INTRODUCTION

Quite a number of colloidal solutions are known to exhibit pronounced changes in their optical transmission and also show birefringence when placed in a magnetic field. Although these effects have been known for a long time (1) their applications to the particle size analysis in colloidal solution are comparatively a novel feature. F.D. Stott (2) has studied the optical transmission of colloidal graphite under a magnetic field and has determined the particle size from the data. He assumes the extinction cross-section of a colloidal particle to be proportional to the geometrical cross-section. Detailed experimental study (3), however, has shown that this assumption is not valid and that the extinction coefficients calculated on the basis of Rayleigh theory show better agreement with the experimental results.

Analytical expressions have also been obtained relating the optical transmission and the birefringence in a colloid on the strength of the applied field (3 4). Applications of these expressions to the problem of particle size analysis has also been discussed (2 Ph.D. thesis 5).

Stott (3), however, has interpreted his results assuming that the extinction coefficient of a colloidal graphite particle is proportional to the projected geometrical cross-section. In general, the experimental data on magneto-optical effects in colloid show good agreement with the expressions derived assuming the colloidal particle to
be independent Rayleigh scatteror (3, 74, 4, Ph.D. thesis of H.S. Shah pp.149). At the same time in a number of colloids the particles may not be sufficiently small for the Rayleigh theory to be accurately applicable. Main deviations can occur in particular cases as described below:

(1) Red Shaped Particles—In this case it would be desirable to use the scattering theory for cylinder. Expressions for the scattering coefficients of arbitrarily oriented infinite cylinders have been worked out by Wait (5). These expressions are, however, too complicated to be of practical use, unless extensive numerical integrations are carried out. It is not possible to obtain simple analytical expressions for magneto-optical behaviour for such particles, as in the case of Rayleigh scatterers. Further the theoretical requirement that the cylinder should be infinite in length is not actually obtained in practice and involves a certain degree of approximation.

(2) Aggregates of Rayleigh Scatterers—Under certain conditions the primary particles may form aggregates and this may lead to additional complications. Certain anomalies observed in the magneto-optical behaviour of colloidal Fe₃O₄ (3, pp.150) indicates evidence of formation of such aggregates in this colloid. In the present work it was decided, therefore, to carry out a detailed investigations of the magneto-optical behaviour of colloidal Fe₃O₄.

Before proceeding further, however, a brief summary of the expressions relating the magneto-optical effects in a colloid containing independent Rayleigh scatterers is given below. Their applications to the particle size analysis is also explained. In the present work, only dipolar particles are considered, though the expressions for magnetically anisotropic particles have also been derived (4).
Under a magnetic field, the colloid exhibits anisotropic light transmission, which is formally similar to the transmission through an uniaxial dichroic crystal. The symmetry axis is parallel to the magnetic field. We assign two complex refractive indices, viz. "extraordinary" $\bar{n}_e$ and "ordinary" $\bar{n}_o$ to the colloid. The extraordinary index $\bar{n}_e$ is applicable when the electric vector of the incident light is parallel to the magnetic field. The ordinary index $\bar{n}_o$ is applicable when the electric vector is perpendicular to the direction of the magnetic field. Expressions for $\bar{n}_e$ and $\bar{n}_o$ are given by

$$
\bar{n}_e = \mu \left[ 1 + 2\pi N \left[ \alpha_\perp + (\alpha_\parallel - \alpha_\perp) \mathcal{L}(h) \right] \right]^2
$$

$$
\bar{n}_o = \mu \left[ 1 + 2\pi N \left( \frac{\alpha_\perp + \alpha_\parallel}{2} - \frac{\alpha_\parallel - \alpha_\perp}{2} \mathcal{L}(h) \right) \right]^2
$$

Here

$\mu$ = refractive index of the surrounding medium.

$N$ = Number of particles per cc.

$\alpha_\perp$ and $\alpha_\parallel$ are the principal components of the complex polarizability of the colloidal particle respectively perpendicular and parallel to its axis of symmetry. For particles of isotropic materials they are determined by the shape coefficients. (§ 22 pp 4).

(Colloidal particles are assumed here to be of a strongly absorbing material so that the extinction in the colloid is mainly due to the

THEORY

...
absorption. Generalisation to include the scattering can readily be done by writing

$$ p_j = \alpha_j - \frac{2}{3} i k^3 |\alpha_j|^2 \text{ for } \alpha_j $$

The function $L(h)$ has the form

$$ L(h) = 1 - \frac{2}{h} \coth h + \frac{2}{h^2} $$

where

$$ h = \frac{\omega H}{KT} $$

$\omega$ being the magnetic moment of the particle.

Birefringence in the colloid is given by

$$ n_e - n_o = \frac{\delta}{2\pi N\lambda^2} \left[ \text{Re} \left( \frac{\alpha_i - \alpha_{ii}}{z} \right) \right] \left[ 3L(h) - 1 \right] $$

$\delta$ is the phase retardation per unit length and is the parameter directly measured in birefringence experiment.

Similarly we define two parameters $Q_{\parallel}$ and $Q_{\perp}$ to describe the transmission measurements.

$$ Q_{\parallel} = \frac{c_{\parallel}}{c_{o}}, \quad Q_{\perp} = \frac{c_{\perp}}{c_{o}} $$

$C_o$ is the extinction coefficient measured without the application of the magnetic field.

$C_{\parallel}$ is the extinction coefficient measured under the applied field when the electric vector of the incident light is parallel to the applied field.

$C_{\perp}$ is the extinction coefficient measured under the applied field.
when the electric vector of the incident light is perpendicular to the applied field.

\[ Q_{\|} - Q_{\perp} = \frac{3}{2} \frac{\text{Im}(\alpha_{\perp} - \alpha_{\|})}{\text{Im}(\alpha_{\perp} + 2\alpha_{\|})} \left[ 3L(h) - 1 \right] \]  

(2)

It is to be noted here that the transmissivity of the colloid when the light path is parallel to the magnetic field (indicated here by subscript K) is same as that under transverse field with electric vector perpendicular to the light path \( Q_{K} = Q_{\perp} \). This equality can serve as a very good check to test whether the optics of the colloid can be described in terms of independent Rayleigh scatterers. Other special relation readily verified is

\[ \frac{Q_{\|} - 1}{1 - Q_{\perp}} = z \left[ \text{Since } Q_{\|} \text{ is proportional to } \frac{\alpha_{\|} + 2\alpha_{\perp}}{3} \right. \]

\[ \text{and } L(0) = \frac{1}{3} \]

APPLICATION:

Equations (1) and (2) are useful in interpreting experimental data. Technique of their application is explained below.

For the birefringence observations we plot

(1) the theoretical curve of \( \log (3L(h)-1) \) vs. \( \log h \) and

(2) the experimental curve of \( \log S \) vs. \( \log h \).

Combining equation (1) with \( h = \frac{\omega H}{kT} \) we see that the two graphs should be identical except that the origin of the experimental
graph is shifted relative to that of the theoretical graph by an amount

(i) \[ \log \frac{\omega}{K_T} \] along the X-axis and
(ii) \[ -\log \frac{\delta_{sa}+}{2} \] along the Y-axis

\[ \delta_{sa}+ \] is the saturation value of the birefringence.

Thus from the transmission data we plot

(1) the theoretical curve of \( \log (3L(b)-1) \) vs. \( \log b \)
(2) the experimental graph of \( \log (Q_{ii}-Q_{ll}) \) vs. \( \log b \)

These two curves should also be similar except that the origin of
the experimental curve is shifted relative to that of the theoretical
graph by an amount

(i) \[ \log \frac{\rho}{K_T} \] along the X-axis
(ii) \[ -\log \frac{(Q_{ii}-Q_{ll})_{sa}+}{2} \] along the Y-axis

Due to polydispersity in the particle sizes, the experimental and
theoretical curves may not match entirely over the whole range of field
strength. For particles of colloidal dimensions one can safely assume
that they exist as individual magnetic domains (9).

**Application to the Determination of the Shape Factor**

From the transmission data the shape factor can be calculated as

under

\[ \left( Q_{ii} - Q_{ll} \right)_{sa}+ = \frac{3 \text{Im}(\alpha_{ll} - \alpha_{ll})}{\text{Im}(\alpha_{ll} + 2\alpha_{ll})} \] \hspace{1cm} (3)

Also (9 pp. 70)
\[
\alpha_j = \frac{V}{4\pi} \left[ \frac{1}{L_j + \frac{1}{m^2 - 1}} \right]
\]

where

\( L_j \) - appropriate depolarisation coefficient of a spheroidal particle with volume \( V \).

\( m \) - the complex refractive index of the material of the particle.

Using the above expression we can calculate \( L_{||} \) and \( L_{\perp} \) and hence the shape factor (i.e., the ratio of the axis).

It is also possible to determine the shape factor from birefringence data. However this requires the knowledge of concentration of the colloid in g/l or cc. In this case

\[
\frac{8 \omega^2}{\lambda} = \frac{2\pi}{\lambda} (n_c - n_0) = 2\pi \frac{n_c n_0}{\lambda} \text{Re} (\alpha_{\perp} - \alpha_{||})
\]
Preparation of Colloidal Fe₃O₄

The following procedure suggested by Kittel (10, pp. 491) was used in preparing colloidal Fe₃O₄:

Equivalent quantities of ferrous chloride and ferric chloride solutions were mixed. (Ferrous chloride was freshly prepared by dissolving pure iron in hot concentrated HCl.) Requisite quantity of hot NaOH solution was added to this mixture. The black precipitate of Fe₃O₄ thus obtained was washed in centrifuge to remove electrolytes. This was then peptized using minimum quantity of HCL. Initially the colloid is black but after about a month it turns to brownish red.

Slight variation in the procedure considerably affects the stability of the colloid.

Technique for the Measurement of Birefringence:

The birefringence in colloidal solution is usually measured by placing the colloid between cross polaroids oriented at 45° to the direction of the field. The light transmitted through the system when the magnetic field is applied is then measured. Since in most of the colloids the birefringence is accompanied by dichroism and hence it is necessary to correct for the latter. The expression for the transmitted light intensity is

\[ I = \frac{I_0}{4} \sin^2 \theta \left[ T_\theta + T_L - 2 \sqrt{T_\theta T_L} \cos S \right] \]
(11)

Where

\[ \phi = \text{the angle between the applied field (i.e., the principle axis of the birefringent colloid) and the axis of the polaroid} = 45^\circ \text{ throughout.} \]

\[ \delta = \delta_{11} - \delta_{11} = \text{is the phase difference produced in the colloid.} \]

\[ T_{11} = \text{is the transmissivity when the electric vector of the incident light is parallel to the applied field.} \]

\[ T_{11} = \text{is the transmissivity when the electric vector of the incident light is perpendicular to the applied magnetic field.} \]

Thus particularly in the case of absorbing colloids which show large dichroism it is necessary to know the ratio \( T_{11} / T_{11} \) accurately at different field strengths. This can lead to large errors in the present case of Fe\(_3\)O\(_4\) where the colloid show anomalous transmission changes under a magnetic field. Following alternative method was therefore used.

The method is an adaptation of one used by Menard (1c) for the determination of optical constants of metals by ellipsometry.

The assembly is as under. Light transmitted through a polariser which can be oriented at desired azimuth is next incident on a retardation plate oriented with its axis at \( 45^\circ \) to the principle axis of the birefringent sample. The elliptically polarised light beam after emerging through the birefringent sample is viewed through an analyser. The polariser and analyser are oriented to obtain complete extinction. The orientation of polariser with respect to the axis of the retardation plate gives the phase retardation in the birefringent sample. Usual practice
in ellipsometry is to use a near quarter wave plate for the retardation plate. For the purpose of measurement of weak birefringent in the colloid it was found however desirable to use smaller values of phase retardation. In our present study a retardation plate prepared of mica giving a phase different of 34° has been used. The birefringence is calculated using the following formula:

\[
\tan 2\Delta = \sin 2\phi \tan 2\theta
\]

Where

\[2\Delta = \text{the phase retardation}\]

\[2\phi = 34° = \text{phase retardation of the compensating mica plate.}\]

\[\theta = \text{the orientation of the polariser with respect to the axis of the compensating plate in the extinction position.}\]

The technique of measuring the changes in optical transmission is discussed earlier in the thesis (pp.43).

(I) Transmission Changes under a Magnetic Field:

Transmission changes were studied with the colloid placed under a magnetic field for the following three cases:

(i) The field applied perpendicular to the direction of propagation of incident light, the incident light being plane polarised with its electric vector parallel to the applied magnetic field.

(ii) The magnetic field applied as in case (i) but the incident light with its electric vector perpendicular to the applied magnetic field.

(iii) The magnetic field applied parallel to the direction of
incident light.

In the case (iii) the changes were found to be independent of the state of polarization.

(a) Transmission in Fresh Colloids:

Freshly prepared colloids exhibited marked changes in their transmissivity in a comparatively weak field, below about 100 gauss. For stronger fields, colloids show continuous increase or decrease in transmission. This may probably be due to a drift of particles towards the region of stronger fields. Hence for fresh colloids the observations were limited to the fields below 100 gauss. Such magnetic fields were applied using a suitable Helmholtz coil. It was generally observed that:

(1) transmission decreased in a longitudinal field.
(2) transmission increased in a transverse field if electric vector of incident light was perpendicular to the applied magnetic field.
(3) transmission decreased by a very small amount in a transverse field if electric vector of incident light was parallel to the applied magnetic field.

The results obtained for three different specimens are represented graphically in figs. 1, 2 and 3.

Fig. 1 shows the transmission changes observed in a colloidal Fe₃O₄ approximately two weeks after preparation. The parameter \( Q \) indicates the ratio of extinction coefficient under applied field to that without the field \( (Q = \frac{\eta_1}{\eta_0}) \). The curve indicated by \( k \) shows the data when the magnetic field is parallel to the direction of incident light.

Fig. 2 shows similar observations for another specimen observed almost immediately after preparation. In this case practically no
Fig. No. 1.

Transmission Changes in a Weak Magnetic Field

\[ \lambda = 5500 \text{ Å} \]

Fe$_3$O$_4$ colloid

Prepared on 25-4-66

Observed on 6-5-66

I amp. = 74 gauss

\[ \text{Current (in amps)} \]
Fe$_3$O$_4$ - Transmission Changes in Weak Magnetic Field

Colloid prepared on 23.5 \text{ and observed on 27.5.}

Helmholtz Coils \text{ in}
\text{(a.c. & d.c.)}

1 amp. = 74 gauss

\text{Coil Current in amps.}

\lambda: 4500 \text{ AU.}

\lambda: 5500 \text{ AU.}

\text{Coil Current in amps.}
transmission changes were exhibited by the colloid when magnetic field was applied perpendicular to light path and electric vector of incident light parallel to the magnetic field. This figure also indicates that the transmission changes under alternating magnetic field (50 c/s) are practically the same as in d.c. field.

Fig. 3 shows the observations in a colloidal solution about one month after the preparation (data and figure are reproduced from the Ph.D. thesis of Shri J.R. Bajaj). The nature of these curves are similar to those in fig. 1.

The results shown in fig. 1, 2 and 3 are quite surprising. They show that the transmission changes exhibited by freshly prepared colloid do not agree with the theoretical expressions (pp. 5 to 9). Thus not only $Q_\perp$ and $Q_\parallel$ are unequal. Also transmission decreases in longitudinal position and it increases in the perpendicular position, the relation $Q_\parallel - 1$ is also obviously not satisfied.

The results appear really anomalous when it is noted that the colloidal particles in Fe$_3$O$_4$ are known to be about 70 Å in radius. It is quite small compared to the wavelength of light used (11, 12), and should therefore act as Rayleigh scatterer. These anomalous results will be discussed after describing the transmission through aged colloids.

(b) Transmission in Aged Colloids

Optical transmission changes in aged colloidal Fe$_3$O$_4$ were studied for two different specimens.
Figure 4

Fe$_3$O$_4$ colloid aged for one year

Transmission Changes in a Strong Magnetic field.
(15)

(1) A specimen aged for about one year (Prepared by a senior worker).

(2) Another specimen aged for about four months.

In aged colloids no drift of particles were observed even at fields as large as 4000 gauss. The effects observed for weak fields below 100 gauss are quite small. Hence observations were taken with stronger fields using an electromagnet.

Results are shown in fig. 4 and 5.

The curves in fig. 4 clearly show that the transmission under magnetic field in an aged Fe₃O₄ colloid is entirely in agreement with the theory presented earlier (pp. 5 to 9). The curves for H position and K position cannot be distinguished. The relation in also seems to be obeyed quite satisfactorily.

Fig. 3 shows similar observations for another specimen of colloidal Fe₃O₄ aged for about four months. In this case also the behaviour of the colloid seems to be quite normal in the sense that it is in agreement with the Rayleigh theory. The same colloid when it was fresh exhibited anomalous behaviour similar to those shown in fig. 1.

Comparison of the optical transmission in the fresh and the aged colloids brings out the following main features.

(1) Transmission changes observed in a magnetic field for the fresh colloids are not in agreement with the expressions based on the Rayleigh theory; on the other hand, the changes observed for the aged colloids are in complete agreement with the theory.
(2) Most marked difference in the behaviour of the fresh and the aged colloids is observed when the applied magnetic field is parallel to the incident light beam. In this position the fresh colloids show a decrease in transmission under a magnetic field while the aged colloids show an increase in the transmission.

(3) The fresh colloids when subjected to a moderately strong field over 100 gauss particularly in k-position, show a continuous change in transmission. No such effects are exhibited by aged colloids. This "cropping" observed in fresh colloid can possibly be due to drifting of the particles towards the region of stronger fields.

**Explanation of the Anomalous Behaviour in Fresh Fe₃O₄ Colloids**

The anomalous transmission changes observed in the fresh Fe₃O₄ colloids can probably be due to the formation of magnetically linked groups of magnetite particles. It has not been possible to give an exact theoretical explanation of this problem of light extinction by such aggregates when the individual particles are orientated under the influence of an applied magnetic field. Qualitatively, however, the behaviour in the case of light propagation parallel to the magnetic field can be understood if we suppose that the primary particles form magnetically linked chains. The extinction cross-section of such a chain will be somewhat similar to that of a long cylinder. Theoretical results on extinction cross-section of thin infinite cylinders (7) show that it has a large value when the propagation direction is parallel to the cylinder axis. These results, however,
Comparison of Theoretical Curve of \( \log h \) vs \( \log \left[ \frac{3L(h)-1}{2} \right] \)

with the Experimental points of \( \log H \).
Comparison of theoretical curve of $\log \frac{h}{v} = \log \left[ \frac{b}{l} (h-1) \right]$ with the experimental points of $\log H$ vs. $\log \delta$.
Graph of Birefringence vs. Magnetic Field.

Fe₃O₄ Colloid: aged and fresh.

λ = 5890 Å

O: aged sol; △: fresh sol
Graph of Birefringence vs. Magnetic Field

Fe$_3$O$_4$ Colloid: aged and fresh

λ = 5890 Å

- ○: aged sol.
- △: fresh sol.

Magnetic field
concentration of HCl which is used for peptization, it follows that the particles will not approach each other by less than about 30 Å distance (30 Å being the extent of double layer at this electrolyte concentration). This double layer repulsion forces would still reduce the chances of formation of such chains.

Thus we conclude that in the equilibrium situation the particles should exist independently. In case of a fresh colloid, linked groups which are formed when Fe₃O₄ is precipitated, may not dissociate immediately on the peptization of the colloid. Fresh colloid may, therefore, contain undissociated chains. On aging, however, gradually the particles dissociate and the particles act as independent scatterers exhibiting transmission changes in the magnetic field. This is in agreement with the theory based on the assumption of independent single particle Rayleigh scattering.

**Birefringence in Colloidal Fe₃O₄**

The birefringent in colloidal Fe₃O₄ was also studied in the case of aged and the fresh colloids by the technique described earlier. In this case no marked difference was observed between the behaviour of fresh and the aged colloids.

**Spectral Transmission**

The spectral transmission curves are shown in Fig. 9 for different specimen both, aged and fresh. In order to make the shapes of the curve independent of the concentration log extinction coefficient is
plotted against the wavelength. It is interesting to note that the aged specimens show a comparatively deeper minimum at about 7500 Å.

Determination of Particle Size:

On page 6 we have explained the technique of determining the magnetic moment per particle from the observations of either the transmission changes or birefringence under a magnetic field. In the case of transmission the method can be applicable only to the aged colloid since the fresh colloid shows anomalous behaviour.

Fig. 6 shows the theoretical graph of log \((3\beta(h-1))\) vs log \(h\). The experimental points of log \((Q_{||} - Q_{\perp})\) vs log \(h\) are shown after shifting the origin. The shift along \(X\) and \(Y\) axes are tabulated on pp. 20.

Both the specimens show the same shift along the \(X\)-axis. With \(KT = 4.1 \times 10^{-14}\) cm we obtain \(\omega = 6.95 \times 10^{-16}\) esu.

As mentioned previously, such small ferromagnetic particles exist as single domains, magnetized to the saturation value (2, 10 pp. Dividing by the saturation intensity of magnetization = 476 esu/cc, the particle size comes out to be

\[ V = 1.46 \times 10^{-18} \text{ cc} \]

\[ \therefore r = 70 \text{ Å} \]

Fig. 7 shows the graph of log \((3\beta(h-1))\) vs log \(h\) and the experimental points of the curve of log \(S\) vs log \(h\) after necessary shift of origin. The results are calculated for both fresh and aged
### TABLE No. 1

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Colloid</th>
<th>X-displacement</th>
<th>Y-displacement</th>
<th>Average Y-displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aged for one year</td>
<td>-1.775</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Aged for four months</td>
<td>-1.775</td>
<td>0.93</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE No. 2

Shifts of origin of the experimental curve of log $\log (Q_{x}+Q_{y})$ vs log $\log (x+y)$ = fig. 6

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Colloid</th>
<th>X-displacement</th>
<th>Y-displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aged for four months</td>
<td>-1.75</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>Fresh</td>
<td>-1.59</td>
<td>0.57</td>
</tr>
</tbody>
</table>
The shifts along both the axes are tabulated on pp. 20.

For aged colloid from \( X \)-displacement = -1.75, we obtain
\[
\omega = 7.35 \times 10^{-16} \text{ cm}
\]
which gives \( r = 72 \text{ A} \).

For fresh colloid from \( X \)-displacement = -1.59, we obtain
\[
\omega = 10.54 \times 10^{-16} \text{ cm} \text{cm}
\]
which gives \( r = 81 \text{ A} \).

Thus it appears that even in a fresh colloid the particle size can be determined fairly accurately from the birefringence measurements. The transmission measurements, however, do not give reliable results.

The particle size obtained by Elsevo (11) is \( (\approx 85 \text{ A}) \),
and that obtained by Garrod (12) is 50 \text{ A}.

**Particle Shape**

To determine particle shape we need two depolarisation coefficients \( D_{||} \) and \( D_{\perp} \). They are obtained from the saturation values of either "\( (Q_{||} - Q_{\perp}) \)" or "\( Q_{||} \)".

Thus from the average \( X \)-displacement = 0.93 in fig. 6, we have
\[
(Q_{||} - Q_{\perp})_{\text{sat}} = 0.235.
\]

Also,
\[
(Q_{||} - Q_{\perp})_{\text{sat}} = \frac{3 I_m (\alpha_{||} - \alpha_{\perp})}{\alpha_{||} + 2 \alpha_{\perp}}
\]

Now \( \alpha_j = \frac{V}{4\pi} \left[ \frac{1}{L_j + \frac{1}{m^2 - 1}} \right] \).
Where
\[ n = n_1 - in_2 = \text{complex refractive index of the material of} \]
particle with respect to the surrounding medium viz. water

when \( n_2 < 0.3 \) we have approximately
\[
\frac{\text{Im}(\alpha_L - \alpha_{\|})}{\text{Im}(\alpha_L + 2\alpha_{\|})} = \frac{2(m_2^2 - 1)}{(m_1^2 + 2)} (L_L - L_{\|})
\]

substituting \( (\alpha_{\|} - \alpha_L)_{\text{ext}} \)
we obtain \( L_L - L_{\|} = 0.096 \) since \( L_{\|} + 2L_L = 1 \)

This gives the ratio of major to minor axis of the spheroid = 1.25

Similarly from the saturation value of \( \delta \) we can determine the
shape using the equations
\[ \delta = \frac{2\pi}{\lambda} (n_e - n_o) \]
\[ n_e - n_o = 2\pi N \mu \left[ \text{Re} \frac{\alpha_L - \alpha_{\|}}{2} \right] \left[ 3L(x) - 1 \right] \]
\[ \text{Re} \left( \frac{\alpha_L - \alpha_{\|}}{2} \right) = \frac{qV}{4\pi} \left[ \frac{m_2^2 - 1}{m_1^2 - 2} \right] \left[ L_L - L_{\|} \right] \]

assuming the imaginary part \( n_2 \) of index \( n < 0.3 \)

In this case it is also necessary to know the concentration of the
colloid in grams/cc.

\[ M = 4/3 \int r^3 f = NV^3 \] in order to eliminate \( NV \).

From \( L \)-displacement in fig. 8 we get \( a = 1.74 \) for the aged
colloid with \( M = 0.7 \) grams/cc this gives \( L_L = L_{\|} = 0.046 \) which
correspond to the ratio of the axis of the particle = 1.11

The experimental curve in fig. 8 have been fitted to the
theoretical curve for the medium field strengths. The experimental curve
falls below the theoretical curve for the high field strength. This is most probably due to the polydispersity of the particle sizes. If we use the extrapolated values for the high field strength, the X-displacement gives the value \( S_{\text{ex}} = 2.344 \). This gives \( L_\perp - L_\parallel = 0.057 \) which corresponds to the ratio of the axis = 1.16

The axial ratio derived from the birefringence data is somewhat smaller than that derived from transmission measurement. The discrepancy may be due to the error in the determination of the concentration. Partly it may also be due to the optical anisotropy in Fe$_3$O$_4$ crystals induced because of the "magnetostriction".

**CONCLUSION**

From our study of magneto-optical effects in fresh and aged colloidal solutions of Fe$_3$O$_4$, the following main features are observed.

(1) Fresh and aged colloid show markedly dissimilar changes in the transmissivity under a magnetic field. Most striking differences are shown in the case when the optical transmission is parallel to the magnetic field. In that case, the two colloids show contrary behaviour. In fresh colloid transmission increases under the applied magnetic field, while it decreases in aged colloid.
(2) In fresh colloids continuous changes in transmission i.e., "creeping" is observed for field strength above 100 gauss, while in aged colloids no such behaviour is noted even at 4000 gauss.

(3) Birefringent behaviour shown by the fresh and aged colloid have similar nature (fig. No.7) and no marked differences are noted.

(4) The magneto-optical effects in aged colloids show complete agreement with the expressions derived under the assumptions that the colloidal particles are independent Rayleigh scatterers. The effects observed in fresh colloids do not agree with these expressions.

It is proposed that the anomalous effects observed in fresh colloids occur because of the existence of magnetically linked chains of primary particles. On subsequent aging these chains dissociate and colloidal particles then act as independent Rayleigh scatterers. This conclusion is also justified if one compares the magnetic potential energy of the linked particles with the thermal excitation energy $kT$ (14).

From the analysis of the data the particle size and shape are inferred. We obtain the average magnetic moment of the particle as $6.95 \times 10^{-16}$ c.g.s. (from transmission measurement) and $7.36 \times 10^{-16}$ c.g.s. (from birefringence measurement). With saturation magnetisation intensity of 476 c.g.s./cm, we get the mean particle radius of 70 A. This may be compared with the value 95 A obtained by Elseor (14) by centrifuge method and 50 A obtained by Garwood (13).
Assuming the particles to be prolate spheroid, the ratio of the two axes of the particle obtained from transmission observations comes out to be 1.35 and that obtained from birefringence observations comes out to be 1.16.

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