Magneto-Optical Properties of Ferromagnetic Suspensions

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Observations on the change of light transmission through magnetite suspensions under the influence of alternating magnetic fields show that the orientation of the particles is not exclusively of dipolar origin, as was assumed by Heaps and Elmore. Fields of frequencies between 500 and 15,000 cycles per sec. produce a steady change of absorption. In fields of lower frequencies ω the change consists of a steady and a fluctuating part. The wave form of the latter is studied with a photo-cell amplifier and an oscillograph. In general, it is given by an equation of the form: $A \cos \omega t + B \cos 2\omega t$. By varying the field intensity, the frequency or the viscosity, either A or B can be made to vanish. This behavior is shown to be characteristic of polar anisotropic particles, for which the torque on the induced dipole is of the same order of magnitude as that due to the permanent dipole. Included is a survey of the work done on the magneto- and electro-optical properties of numerous other colloids and suspensions.

INTRODUCTION

THE optical properties of many colloids and suspensions undergo marked changes under the influence of uniform magnetic or electric fields. Clear, transparent colloids made up of small particles with an average diameter less than about 0.1μ become birefringent, while the predominant optical effect in suspensions with large particles is a change in the intensity and angular distribution of the scattered Tyndall light. Frequently, when the integrated intensity of the scattered light is altered, the field changes the intensity of the transmitted light, i.e., it influences the absorption. In fine dispersions the latter effects are small, whereas the birefringence is negligible in coarse suspensions. An intermediate case arises when the linear dimensions of the particles are of the same order of magnitude as the wave-length of light. These sols show both an appreciable birefringence and a large change of absorption. Moreover, the change of absorption depends upon the state of polarization of the light, i.e., for light traveling normal to the direction of the field the colloid becomes dichroic, even when the micelles are not of a dichroic material. In coarse suspensions, however, this dichroism disappears.

The magnitudes of the various effects vary considerably with the sol concentration, the shape, and the optical, magnetic, and electrical properties of the micelles. Of the numerous colloids examined by one of us, only two, milk and a suspension of carbon-black in Nujol, show no effects. Electric birefringence is known to occur in suspensions of ground calcite, mica, and other minerals (see Procupju),[1] in various solvents, in smokes, in the metallic colloids of Au, Pt, Ag, and Hg, and it is especially large in the sols of bentonite, V_2O_5, and the mosaic virus proteins. It has also been observed in collagen, pseudo-globulin, soap solutions, inks, and diluted paints. The change of scattering and of absorption in an electric field is particularly large in aqueous suspensions of kaolin clays, of ZnO in Nujol, and in colloids of $PbCO_3$. The effects are readily observable in fields of 100 volts/cm, and, for the coarse suspensions, fields as low as 10 volts/cm produce noticeable changes. In many instances the effects are extremely large; for example, the intensity of Krishnan's H_h component[2] of the scattered light can be increased by a factor of 10, and, in the kaolin suspensions, the absorption coefficient can be decreased more than 30 percent.

The magneto-optical effects have been studied for only a few colloids. In fields of several thousand gauss they are usually much smaller than the corresponding electro-optical effects, with the following exceptions: Colloidal graphite (aquadag) shows a large change of scattering and of absorption in fields of less than 1000 gauss. Especially famous for their large magneto-

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[1] S. Procupju, Ann. de physique **10**, 213 (1924).
[2] R. S. Krishnan, Proc. Ind. Acad. Sci. **7**, 91 (1938).

optical birefringence are colloidal solutions of the iron oxides, studied by Majorana,[3] Cotton and Mouton,[4] Schmaus,[5] and Heller and Zocher.[6] These solutions also exhibit a small change of absorption, and become dichroic in the magnetic field. Suspensions composed of larger particles of magnetite show a marked change of absorption. According to McKeehan,[7] this magneto-optical effect was discovered first by W. R. Grove in 1845. It was rediscovered by Heaps[8] in 1938, and has been the topic of a recent discussion by Elmore.[9] It is with the interpretation of this effect offered by the latter two authors that we should like to take issue here.

THEORETICAL

The magneto- and electro-optical effects in colloids are due to the orientation of anisometric particles. With increasing field intensity all the effects tend toward saturation, corresponding to complete orientation of all particles. Both Heaps and Elmore have assumed that, since Fe_2O_3 is ferromagnetic, we have to deal only with the orientation of permanent dipoles, i.e., that the torque on a single particle is given by

$$T=\mu H \sin\theta$$

where H is the applied field. The particles of all the other colloids studied are neither magnetic nor electric dipoles. In these colloids a major part of the torque arises from the action of the field on the induced rather than the permanent dipoles. Therefore, for particles with an axis of symmetry which forms the angle θ with the direction of the field, the torque is

$$T=\gamma H^2 \sin\theta\cos\theta.$$

Although the particles of Fe_2O_3 are oriented by very weak magnetic fields of one to ten Gauss (depending on particle size and heat treatment of the material) the possibility that the observed effect is not of ferromagnetic origin cannot be excluded. Hence the question arises: Is the magneto-optical effect in Fe_2O_3 due entirely to dipolar orientations, or is it in part due to the fact that the magnetic polarizability of the particles is anisotropic?

This problem can be solved on the basis of the following considerations: If the energy of orientation U is large compared to kT we must distinguish, as Elmore has pointed out, between two separate relaxation times. The short relaxation time $\tau_1=\rho/U$ is the time required for the absorption effect to reach a maximum when a steady field is applied suddenly, or when its direction is changed. However, when the field is removed, the decay of the effect is determined by the rotational Brownian motion, and thus the relaxation time is longer. This second relaxation time $\tau_2=\rho/kT$ (where ρ is the friction constant $8\pi\eta r^3$) will be called the decay time, and τ_1 the orientation time. The relaxation time τ_2 is used in Debye's theory. For dipoles $\tau_2/\tau_1=\mu H/kT$.

Now, if the suspension is subjected to an alternating field $H_0\cos 2\pi\nu t$ with period $1/\nu \gg \tau_2$ it is obvious, since the change of absorption depends upon H^2, that in the first approximation the intensity of the transmitted light will vary according to a law of the form:

$$\begin{aligned} I &= I_0 + A\cos^2 2\pi\nu t \\ &= (I_0 + A/2) + A/2\cdot\cos 4\pi\nu t \end{aligned}$$

where I_0 is the transmitted intensity when no field is acting, and A is the change for a steady field H_0. Actually, when saturation is approached the variation is not sinusoidal, although the period remains $1/2\nu$. When the frequency is increased, deviations from the above law are to be expected as ν approaches a critical frequency. The types of deviations and the frequencies at which they occur depend upon the origin of the orienting torque. In this respect, three possibilities will be considered.

(A) Dipolar Orientation

According to Debye's theory, the orientation and hence the optical effects disappear for high frequency fields. When $\mu H < kT$ the critical frequency is $1/\tau_2$, but in strong fields the critical period depends upon the orientation time τ_1, since the direction of the dipoles is reversed

[3] Q. Majorana, Comptes rendus **135**, 159, 235 (1902); Rend. Accad. Linc., [5], **11** (1), 374, 463, 531; (2), 90, 139 (1902); Physik. Zeits. **4**, 145 (1902).
[4] A. Cotton and H. Mouton, Ann. Chim. Phys. [8] **11**, 145, 289 (1907).
[5] A. Schmaus, Ann. d. Physik **10**, 658 (1903); **12**, 180 (1903).
[6] W. Heller and H. Zocher, Zeits. f. physik. Chemie **A164**, 55 (1933). (For a comprehensive study of these effects see: W. Heller, Kolloid Beihefte **39**, 1–4 (1933).)
[7] L. W. McKeehan, Phys. Rev. **57**, 1177 (1940).
[8] C. W. Heaps, Phys. Rev. **57**, 528 (1940).
[9] W. C. Elmore, Phys. Rev. **60**, 593 (1941).

after every half-cycle, and this reversal can take place in strong fields when $1/\nu > \tau_1$. In the first approximation, then, the intensity variation is of the form:

$$I = I_0 + B + C\cos(4\pi\nu t - \psi), \qquad (1)$$

where B and C approach zero at high frequencies. Notice that the periodic part has twice the frequency of the applied field, and is shifted in phase.

(B) Orientation of Anisotropic Non-Polar Particles

This case has been treated by Tummers[10] for small fields. In high frequency fields the particles are oriented, but the change of absorption is steady. The critical relaxation period is the decay time τ_2, for in this case the torque is proportional to H^2 and the orientation of the particles is not reversed. Hence the transmitted intensity can fluctuate only when the time between successive half-cycles is sufficiently large to allow the orientation to decay. Again, in the first approximation the intensity variation is given by Eq. (1), but, for nonpolar particles, only C vanishes at high frequencies, while the magnitude of the steady change B is equal to that produced by a steady field $H = H_0/\sqrt{2}$.

(C) Orientation of Anisotropic Polar Particles

For $1/\nu < \tau_1$, where the dipoles are ineffective, the alternating field creates a steady change in the transmitted light, as in case B. For $1/\nu > \tau_2$ the intensity is given by Eq. (1). In the intermediate case, however, where $\tau_2 > 1/\nu > \tau_1$, the particles are too sluggish to follow the variations of the torque $\gamma H^2 \sin\theta\cos\theta$, but they are sufficiently mobile to follow the variations of the torque on the dipoles. Since the quadratic torque creates a steady deflection, the combined effect of both torques is analogous to that produced in a polar colloid by the superposition of a steady and an alternating field:

$$H = H_1 + H_2\cos 2\pi\nu t.$$

This implies that, in the intermediate range, the transmitted intensity fluctuates according to a law which, in the first approximation, is of the form:

$$\begin{aligned} I &= I_0 + [\alpha + \beta\cos(2\pi\nu t - \psi)]^2 \\ &= (I_0 + \alpha + \beta^2/2) + 2\alpha\beta\cos(2\pi\nu t - \psi) \\ &\qquad + \beta^2/2\cdot\cos(4\pi\nu t - 2\psi). \end{aligned} \qquad (2)$$

Hence, if the influence of the anisotropy, i.e., the quantity α, is not small in comparison with the dipolar effect β, an appreciable fraction of the intensity variation has the same frequency as the applied field. In contrast to the two previous cases, the variation of the transmitted light may show no frequency doubling in strong alternating fields, when the dipole and the anisotropy play roles of equal importance—and when the frequency lies within the critical range.

Magneto- and electro-optical investigations in alternating fields, therefore, offer a very simple method for determining the origin of the torques on the micelles. Only when all the optical changes vanish at high frequencies can we be sure that the torque is of a purely dipolar origin. For most aqueous colloids frequencies of several kilocycles are to be considered high; for coarse suspensions in viscous media 60-cycle a.c. is sufficiently high. The numerous colloids for which the electro-optical effects have been investigated show the following changes: At high frequencies, steady changes in the birefringence, scattering, absorption, and dichroism occur. In fields of low frequency the change consists of both a steady and an alternating part, the latter having twice the frequency of the applied field. This behavior is characteristic of anisotropic nonpolar particles.

EXPERIMENTAL

Suspensions of Fe_2O_3 were prepared from a red powder, supplied to us by Dr. Benedikt of the magnetic laboratory of our Institute. This powder is derived from black Magnaflux powder No. 10 by annealing at 300°C in air. The particles were suspended in Nujol and the viscosity was varied either by heating or by diluting with CCl_4. The larger particles were allowed to settle out. From the decay time we estimate an average particle radius of about 10μ. The suspensions were placed in a rectangular glass trough of 5-cm length within a coil of 30 turns, and the radius of the coil was 3 cm. The current used was between 0.1 and 2 amp. Thus the range of field intensities was between

[10] J. H. Tummers, Diss. Utrecht, 1914.

FIG. 1. Wave form of intensity fluctuations of the light transmitted by a suspension of magnetite in an alternating magnetic field of 90 cycles/sec.

$\frac{1}{2}$ to 10 gauss. Alternating current was supplied by an audio-amplifier and a beat frequency oscillator as source of constant frequencies. The light source was a d.c. operated incandescent lamp, the beam passing through the cell parallel to the magnetic field. In order to study the intensity variations of the transmitted light, a photo-tube amplifier was connected to a cathode-ray oscillograph, thereby obtaining a clear record of the alternating part of the photo-current.

RESULTS AND DISCUSSION

Visual observation showed an appreciable increase in the transmitted intensity when a steady field H was applied, and, except for the very viscous solutions, the change took place very quickly; i.e., the orientation time was a small fraction of 1 sec. The decay time, however, was noticeably longer; in most suspensions it was longer than 1 sec. The dependence of the effect on the field intensity is similar to that reported by Heaps, but our suspensions require a field of about 10 gauss for saturation,[11] whereas the more finely dispersed colloids used by Heaps become saturated in fields of 1 gauss. In spite of this difference it seems reasonably safe to assume that the origin of the optical effect is the same in both types of suspensions.

Alternating fields of frequencies up to 15 kc produced the same sort of visual changes as were observed for steady fields. For frequencies above 500 cycles the intensity change was steady, this fact alone indicating that for our suspensions the assumption of Heaps and Elmore is not tenable. The orientation of the particles is due, at least partly, to their anisotropic polarizability. On the other hand, this anisotropy is not sufficient to account for the observations in fields between 50 and 300 cycles, for in this range the transmitted intensity possesses a fluctuating component. Since the decay time is longer than 1 sec., this fact indicates that the particles are permanent dipoles. Hence, we conclude that we are dealing with polar anisotropic particles, for which the torque on the induced dipoles is of the same order of magnitude as that due to the permanent dipoles. This conclusion is supported by observations made upon the wave form of the intensity fluctuations. The shape of the oscillograph curve changes with the frequency, the field intensity, the temperature, and consequently the viscosity of the solution. It can be varied from a sine curve with twice the frequency of the oscillator to a sine curve with the same frequency as the applied field. In general, as shown by the photograph, Fig. 1, the curve represents the superposition of a sin ωt and a sin $2\omega t$ term. This type of curve can be explained very readily on the basis of Eq. (2), when the dipolar contribution β is somewhat larger than α.

Thus, for the more coarsely dispersed suspensions of Fe_2O_3, it is necessary to modify the theoretical considerations of Elmore by taking into account an additional term proportional to H^2 in the expression for the orientation energy. This introduces considerable complications into the theory: Several conclusions reached by Heaps and by Elmore must be invalidated, and the problem of the relaxation phenomena in strong fields becomes extremely complex. Observations in alternating fields can be used to decide whether a similar correction is necessary for the fine disperse suspensions. Since they are saturated by weaker fields it is possible that the quadratic term plays a negligible role for the smaller particles.

Recently, Benedikt[12] has devised a more direct method for measuring the magnetic torque on colloidal particles. His results on Fe_2O_3 and other ferromagnetic suspensions lead to conclusions which are identical with those derived from our optical investigation. We are indebted to Dr. Benedikt for supplying us with the magnetite powder.

[11] According to private communication this result agrees with observations of Dr. Elmore on similar suspensions.

[12] E. T. Benedikt, J. App. Phys. **13**, 105 (1942).