCl	1.45c.c.	0.0725	0.15 c.c.	0.0075
	N/5 HCl	1.4 c.c.	0.028	0.04 c.c.	0.0008
	N/100 $Bacl_2$	0.9 c.c.	0.0009	-	-
	N/50 $CaCl_2$	0.9 c.c.	0.0018	0.05 c.c.	0.0001

Manganese ferrocyanide sol:

TABLE No.2

Strength of manganese ferrocyanide sol = 2.5 gms per litre.

Vol. of sol + electrolyte + water = 10 c.c.

Sol was stabilized by adding 1 c.c. of $K_4Fe(CN)_6$ to 250 c.c. of the original sol.

Sol.A Temperature = 31 ± 0.1°C

Electrolyte	Volume of the electrolyte.	Precipitation conc. in gms. equivalent per litre	Volume which gave maximum acclimatisation effect	Maximum acclimatisation in gms. equivalent per litre
N NaCl	1.35 c.c.	0.135	0.04 c.c.	0.004
N/2 KCl	2.3 c.c.	0.115	0.06 c.c.	0.003
N/5 HCl	0.8 c.c.	0.016	0.05 c.c.	0.001
N/100 $BaCl_2$	1.3 c.c.	0.0013	0.10 c.c.	0.0001
N/50 $CaCl_2$	0.9 c.c.	0.0018	0.05 c.c.	0.0001
N/200 Al_2Cl_6	2.3 c.c.	0.00115	0.08 c.c.	0.00004

Zinc ferrocyanide sol:

TABLE No.3

Strength of zinc ferrocyanide sol = 2.5 gms per litre.

Vol. of sol + electrolyte + water = 10 c.c., Tempt.=31±0.1°C

Sol.A	Electrolyte	Volume of the electrolyte	Precipitation conc. in gms. equivalent per litre	Volume which gave maximum acclimatisation effect	Maximum acclimatisation in gms equivalent per litre.
	2N NaCl	0.85 c.c.	0.17	0.15 c.c.	0.03
	N/2 KCl	2.1 c.c.	0.105	0.3 c.c.	0.015
	N HCl	1.0 c.c.	0.1	0.02 c.c.	0.002
	N/100 $BaCl_2$	3.25 c.c.	0.00325	0.1 c.c.	0.0001
	N/50 $CaCl_2$	1.35 c.c.	0.0027	0.1 c.c.	0.0002
	N/200 Al_2Cl_6	1.8 c.c.	0.0009	0.05 c.c.	0.000025
Sol.$\frac{A}{2}$	2N NaCl	0.95 c.c.	0.19	0.1 c.c.	0.02
	N/2 KCl	1.9 c.c.	0.095	0.2 c.c.	0.01
	N/100 $BaCl_2$	2.3 c.c.	0.0023	0.2 c.c.	0.0002
	N/50 $CaCl_2$	1.3 c.c.	0.0026	0.1 c.c.	0.0002
	N/200 Al_2Cl_6	1.1 c.c.	0.00055	0.03 c.c.	0.000015

Ionic antagonism:

The table given below shows the phenomenon of ionic antagonism with mixed electrolytes in the case of nickel, manganese and zinc ferrocyanide sols.

TABLE No.4

Strength of nickel ferrocyanide sol = 2.5 gms per litre

Vol. of the sol + electrolyte + water = 10 c.c.

Time of coagulation = 1 hour, Tempt. = 31 ± 0.1°C

Volume and precipitation conc. of primary electrolyte		Secondary electrolyte	Volume of secondary electrolyte	Conc. of secondary electrolyte in gms per litre
N/2 KCl	1.5 c.c. 0.075	2N NaCl	0.1 c.c.	0.02
		N/5 HCl	0.05 c.c.	0.001
		N/50 $CaCl_2$	0.15 c.c.	0.0003
		N/200 Al_2Cl_6	0.10 c.c.	0.00005
N/50 $CaCl_2$	1.4 c.c. 0.0028	2N NaCl	0.05 c.c.	0.01
		N/2 KCl	0.2 c.c.	0.01
		N/5 HCl	0.05 c.c.	0.001
		N/100 $BaCl_2$	0.05 c.c.	0.00005
		N/200 Al_2Cl_6	0.1 c.c.	0.00005
N/200 Al_2Cl_6	2.2 c.c. 0.0011	N/2 KCl	0.15 c.c.	0.0075
		N/50 $CaCl_2$	0.15 c.c.	0.0003

TABLE No.5

Manganese ferrocyanide sol:

Strength of manganese ferrocyanide sol = 2.5 gms per litre

Vol. of the sol + electrolyte + water = 10 c.c.

Time of coagulation = 1 hour, Tempt. = 31 ± 0.1°C

Volume and precipitation conc. of primary electrolyte		Secondary electrolyte	Volume of secondary electrolyte	Conc. of secondary electrolyte in gms. per litre.
N/2 KCl	1.0 c.c. 0.055	N/2 NaCl	0.05 c.c.	0.0025
		N/100 $BaCl_2$	0.02 c.c.	0.000004
		N/200 Al_2Cl_6	0.04 c.c.	0.00002
N/50 $BaCl_2$	0.8 c.c. 0.00016	N/2 NaCl	0.03 c.c.	0.0015
		N/2 KCl	0.06 c.c.	0.003
		N/50 $CaCl_2$	0.04 c.c.	0.00008
		N/200 Al_2Cl_6	0.05 c.c.	0.000025
N/200 Al_2Cl_6	0.65 c.c. 0.000325	N/2 NaCl	0.02 c.c.	0.001
		N/2 KCl	0.04 c.c.	0.0002
		N/50 $CaCl_2$	0.02 c.c.	0.0004

TABLE No.6

Zinc. ferrocyanide sol:

Strength of zinc ferrocyanide sol = 2.5 gms per litre

Vol. of sol + electrolyte + water = 10 c.c.

Time of coagulation = 1 hour, Tempt. = 31 ± 0.1°C

Volume and precipitation conc. of primary electrolyte		Secondary electrolyte	Vol. of secondary electrolyte.	Conc. of secondary electrolyte in gms. per litre
N/2 KCl	2.1 c.c. 0.105	2N NaCl	0.15 c.c.	0.03
		N/100 $BaCl_2$	0.2 c.c.	0.0002
		N/200 Al_2Cl_6	0.05 c.c.	0.000025
N/100 $BaCl_2$	3.25 c.c. 0.00325	N/2 KCl	1.1 c.c.	0.0055
		N/50 $CaCl_2$	0.05 c.c.	0.0001
		N/200 Al_2Cl_6	0.04 c.c.	0.00002
N/200 Al_2Cl_6	1.8 c.c. 0.0009	N/2 KCl	0.1 c.c.	0.005
		N/100 $BaCl_2$	0.1 c.c.	0.0001

1 ○ = NICKEL FERROCYANIDE SOL A, $\frac{M}{2}$ Kcl.
2 • = " " sol A/2, $\frac{M}{2}$ Kcl.
3 ⊙ = MN " sol A, $\frac{M}{2}$ Kcl.
4 ● = " " sol A/2, $\frac{M}{2}$ Kcl.
5 ⊡ = Zn. " sol A, $\frac{M}{2}$ Kcl.
6 ■ = " " sol A/2, $\frac{M}{2}$ Kcl.
7 • = NICKEL " sol A, $\frac{M}{200}$ Bacl$_2$
8 ▭ = " " sol A, $\frac{M}{400}$ Alcl$_3$
9 ▬ = " " sol A/2 $\frac{M}{200}$ Bacl$_2$
10 ◨ = " " sol $\frac{A}{2}$ $\frac{M}{400}$ Alcl$_3$
11 ▮ = Mn. " Sol A $\frac{M}{200}$ Bacl$_2$
12 ○ = Mn. " sol A $\frac{M}{400}$ Alcl$_3$
13 △ = Zn. " sol A $\frac{M}{200}$ Bacl$_2$
14 ▲ = Zn. " sol A $\frac{M}{400}$ Alcl$_3$
15 ▽ = " " sol $\frac{A}{2}$ $\frac{M}{200}$ Bacl$_2$
16 ▼ = " " sol $\frac{A}{2}$ $\frac{M}{200}$ Alcl$_3$
17 ▨ = Mn " sol $\frac{A}{2}$ $\frac{M}{200}$ Bacl$_2$
18 ⊠ = Mn " sol $\frac{A}{2}$ $\frac{M}{400}$ Alcl$_3$

COAGULATION OF Ni, Mn, Zn FERROCYANIDE SOLS BY K^+, Ba^{++} and Al^{+++}

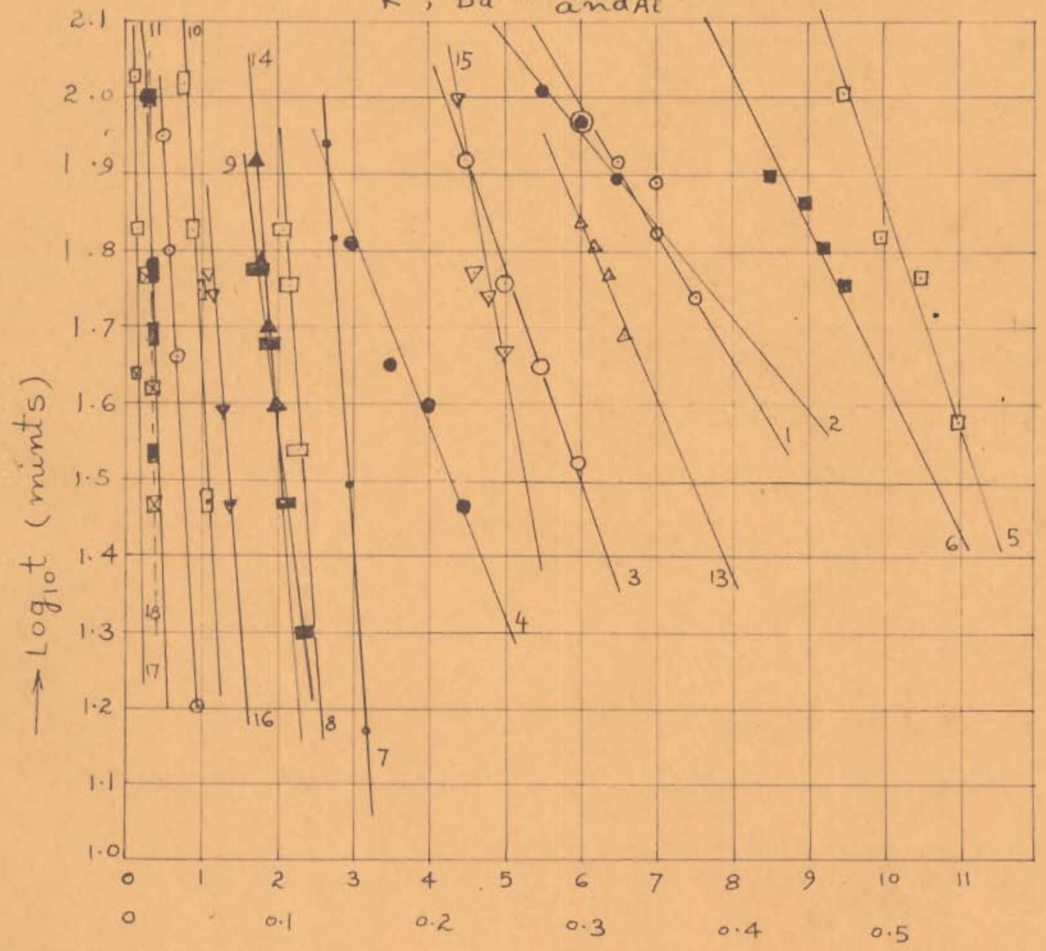


FIG-65. → $100\sqrt{Ce}$ (gms equiv. per Litre)$^{1/2}$

RESULTS AND DISCUSSION

The precipitation concentrations in mM/litre for the various electrolytes required for coagulating the sol in one hour are given below.

TABLE No.7

Precipitation concentrations in mM/litre for different electrolytes for coagulating the sol in one hour.

Nickel ferrocyanide sol	KCl	HCl	$BaCl_2$	$AlCl_3$
A(2.5 gms per litre)	75.0	34	1.4	1.1
A/2(1.25 gms per litre)	70.0	32	0.50	0.45
Manganese ferrocyanide sol				
A(2.5 gms per litre)	50.0	4.0	0.80	0.30
A/2(1.25 gms per litre)	30.0	2.7	0.40	0.15
Zinc ferrocyanide sol				
A(2.5 gms per litre)	105.0	100.0	1.60	0.90
A/2(1.25 gms per litre)	95.0	90.0	1.15	0.55

From the above table (No.7), it is evident that the Hardy Schulze rule is followed for all the different concentrations of sol used, the order of coagulating power being $Al^{+++} > Ba^{++} > H^{+} > Na^{+}$.

The applicability of Bhattacharya's equation has been examined with different concentrations of the sols and electrolytes. Empirical relation proposed by Bhattacharya et.al (2) is $1/c-a = \frac{n.t}{m} + 1/m$, where n and m are empirical constants, c is the concentration of the electrolyte added for coagulation, a the critical stability concentration and t the time of coagulation. This equation has been found to agree with the experimental results. The values of a of the

Mn, Ni and Zn FERROCYANIDES

1 ⊙ = Zn Ferrocyanide. sol A, $\frac{M}{2}$ KCl → a = 87 mM/litre
2 • = " sol $A/_2$, $\frac{M}{2}$ Kcl → a = 65 mM/litre
3 ◉ = Mn " sol A, $\frac{M}{2}$ Kcl → a = 36 mM/litre
4 ● = Mn " sol $A/_2$, $\frac{M}{2}$ kcl → a = 19 mM/litre
5 △ = Ni " sol A, $\frac{M}{2}$ kcl → a = 40 mM/litre
6 ▲ = Ni " sol $A/_2$, $M/_2$ kcl → a = 34 mM/litre
---7 ⊡ = Zn " sol A, $\frac{M}{200}$ $BaCl_2$ → a = 1.18 mM/litre
---8 ■ = Zn " sol $\frac{A}{2}$ " " → a = 0.94 mM/litre
9 ▽ = Mn " sol A $\frac{M}{200}$ " → a = 0.28 mM/litre
10 ▼ = Mn " sol $\frac{A}{2}$ " " → a = 0.14 mM/litre
11 ⊙ = Ni " sol A $\frac{M}{200}$ " → a = 0.64 mM/ "
12 ○ = Ni " sol $A/_2$ " " → a = 0.36 " "
13 × = Ni " sol A $\frac{M}{400}$ $AlCl_3$ → a = 0.465 mM/liter.
14 ⁎ = Ni " sol $\frac{A}{2}$ $\frac{M}{400}$ " → a = 0.17 mM/liter.
15 ✳ = Mn " sol A $\frac{M}{400}$ $AlCl_3$ → a = 0.075 mM/liter
16 + = Mn " sol $A/_2$ $\frac{M}{400}$ " → a = 0.055 mM/liter
17 ⊟ = Zn " sol A → a = 0.355 mM/liter
18 ▮ = Zn " sol $M/_2$ → a = 0.21 mM/liter

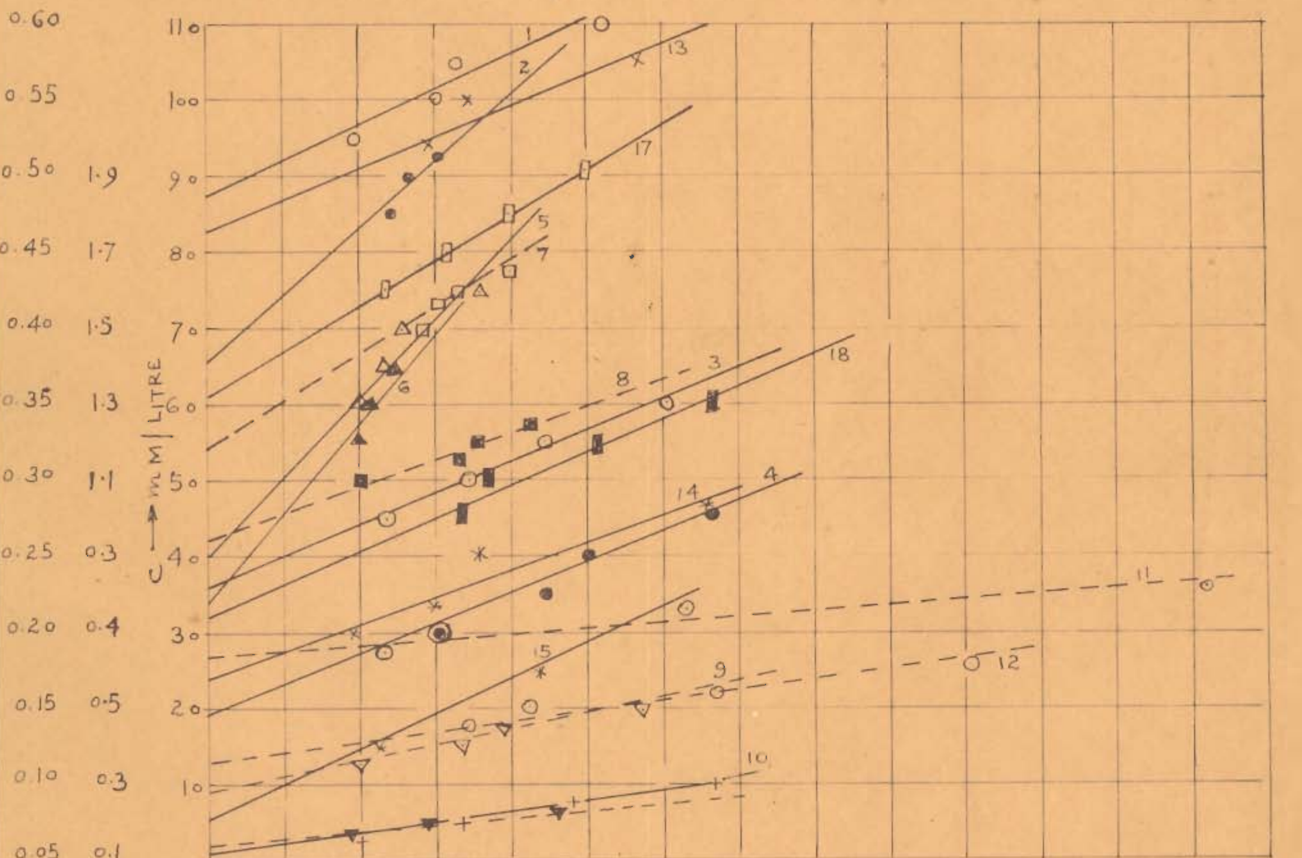


FIG - 66

said relation have been obtained from the intercepts on the c axis from the plots of c and 1/t (fig.66). The plot of 1/c-a and t (fig.67) is a straight line showing the applicability of the above relation. The slope of the straight lines, thus obtained gives the value of n/m and the intercept on 1/c-a axis gives 1/m. The values of the constants a,m and n obtained from figs.66 and67are recorded in subsequent tables (8,9,10) for nickel, manganese and zinc ferrocyanide sols respectively. The straight lines obtained from the plots of 1/c-a and t in the case of all the three sols of the two dilutions (A, A/2) show the validity of the equation.

TABLE No.8

Constants of the Bhattacharya's equation for nickel ferrocyanide sol:

Electrolyte used	Sol A			Sol A/2		
	a (mM/litre)	m (mM/litre)	n (minute^{-1})	a (mM/litre)	m (mM/litre)	n (minute^{-1})
M/2 KCl	40.0	200	80.0	34.0	333.3	124.8
M/200 $BaCl_2$	0.64	0.31	0.31	0.36	1.25	1.0
M/400 $AlCl_3$	0.465	0.19	0.10	0.17	1.0	1.0

TABLE No.9

Constants of Bhattacharya's equation for manganese ferrocyanide sol:

Electrolyte used	Sol A			Sol A/2		
	a (mM/litre)	m (mM/litre)	n (minute^{-1})	a (mM/litre)	m (mM/litre)	n (minute^{-1})
M/2 KCl	36.0	333	416.2	19.0	666.6	874.5
M/200 $BaCl_2$	0.28	5.0	4.5	0.14	10.0	12.8
M/400 $AlCl_3$	0.075	0.5	0.4	0.055	5.0	3.5

TABLE No.10

Constants of Bhattacharya's equation for zinc ferrocyanide sol.

Electrolyte used	Sol A			Sol A/2		
	a (mM/litre)	m (mM/litre)	n (minute^{-1})	a (mM/litre)	m (mM/litre)	n (minute^{-1})
M/2 KCl	87.0	660	775	65.0	166.0	157.7
M/200 $BaCl_2$	1.18	2.5	0.5	0.94	1.25	0.34
M/400 $AlCl_3$	0.355	2.0	0.4	0.21	0.38	0.28

A perusal of tables 8 to 10 lead to the following conclusions.

The values of the empirical constants a, m and n decrease with increasing valency of the coagulating ions, so that these are more when coagulation is effected by monovalent ion than by a polyvalent one.

The stability of dilute lyophobic sols depends on the energy of interaction between two approaching particles, according to Verwey and Overbeek(3) this energy is composed of long range electrical repulsion and a long range Vander-waal's attraction. For one given sol, the attraction is assumed to be constant, while the repulsion changes with electrolyte content of the system and compression of the electrical double layer. With decreasing repulsion the rate of coagulation increases.

From the curves (fig.65) plotted against stability (4) $\log_{10} t$ or log W and $\sqrt{C_e}$ it is observed that stability of sol decreases with increasing electrolyte concentration and with increase in the valency of the coagulating ions.

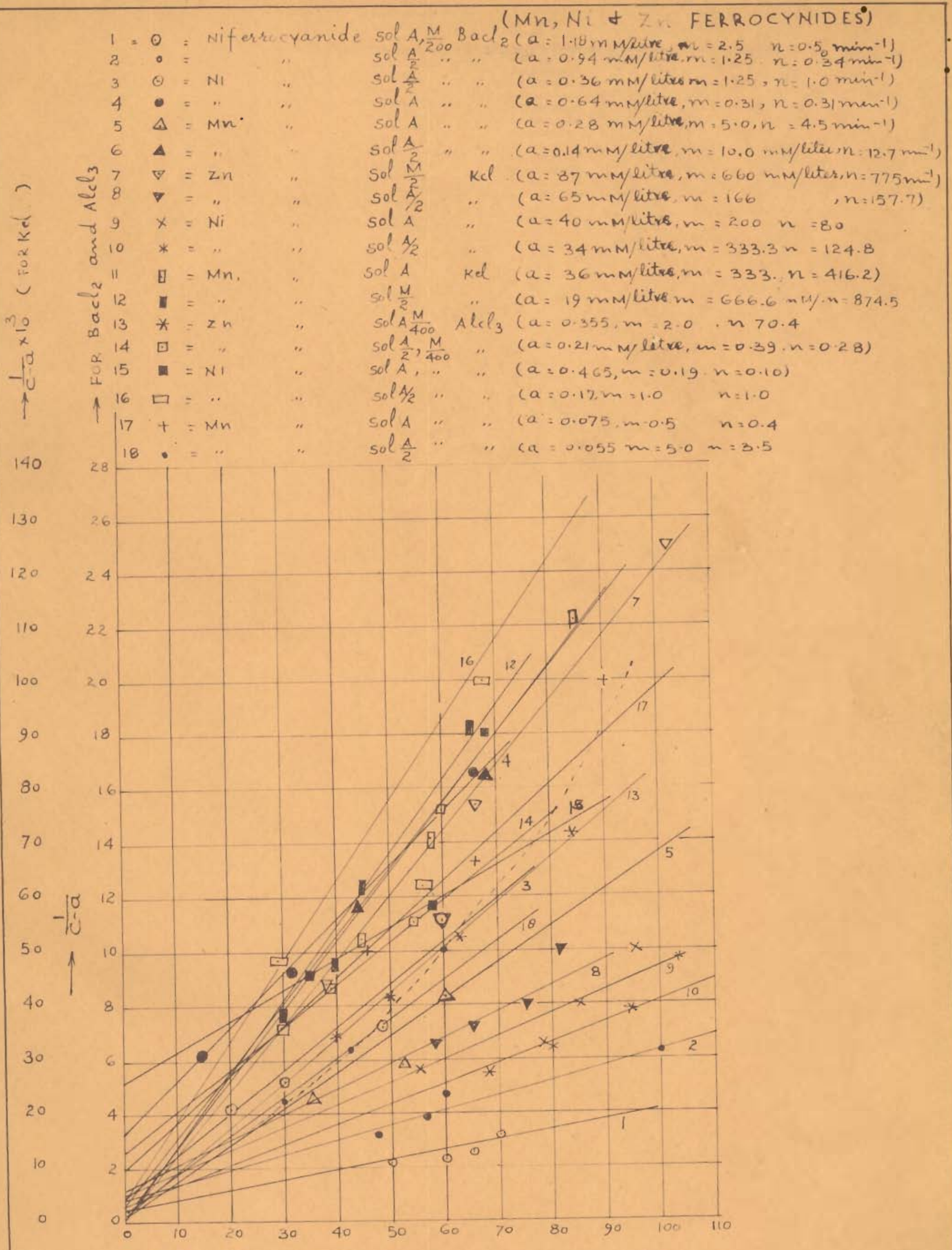
(Mn, Ni & Zn FERROCYNIDES)
1 = ⊙ : Niferrocyanide sol A, M/200 Bacl2 (a = 1.18 mM/litre, m = 2.5 n = 0.50 min-1)
2 ∘ = " sol A/2 " " (a = 0.94 mM/litre m = 1.25 n = 0.34 min-1)
3 ⊙ = Ni " sol A/2 " " (a = 0.36 mM/litre m = 1.25, n = 1.0 min-1)
4 ● = " " sol A " " (a = 0.64 mM/litre, m = 0.31, n = 0.31 min-1)
5 △ = Mn " sol A " " (a = 0.28 mM/litre, m = 5.0, n = 4.5 min-1)
6 ▲ = " " sol A/2 " " (a = 0.14 mM/litre, m = 10.0 mM/liter n = 12.7 m-1)
7 ▽ = Zn " Sol M/2 Kcl (a = 87 mM/litre, m = 660 mM/liter, n = 775 m-1)
8 ▼ = " " sol A/2 " (a = 65 mM/litre, m = 166 , n = 157.7)
9 × = Ni " sol A " (a = 40 mM/litre, m = 200 n = 80
10 ✳ = " " sol A/2 " (a = 34 mM/litre, m = 333.3 n = 124.8
11 ▯ = Mn. " sol A Kcl (a = 36 mM/litre, m = 333. n = 416.2)
12 ▮ = " " sol M/2 " (a = 19 mM/litre m = 666.6 mM/ n = 874.5
13 ✳ = Zn " sol A M/400 Alcl3 (a = 0.355, m = 2.0 . n 70.4
14 ⊡ = " " sol A/2, M/400 " (a = 0.21 mM/litre, m = 0.39 . n = 0.28)
15 ■ = Ni " sol A, " " (a = 0.465, m = 0.19 n = 0.10)
16 ▭ = " " sol A/2 " " (a = 0.17, m = 1.0 n = 1.0
17 + = Mn " sol A " " (a = 0.075, m = 0.5 n = 0.4
18 • = " " sol A/2 " " (a = 0.055 m = 5.0 n = 3.5
→ 1/(C-a) ×10³ (FOR Kcl)
→ FOR Bacl2 and Alcl3
→ 1/(C-a)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
70
80
90
100
110
1
2
3
4
5
7
8
9
10
12
13
14
16
17
18
→ t (TIME OF COAGULATION mts)

FIG- 67

Hence it can be concluded that the values of the constants vary directly with the stability of sol and with the variation in the valency of the coagulating ion. The value of m decreases with decreasing stability of a sol. These results are quite in good agreement with the view of Ghosh and Coworkers (7).

The empirical equation of Bhattacharya et.al (2) may be based on the theoritical considerations developed by Verwey and Overbeek for the interaction of two charged units as shown by Ghosh et.al (5). They have written this equation in the form $t/T + 1 = 1/Ka_1^{\beta-1} (c-a)^{\beta}$.....(1) where a is a constant given by $\left(\frac{a_1(\beta-1)}{\beta}\right)$ and K is a constant. The value of β by Verwey and Overbeek is given as $\left(\frac{0.85\times10^{6} a' r^{2}}{kTZ^{2}} + \frac{1}{2}\right)$ where a' is the particle radius and the value of the constant r is given as $\left(\frac{e^{z/2}-1}{e^{z/2}+1}\right)$, where $z = \frac{Ze\Psi_0}{kT}$ here e being the electric charge, Z the valency of the coagulating ion and Ψ_0 the surface potential. From equation (1) the value of the constant n could be equated to 1/T (where, $T=1/8\pi RDn_0$) of Smoluchowski equation (6). Therefore n has the dimension of frequency, while m has the dimension of concentration. Hence the value of the constant n is directly related to RD which defines the attractive force between two aggregating colloidal particles. Further for rapid coagulation c=a+m but since a is very very small compared to the coagulation concentration c therefore m equals to c i.e., m refers to the concentration of the coagulating electrolyte when the stability factor W is unity. Now the value of W is defined to a great extent by the repulsive force V_R as given by the relation (7) $V_R = \frac{8\varepsilon K^2 T^2 x}{\pi (Ze)^2} r^2 e^{-2xd}$. Thus we see from this equation that the repulsive potential V_R decays exponentially and the rate of decay is independent of the value of the surface potential and is determined by the quantity x given by the factor ($\sqrt{\frac{8\pi n}{\varepsilon KT}} Ze$). Here ε (dielectric constant), K,T, $8\pi n$ are constants. Therefore an increase in Z (valency of the ion-increasing from monovalent to polyvalent) will result in the decrease of V_R and since the stability of a colloidal system is directly related to V_R, therefore value of m will decrease as the valency of the ion will increase.

The experiments on acclimatisation show that the stability of zinc, manganese and nickel ferrocyanide sols gradually increases with gradual addition of the electrolytes upto a certain concentration beyond which the stability of the sols begin to decrease (tables 1,2 and 3). Hence there is an optimum concentration of the electrolyte to produce maximum stability and may be named as maximum acclimatisation concentration of the electrolyte.

Various theories have been, viz., those of fractional precipitation and formation of soluble salt with the material of the colloidal micelle. To us it appears that preferential adsorption of similarly charged ions also play a vital role in the acclimatisation phenomenon. On the addition of small quantity of the electrolyte, much less than its precipitation concentration, partial coalescence of some particles may reasonably take place and the released stabilizing ions ($FeCy_6^{==}$) may get adsorbed on the colloidal material resulting in its enhanced stability.

The results on ionic antagonism (tables 4,5 and 6) show that the total amount of mixed electrolyte required to coagulate the sol in one hour is greater than the precipitation concentration of the primary electrolyte. Many authors have suggested that the adsorption of ions carrying the same charge as the colloid may very well explain these results. Attention may be drawn to another important factor, viz., the change in the ionic concentration of the ions take place when electrolytes are mixed together and it is this effective ion concentration of the mixed electrolytes which should be given due consideration while explaining the results on ionic antagonism.

RESUMÉ

The hydrous oxides of iron, chromium and aluminium are well known for their high adsorptive capacity. Their interaction with dyes has not been comprehensively studied except for alizarin Red S. The phenomenon of lake formation in the case of this dye has attracted the attention of a number of workers like Biltz (1905), Ackerman (1932), Bancroft and Farnham (1932). However, the nature of the binding involved even in the case of this dye is in a controversial stage. It was, therefore, considered worthwhile to study the problem of the dye-hydrophobic sol interaction in a more systematic and comprehensive manner than taken up so far. On considering a number of combinations of sols and dyes as the reactants and studying their coagulation and gelation phenomenon it was expected that some new and useful information might be obtained regarding the nature of their binding. The results of the investigations are reviewed in the description to follow.

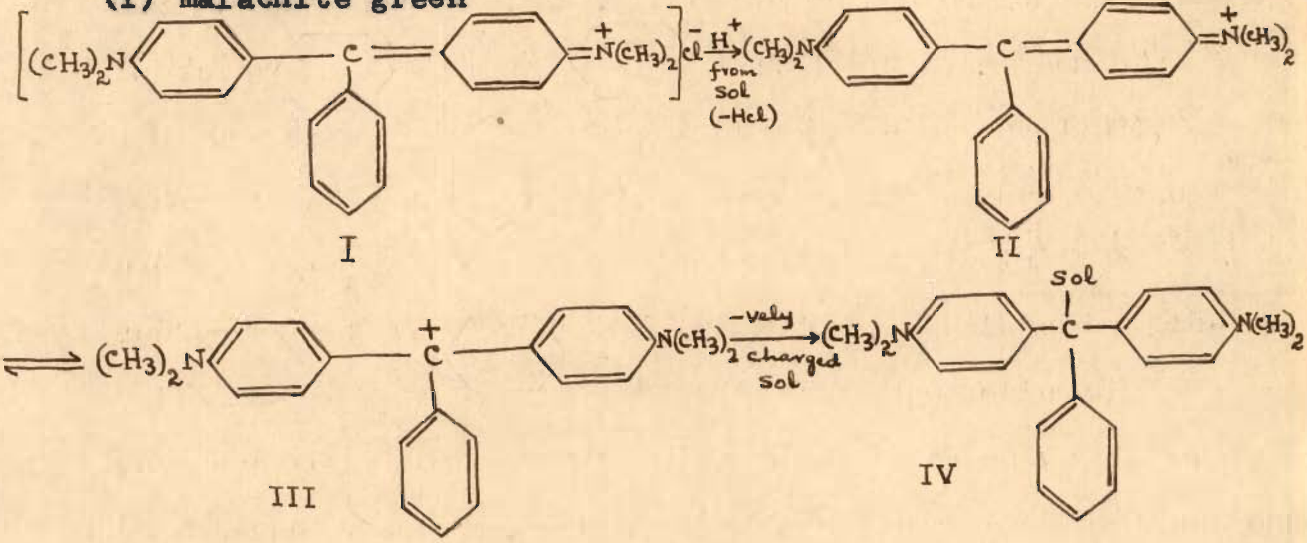
1. <u>Interaction of dyes with arsenic sulphide sol</u>:

The interaction of arsenic sulphide sol with anionic and cationic dyes, viz., alizarin sulphonic acid, methyl orange, malachite green and methylene blue interms of the dye binding capacity of the sol had been studied with the help of spectrophotometric, cataphoretic, conductometric, viscometric and pH metric methods. Klotz's method (1946), usually employed to study protein-metal ion binding, was found to be suitable in such interactions also. The binding data were calculated employing the equation $\alpha = \frac{\epsilon_{app} - \epsilon_B}{\epsilon_F - \epsilon_B}$, where α is the fraction of the dye which is free or extent of binding. ϵapp is the apparent molar extinction coefficient of the bound dye, ϵ_B is the molar extinction coefficient of the bound dye and ϵ_F is the molar extinction coefficient of the free dye.

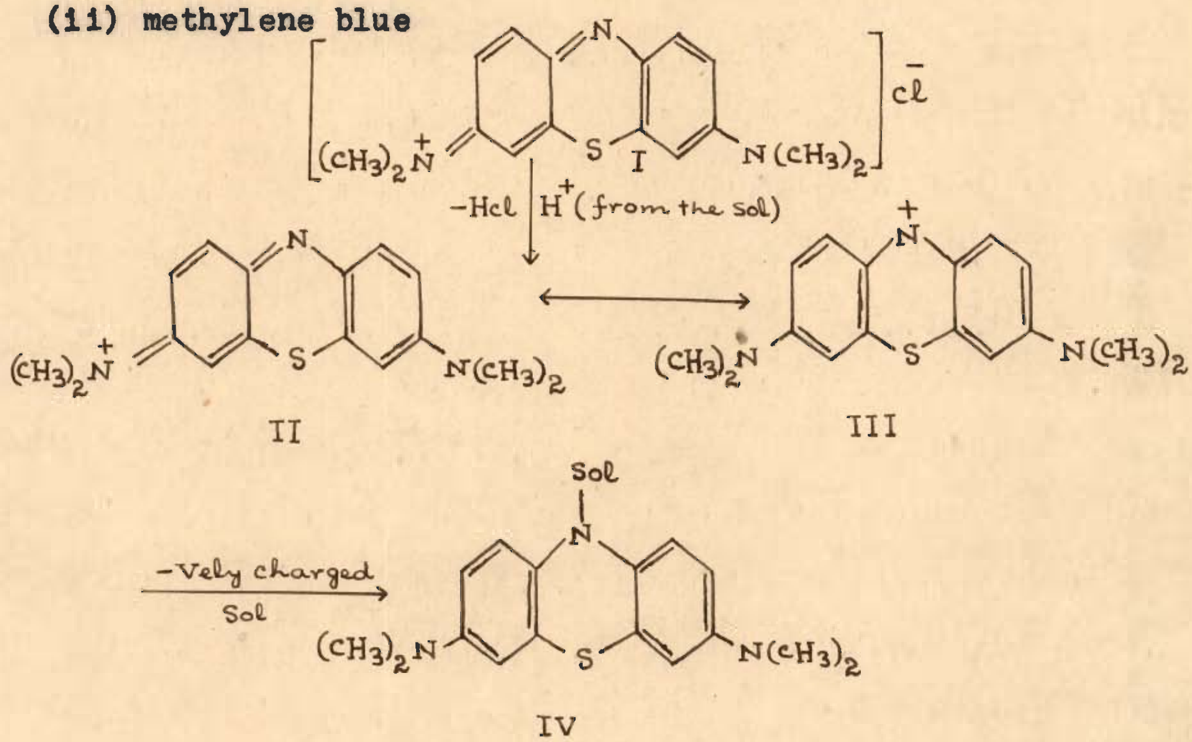
Experiments carried out with varying concentration of the dyes with sols had shown that although the behaviour of both the basic dyes was almost the same, it differed markedly from each other in the case of the acid dyes (methyl orange and alizarin sulphonic acid). For example, it was observed that the ζ-potential, viscosity and conductivity continuously increased with increase in the concentration of the alizarin sulphonic acid while with methyl orange a reverse behaviour was observed. The same dissimilarity was observed regarding the variations in pH. From the results on the variations in pH, ζ-potential, viscosity and conductivity the following information was obtained.

(a) It was observed that although the dye cations carrying a charge opposite in sign to that of the sol, were effective in bringing about the coagulation, the behaviour was not just the same as in the case of ordinary electrolytes. Here instead of a continuous decrease in ζ-potential an initial increase (upto a concentration of 0.0133×10^{-3}M of malachite green and 0.0100×10^{-3}M methylene blue) followed by a decrease was observed. This was explained by assuming that the big cations compete with the hydrogen ions in the diffused part of the double layer. When sufficient dye had been taken up by the sol, the hydrogen ions were released resulting in the decrease in pH. The released hydrogen ions, however, bring about orientation in the dye molecule making it susceptible for interaction with the sol. The following mechanisms may be proposed for the two dyes.

(i) malachite green



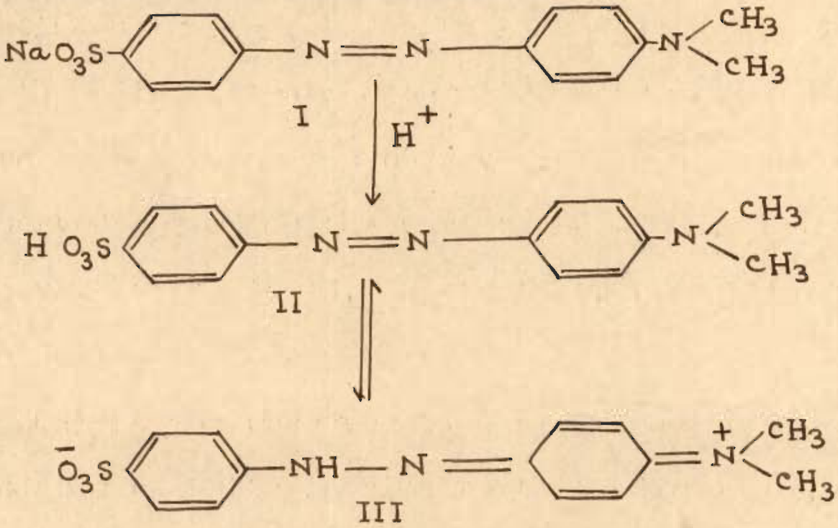
(ii) methylene blue



The structure III was reached in presence of hydrogen ions and the interaction between the dye and the negatively charged sol would take place resulting in its coagulation (hence a decrease in ζ-potential).

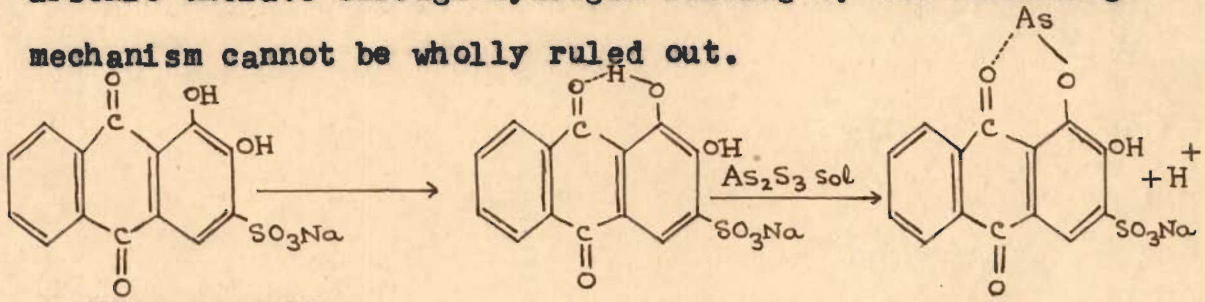
The possibility of compound formation between the sol and dye would exist since an abrupt change in pH, viscosity, conductivity and ζ-potential was observed (table 1,2 , fig5,1,3,7) after the addition of 0.0133×10^{-3}M of malachite green and 0.0100×10^{-3} M methylene blue.

(b) With methyl orange stabilization of the sol took place due to the adsorption of the dye anion. This was accompanied by the increase in ζ-potential, the following structural changes could be contemplated in the methyl orange in presence of this acidoid sol.



Since, the compound III would be electrically neutral, the possibility for the formation of adsorption or ordinary complexes of arsenic sulphide with methyl orange was, therefore, ruled out. Moreover the addition of the dye did not bring any change in the viscosity. This observation was taken as an indication of the fact that neither the aggregation of the sol particles took place nor big particles due to the formation of dye-sol complex were formed.

(c) The addition of gradually increasing amount of the alizarate ion to the sol would also result in the adsorption of these ions by the colloidal micelle (arsenic particle with adsorbed HS^- ions). This could be through exchange, since the decrease in pH (table 4 , fig 1) took place which could take place by gradual exchange of the HS^-(HS^- $H^+ + S^=$) from the surface of sol particles. The results on the variations in pH and ζ-potential support the above mechanism. The conductivity and viscosity data also support the above view. However, the possibility of the formation of an arsenic chelate through hydrogen bonding by the following mechanism cannot be wholly ruled out.



aliz. s. acid

(d) The spectrophotometric data could be used to determine the quantitative binding of the sol by these dyes.

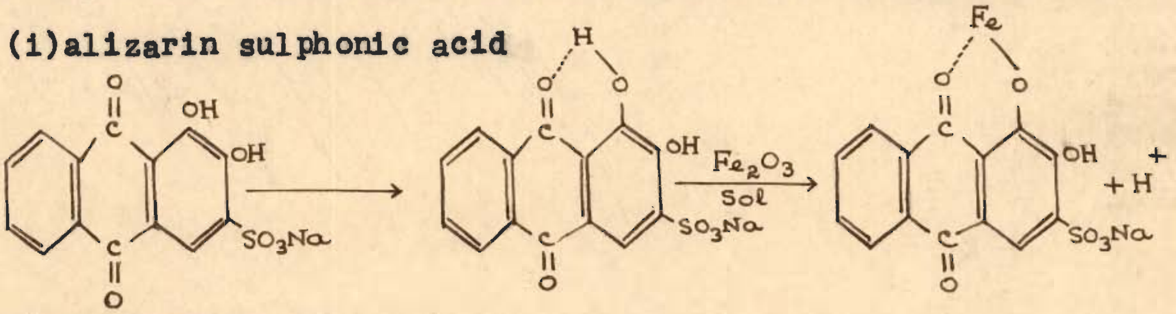
The shifts in absorption maxima and decrease in O.D. values in dye-sol mixtures (unlike that of buffers of the same pH as that of the sol) gave the idea of the binding of the dyes by the sol. The combining ratios were found to be 8 sol:1 dye in the case of malachite green and 5 sol: 1 dye in the case of methylene blue. Almost similar combining ratio (6 sol:1 dye in the case of malachite green, 8 sol:1 dye in the case of methylene blue) were obtained when calculations were carried out from the data corresponding to the abrupt changes of pH, ζ-potential, conductivity and viscosity (tables 1, 2 , page 48,49).

2. <u>Interaction of dyes with ferric oxide and alumina sols</u>:

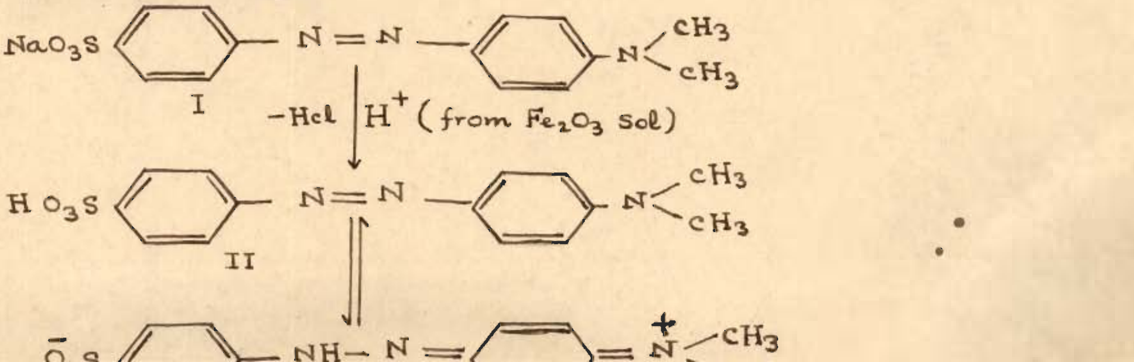
The following generalizations were arrived at on the basis of above studies:

(a) The behaviour of ferric oxide sol was different from that of arsenic sulphide sol. For example, a decrease in ζ-potential was observed in the case of Fe_2O_3 sol irrespective of the dye used (in the case of arsenic sulphide these variations were dependent on the dye used). Unlike arsenic sulphide there was little difference in the behaviour of methyl orange and alizarin sulphonic acid. For example, a decrease in pH and ζ-potential was observed in both the cases. Sensitization of the sol resulting in the release of H^+ ion from the inner part of the double layer could explain the decrease in pH. The viscosity variations in the case of methyl orange were the same as could be expected during the sensitization of the sol. Marked increase in viscosity in the case of alizarin sulphonic acid could be attributed to the hydration of sol particles accompanied by chemical interaction. The possibility of the formation of iron chelate through hydrogen bonding should, therefore, exist. The possible mechanisms in the two cases are given below.

(i)alizarin sulphonic acid



(ii) methyl orange



(b) The contention that factors other than charge neutralization were operative in the case of the coagulation of sols by dyes is again borne out from the results on the interaction of basic dyes with ferric oxide sol. Normally the cation of the added dye should bring about little variation (or a slight increase) in the ζ-potential of the positively charged ferric oxide sol but the results showed that there was a continuous decrease in ζ-potential and only when sufficient amount of the dye had been added that a constancy was observed. It was apparent that both the dyes were strongly adsorbed by the ferric oxide sol.

There was an initial decrease in pH in both cases (although it was much larger in the case of malachite green, pointing towards its greater adsorption) followed by a constancy. Structural changes in the two dyes by taking up the released hydrogen ions (as described under As_2S_3, chapter I, page 64,65) are likely to take place here also. Adsorption of the dye by the sol particles resulted in the formation of bigger aggregates and hence viscosity values were higher. Coagulation of the sol took place by the addition of malachite green whereas in methylene blue the sol remained in the suspended state for a long time which very well explained the differences of the nature of viscosity variations in the two cases. Conductivity variations lend support to the above view.

(c) Shifts in maxima from 425 to 500 mμ in the case of alizarin sulphonic acid and 450 to 475 mμ in the case of methyl orange took place on mixing these dyes with ferric oxide sol, while for basic dyes there was no shift in maxima, although O.D. values were appreciably lowered. These results provided evidence for the binding of the dye by the sol accompanied in certain cases by structural changes (where shifts in maxima occurred).

Quantitative data on the extent of binding are summarised in the tables 19-23, page 109 gave 7 moles, 40.5 moles, 59.9 moles and 47.1 moles of ferric oxide bound per ionic micelle of alizarin sulphonic acid, methyl orange, methylene blue and malachite green respectively.

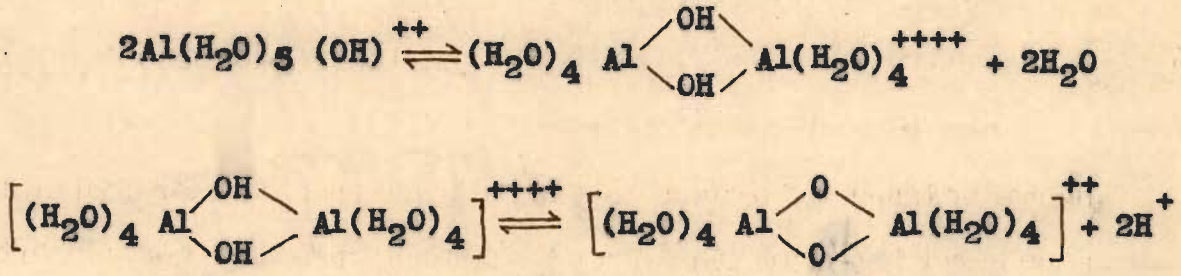
Alumina sol:-

The behaviour of this sol differed from that of ferric oxide or arsenic sulphide. In the case of alizarin sulphonic acid marked variations in pH, viscosity and conductivity were observed. With methyl orange pH and conductivity variations were negligible although slight changes in viscosity did take place. On the other hand, basic dyes did not influence these physical properties to any appreciable extent. It was, therefore, inferred that out of the four dyes alizarin sulphonic acid was most strongly bound to the alumina sol. The variations in viscosity and pH were of the same type as with ferric oxide sol. Spectrophotometric studies provided evidence of the shift in maxima from 425 to 475 mμ with a decrease in O.D. values in the case of alizarin sulphonic acid and methyl orange, while with basic dyes neither any change in O.D. is observed nor a shift in maxima took place which showed the inertness of alumina towards these two basic dyes. The binding data based on

Klotz's equation are given in tables 24-26, page 112 from which the moles of alumina bound per mole of dye were calculated.

The large variations in viscosity in the case of alumina as compared to ferric oxide sol may be attributed to the existence of polymeric Ol and Oxo compounds in the sol, which were formed by the gradual loss of protons according to the following mechanism.

$$Al(H_2O)_6^{+++} \rightleftharpoons Al(H_2O)_5(OH)^{++} + H^+$$



$$2Al(H_2O)_5(OH)^{++} \rightleftharpoons (H_2O)_4\,Al\genfrac{}{}{0pt}{}{\diagup OH \diagdown}{\diagdown OH \diagup}Al(H_2O)_4^{++++} + 2H_2O$$

$$\left[(H_2O)_4\,Al\genfrac{}{}{0pt}{}{\diagup OH \diagdown}{\diagdown OH \diagup}Al(H_2O)_4\right]^{++++} \rightleftharpoons \left[(H_2O)_4\,Al\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}Al(H_2O)_4\right]^{++} + 2H^+$$

Since the variations in pH in the case of ferric oxide were much less than in the case of alumina, the existence of Oxo-complexes in the former would not exist. Highly polymerising complexes would not, therefore, be formed in this case and the viscosity values should be lower in this case as compared to alumina sol.

3. Adsorption of the dyes by silica, ferric oxide and alumina gels:

(a) Silica gel:

In the case of alizarin sulphonic acid, malachite green and methylene blue the adsorption data were found to fit in well in Langmuir adsorption equation. Interestingly enough methyl orange was found to be negatively adsorbed.

(b) Ferric oxide gel:

The datas in the case of methyl orange and methylene blue fit in well in Langmuir adsorption isotherm equation. No such simple relationship was observed in the case of alizarin sulphonic acid. Malachite green was found to be negatively adsorbed on the gel.

(c) Alumina gel:

In the case of methylene blue, malachite green and methyl orange Langmuir equation was followed. In the case of alizarin sulphonic acid the data could not be fitted in Langmuir or Freundlich adsorption equation.

4. Sol-gel transformation of silicic acid, ferric oxide and alumina in presence of dyes:

(a) The influence of these dyes on the gelation of silicic acid sol using viscometric, pH metric and conductometric method was studied. It was found that the gelation time decreased in presence of basic dyes and increased with acid dyes. It was also observed that methylene blue was adsorbed by replacement of H^+ ions by a big cation of the dye followed by a possible combination between the sulphur of the dye and OH of the silanol group of silicic acid. The results on the variations in pH had also provided support to this view point. Similar results were obtained with malachite green. The interaction of alizarin sulphonic acid with silicic acid appeared to take place through compound formation between silanol and phenolic group. Methyl orange seems to attain a quinonoid structure in presence of silicic acid.

(b) In the case of ferric oxide sol a continuous increase in viscosity with dialysis (for a period larger than the time of gelation) was observed in all cases, the extent to which this change took place was found to be dependent on the nature of the dye employed. Thus for a fixed concentration of the acid dye, viz., 1.0 mM/litre and 2.33 mM/litre of the basic dyes (higher concentration of the basic dyes had to be used for the positively charged ferric oxide sol) the increase in viscosity in the case of methyl orange and alizarin sulphonic acid (anionic dyes) was 8.9% and 25% respectively as against 10.4% for the pure sol. With basic dyes e.g. methylene blue and malachite green the increase in viscosity was 7.7% and 8.7% respectively. From these results it was inferred that out of the four dyes alizarin sulphonic acid brought about appreciable increase in viscosity.

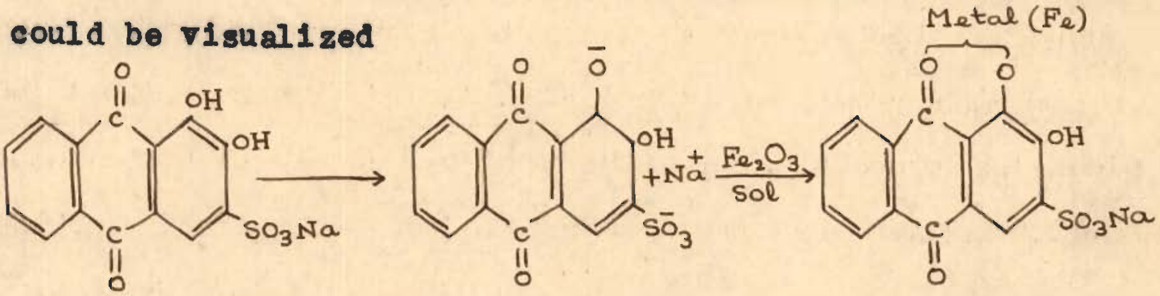
Cataphoretic studies under similar conditions had revealed that there was a decrease in ζ-potential for pure sol to the extent of 62.4%, the extent of increase in ζ-potential in the case of methyl orange, alizarin sulphonic acid, methylene blue and malachite green were 63.2%, 2.9%, 69.0% and 45.2% respectively.

The increase in viscosity and the decrease in ζ-potential in the case of pure sol may be explained simply interms of hydration or solvation although electroviscous effects may also be operative.

In the case of complex systems the only effective way of having such an increase in viscosity and ζ-potential with small amount of suspended material (2.49% Fe_2O_3) could be explained interms of the aggregates formed by the interaction of the dyes with the sol. For ascertaining this the results on the change in viscosity and ζ-potential with varying concentration of the dyes after a fixed period of dialysis were carried out. It was observed that (i) the viscosity of the sol was not found to change with the increase in the concentration of the dye. From these results it was concluded that the gelation of ferric oxide sol was independent of the concentration of the dye present (in alizarin sulphonic acid the presence of even a small amount of the dye was quite enough to make it more viscous on dialysis than the untreated sol). The variations in ζ-potential also supported the fact that the gelation tendency of the sol could not be enhanced merely by increasing the amount of the dye. On the other hand, the sol after attaining on dialysis optimum condition for gelation got more peptized on the addition of the dye. The fact that the dialysed sample of ferric oxide remained unattacked by the dye also got support from the fact that no appreciable change in pH took place on the gradual addition of the dye.

Another factor worth taking into account while explaining the gelation tendency of ferric oxide sol in presence of dyes was the structure of the dyes and the molecular rearrangements they have undergone in the different pH ranges. Since the ferric oxide sol had a fairly low pH (3.76), the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

From the preliminary experiments it was observed that methylene blue did not change its colour either in the acid or basic medium, the addition of the sol brought about a deepening of the colour resulting into bluish pink which could be due to the adsorption of cationic part on the sol particles. Similar change with malachite green was observed after keeping the sol-dye mixture for some time. The colour of the sol changed from light yellow to blood red and deep red in the case of alizarin sulphonic acid and methyl orange respectively. Since alizarin Red S is known for its tendency to form colour lakes with hydrous oxide sols through exchange adsorption, the only possible way in which alizarin sulphonic acid could influence the gelation of Fe_2O_3 was therefore through compound formation. Since a change in the colour of the dye from light yellow to blood red took place on the addition of the sol, a mechanism involving the combination of the sol particles with the dye could be visualized



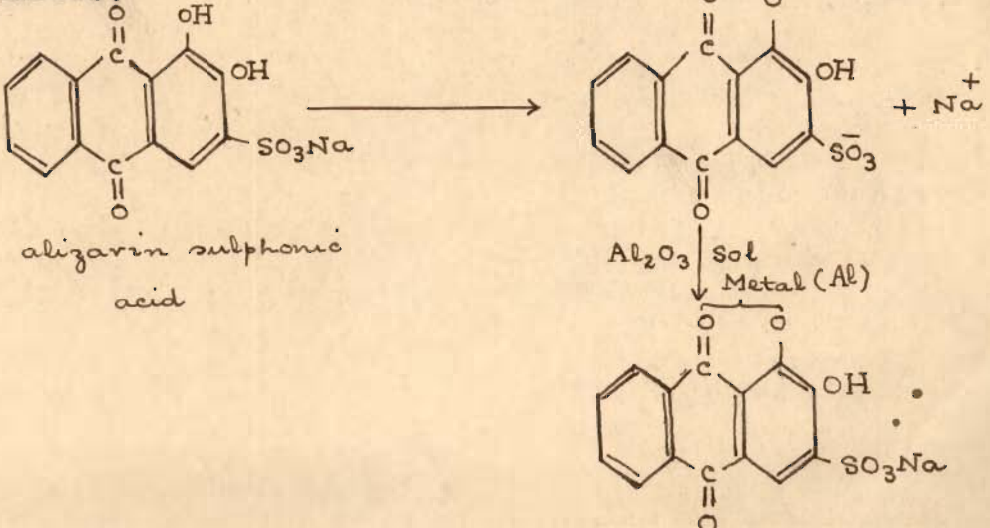
aliz. s. acid

(c) The following conclusions were arrived at in the case of Al_2O_3 sol.

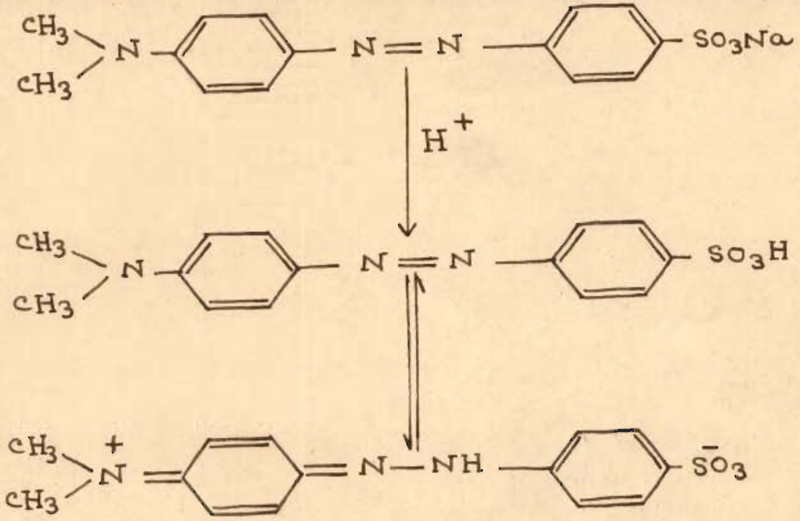
With the acid dyes the viscosity of the mixture decreased first and then increased. The behaviour was different with basic dyes where a slight initial decrease followed by an abrupt increase was observed. Thus in presence of a fixed concentration of the dyes, viz., 1.0 mM/litre, the variations in viscosity were: methyl orange (42.5% decrease), alizarin sulphonic acid (36.0% decrease), malachite green (3.4% increase), methylene blue (0.18% increase) and pure sol (0.92% increase). From these results it was concluded that small concentrations of the acid dyes checked the gel forming tendency of the alumina sol while the basic dyes did not influence the sol at this concentration.

The results of the variations in viscosity and pH with increase in concentration of the dye after a fixed period of dialysis had shown that there was an increase in viscosity in the case of methyl orange and alizarin sulphonic acid while with basic dyes, the concentration viscosity curves showed decrease over a long concentration range followed by an abrupt increase in the case of malachite green.

Preliminary experiments showed that a slight fading of the colour of the basic dyes in presence of sol took place indicating the possibility of adsorption. The results on pH variations also gave support to this view point. With acid dyes like alizarin sulphonic acid (alizarin Red.S) lake formation takes place involving exchange adsorption process, the relatively strongly adsorbed alizarate ion displacing the more weakly adsorbed ion. The change may be depicted as follows.



For methyl orange the following mechanism had been given.



In the appendix are included the results on slow coagulation, ionic antagonism and acclimatization of CO, Ni, Zn and Mn ferrocyanide sols.

Different aspects of the colloidal properties of cobalt, nickel, zinc and manganese ferrocyanides have been studied. With the help of coagulation experiments the values of the constants of the empirical relation proposed by Bhattacharya (1951) have been calculated for the above mentioned sols of different dilutions using uni-, bi-, and trivalent ions. It was found that the values of the constants decreased with increasing valency of the coagulating ion. The values of the parameters are found to be related to the stability of sols. The phenomenon of acclimatisation and ionic antagonism was also well exhibited by these sols.

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CHAPTER I:

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