ELLIPTIC POLARISATION OF LIGHT SCATTERED BY COLLOIDAL SOLUTIONS

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1. INTRODUCTION

IT is well known that the important conclusions derived from Mie's theory (1908) of light-scattering by large spherical particles are the finite depolarisation of the transversely scattered radiation when the incident light is unpolarised, the dissymmetry of the angular distribution of scattering and the ellipticity of the transversely scattered radiation when the exciting radiation is plane polarised in an arbitrary azimuth. Of these the last, namely the ellipticity, has been shown on theoretical grounds to be a sure test of the multipolar character of the scattering of light by any isotropic symmetric medium (Perrin, 1939, 1942). Nevertheless, experimental studies on the elliptic polarisation of light scattered by colloidal media are few. Using the Babinet Compensator method suggested by Sir C. V. Raman (1941) the light scattered by certain heterogeneous media was shown to be elliptically polarised by Darbara Singh (1942), Hariharan (1942), R. S. Krishnan and Venkata Rao (1944), and A. George (1950). Conclusions of a qualitative nature were drawn by them regarding the size of the scattering particles from the range of angles of polarisation of the incident light over which they were able to observe any ellipticity in the transversely scattered light. As will be shown later in the paper, their experimental approach to the problem of the elliptic polarisation of the scattered light was such as not to bring out clearly the implications of Mie's theory. The present investigation has therefore been undertaken in order to examine in greater detail the theoretical conclusions concerning the phase difference and the amplitudes of the vertical and the horizontal components of the scattered radiation when the azimuth of polarisation of the incident radiation is varied. Suitable experimental methods have been used to analyse the scattered radiation in some emulsions and sulphur sols containing particles which are known to be spherically symmetric and of uniform size.

2. THEORETICAL CONSIDERATIONS

According to Mie's theory, if the incident beam of light is polarised with vibrations vertical or horizontal, the light scattered in the transverse

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horizontal direction will be completely polarised. In the former case, the electric vector of the scattered light will be perpendicular to the plane of scattering, while in the latter it will be in the plane of scattering. The corresponding intensities are given by equations (1) and (2).

$$J_{\perp} = K \left| \sum_{1}^{\infty} - (A_\nu \pi_\nu - P_\nu \pi_\nu') \right|^2 = K \left| (a + ib) \right|^2 \qquad (1)$$

$$J_{\parallel} = K \left| \sum_{1}^{\infty} (A_\nu \pi_\nu' - P_\nu \pi_\nu) \right|^2 = K \left| (c + id) \right|^2 \qquad (2)$$

where K is a constant equal to $\lambda^2/4\pi^2 r^2$, r being the distance of the observer from the centre of the particle. π_ν is an easily calculable function of the angle of scattering γ, and π_ν' is its derivative. A_ν and P_ν are complicated functions of $2\pi R/\lambda$ and m, where R is the radius of the spherical particle, λ the wavelength of light and m the relative refractive index of the particle. Several numerical computations of A_ν and P_ν for particles of different sizes and relative refractive index exist in the literature which render quantitative comparison with theory possible. [Blumer (1925, 1926), Lowan (1948), R. O. Gumprecht and C. M. Sliepcevich (1951, 1952), Bernice Goldberg (1953), Kerker and Perlee (1953), Gucker and Cohn (1953) and Boll, Gumprecht and Sliepcevich (1954)].

In formulæ (1) and (2) the quantities within brackets are complex quantities whose absolute values are to be taken for evaluating the intensities of scattering. But the amplitudes of vibration corresponding to $J_\perp$ and $J_\parallel$ which may be put in the form $a + ib$ [see equations (1) and (2)] have in general a certain difference of phase with respect to the components of the incident electric vectors which give rise to them, the phase of these vibrations being with respect to the centre of the spherical particle.

Let us now suppose that the particle is illuminated by a beam of light polarised at an angle α to the vertical. The incident electric vector of unit intensity may be resolved into two components $\sin \alpha$, in the plane of observation and $\cos \alpha$ perpendicular to it. These components of the incident vibration are in phase. In the transverse horizontal direction the intensities of the perpendicular and parallel components of the scattered radiation are given by

$$J_{\perp} = K \left| (a + ib) \right|^2 \cos^2 \alpha \qquad (3)$$

$$J_{\parallel} = K \left| (c + id) \right|^2 \sin^2 \alpha \qquad (4)$$

These two components combine to form an elliptically polarised radiation and the phase difference δ between the vertical and horizontal components

is then given by

$$\delta = \tan^{-1} b/a - \tan^{-1} d/c \qquad (5)$$

δ may however be positive or negative depending on the size and refractive index of the scattering particles (Kastler, 1952). It is to be pointed out that δ the phase difference is independent of the angle of polarisation α and depends only on the size and relative refractive index of the scattering particle and the angle of scattering γ. Thus as α is varied from 0 to 90°, one observes in the transverse horizontal direction a continuous variation of the ellipticity, namely the ratio of the minor to the major axis of the ellipse, which increases first from 0 to a finite value depending on ρ_u and then decreases to zero again, *the phase difference between the vertical and the horizontal components remaining however constant.* It follows from Mie's theory that this phase difference is a characteristic quantity of the scattering element like intensity of scattering and depolarisation.

If the observation is not restricted to the transverse horizontal direction alone, as the phase difference fluctuates with the angle of scattering (Van de Hulst, 1947), for certain angles of observation depending on the size and relative refractive index, the incident linearly polarised light can give rise to circularly polarised light. A complete study of the elliptic polarisation of the scattered light should therefore include a measurement of the phase difference δ, and a determination of its sign, a determination of the orientation of the axes of the ellipse with respect to the horizontal and vertical, the ellipticity or the ratio of the axes and its variation with the angle of polarisation of the incident beam.

If the direction of incidence be along OZ of a rectangular co-ordinate system, and the observation along OY, then the elliptic vibration representing the scattered radiation, when the plane of polarisation of the incident light is inclined at an angle α to the vertical (OX) has for its components

$$z = p_1 \sin \alpha \sin \omega t$$

$$x = p_2 \cos \alpha \sin (\omega t + \delta) \qquad (6)$$

where $p_1 \sin \alpha$ and $p_2 \cos \alpha$ are the complex amplitudes, δ the phase difference and ω the circular frequency. Then θ the inclination of the axis of the ellipse to the horizontal is given by (Theory of Optics—Schuster and Nicholson, 1924).

$$\tan 2\theta = \frac{\sqrt{\rho_u} \sin 2\alpha}{(1+\rho_u)\sin^2 \alpha - 1} \cos \delta \qquad (7)$$

since $\rho_u = (p_1)^2/(p_2)^2$. From this it is seen that there exists a relation between the orientation of the ellipse, the phase difference between the vertical and the horizontal components, the depolarisation factor ρ_u and the angle of polarisation α. Thus as stated earlier, if the scattering medium consists of large spherically symmetric particles of uniform size, δ is the same and is a constant and the result of varying α would be to produce elliptically polarised radiation of different orientations and axial ratios. It follows from equation (7) that for a value of α given by $\cot^{-1} \sqrt{\rho_u}$, θ the inclination of the axis of the ellipse is 45° and the corresponding value of ρ_a is 100%.

If one analyses the scattered light using a Babinet Compensator set with its axes vertical and horizontal, then as the plane of polarisation of the incident beam is rotated, the fringes due to the elliptically polarised scattered radiation will not show a continuous shift with respect to the cross-wire. On the other hand, if the compensator is set with its axes at 45° to the vertical as was done by the earlier workers [Darbara Singh (1942), Hariharan (1942), R. S. Krishnan and Venkata Rao (1944) and A. George (1950)] the fringes as seen through the Compensator will shift continuously with reference to the crosswire in spite of the fact that δ is a constant. The phase difference $(\phi_2 - \phi_1)$ with respect to the axes of the Compensator, which was the quantity measured by the earlier workers is given by

$$\tan(\phi_2 - \phi_1) = \frac{\sqrt{\rho_u} \sin 2\alpha}{1 - (1 + \rho_u) \sin^2\alpha} \sin \delta. \tag{8}$$

It is also possible to evaluate δ from the above equation using the measured values of ρ_u, α and the corresponding $(\phi_2 - \phi_1)$. But this is not the direct method of measurement of δ, which is a characteristic parameter of the scattering particle.

3. EXPERIMENTAL DETAILS

To carry out visual observations a strong source of light was necessary. Consequently in all the measurements to be described below, sunlight reflected by means of a Foucault single mirror Heliostat was used as the source of illumination. The light was condensed by means of a Dallmeyer photographic lens of focal length $12''$ fixed to cover an aperture in the wall of a darkened room. By using a small aperture a nearly parallel beam was obtained and this was allowed to fall on the colloid contained in an optical glass cell, suitable precautions being taken to avoid errors due to stray light, etc. Since the orientation of the elliptic vibration had to be determined it was necessary to rotate the Babinet Compensator about the direction of the scattered radiation and know accurately the orientation of the principal

axes of the Compensator. This was achieved by the use of a Fuess polaris-ing microscope kept with its axis horizontal in conjunction with a Fuess Babinet Compensator analyser combination. The orientation of the principal axes could be accurately read off from the graduated circle of the microscope. A green filter was placed in the path of the incident beam to obtain a narrow band of wavelengths of high intensity. This was essential for accurate measurements since the fringes are well defined only for monochromatic or nearly monochromatic radiations. A cell containing alum solution was used to cut off the heat radiations in the incident light. A large square ended nicol was used to polarise the incident beam and the angle of polarisa-tion could be read off on a graduated circle.

A direct measurement of δ was also made by using the Babinet Com-pensator with its axes vertical and horizontal. For any arbitrary angle of polarisation, if there exists a measurable difference of phase between the vertical and the horizontal components of the scattered light the crosswire would no longer be at the centre of a dark or bright band but would have shifted to some other position depending on δ. The shift which gives the phase difference will be constant when the angle of polarisation is varied; only the visibility of the fringes will undergo a change. The sign of the phase difference as well as the other characteristics of the elliptically pola-rised radiation may easily be determined with the help of a quarter wave plate and a nicol. As such observations on the sign of δ, etc., were made using also a $\lambda/4$ plate and an analyser mounted on graduated circles, by methods which may be found in any standard treatise on optics.

4. PREPARATION OF EMULSIONS AND SOLS

Two different emulsions were prepared for the study, namely (1) Berga-mont oil in water, (2) Lemon oil in water. The uniformity of the droplets and the stability of the emulsion depend on the mode of preparation. Con-sequently to obtain stable emulsions the following method was adopted.

About 400 c.c. of pure double-distilled water was rendered dust-free by slow distillation for a third time after carefully filtering the water through a fritted glass funnel which also contained a pad of Seitz bacterial filter. To this water was added a solution of 1 c.c. of the oil in 5 c.c. of alcohol and then the whole thing was refluxed for about 36 hours in a ground glass apparatus. During this process the alcohol was completely removed and the initial thick emulsion was broken up into one containing more finely divided oil droplets. The emulsion was then filtered through a pyrex glass porous filter in order to homogenise the emulsion. The emulsions were

then examined under a high power microscope having an eyepiece with a micrometer scale and the size of the droplets estimated.

The preparation of sulphur sols by a wide variety of methods is well known. However, it was only recently that strictly monodisperse stable sols of sulphur containing spherical particles were prepared by La Mer and Co-workers (1946 *et seq.*) and their optical properties studied in detail. Since such sols are ideal for measurements, the results of which are to be compared with those of Mie's theory, three different sulphur sols were prepared for the present work using the method of La Mer and Barnes (1946). Initially two solutions, one of A. R. sodium thiosulphate and the other A. R. sulphuric acid were prepared, the strength of each solution being 1·5 N. To 995 c.c. of pure dust-free distilled water kept in a litre resistance glass volumetric flask, 1 c.c. of the 1·5 N acid solution was added. The flask with its contents was then thermostated at 26° C. To this dilute acid solution 1 c.c. of the 1·5 N thiosulphate solution was added rapidly and the volume made up at once to a litre. The solution was mixed thoroughly and returned to the thermostat. Portions of the solution were examined optically at different time intervals. The sulphur particles were found to grow at a uniform rate, at any instant the sol being strictly monodisperse. The appearance of well-defined Tyndall spectra as the particles continued to grow was used as a criterion of monodispersivity. The number of spectral orders and their position vary with the particle radius. All the phenomena of this nature recorded by La Mer and Barnes were reproduced in the sols prepared for the present study and it was therefore concluded that these sols were also strictly monodisperse and contained spherical particles. In order to preserve the stability of the sols during the period of measurement the sols obtained by removal of aliquot portions from the litre flask at different time intervals were titrated with very dilute iodine solution until about 70% of the free thiosulphate was neutralised.

Upto a radius of ·2 μ the depolarisation factor for a sulphur sol is a monotonic function of size. The radius of the particles in sol A which contained the smallest particles was found to be in this range and hence the radius of the particle was determined by measuring the depolarisation factor ρ_u for incident unpolarised green light, using the well-known Cornu method. From the value of ρ_u the particle radius was found to be about ·184 μ. For the other two sols B and C, which were obtained by allowing the particles to grow further, this method of size determination could not be used since ρ_u is no longer a monotonic function of the size but fluctuates violently beyond the size limit of about ·2 μ. Hence the radius was determined from observations on a number of orders of Tyndall spectra. Sol B

gave four well-defined red orders and the particle radius was estimated to be between $\cdot31\,\mu$–$\cdot34\,\mu$. Sol C gave five red orders and so the radius was taken to be between $\cdot33\,\mu$–$\cdot39\,\mu$ (Barnes *et al.* 1947).

5. RESULTS AND DISCUSSION

The experimental results of the measurements on the elliptic polarisation of the scattered light are given in Tables I and II and Fig. 1. In the tables for each sol the experimental values of ϕ defining the orientation of the elliptic vibration for different angles of polarisation α are given in the second column. In the next column are given the values of δ calculated from equation 7 using the experimentally measured value of ρ_u. Finally in each case the average value of the phase difference δ determined by using the Compensator with its axes vertical and horizontal has also been given.

In Fig. 1 the experimentally measured values of $(\phi_2 - \phi_1)$ in the case of emulsions have been plotted against the angle $(90 - \alpha)$ (circles and squares)
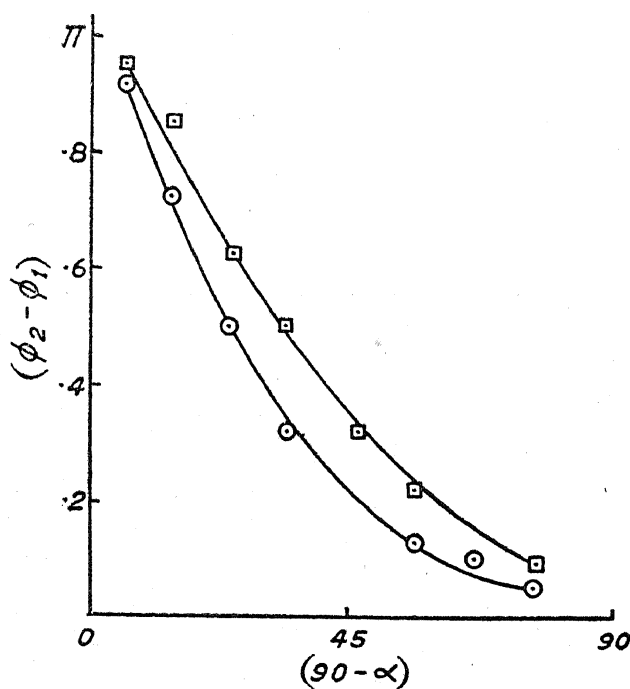

FIG. 1. Variation of $(\phi_2 - \phi_1)$ with $(90-\alpha)$ where α is the angle of polarisation.

and the smooth curves represent the theoretical relation between $(\phi_2 - \phi_1)$ and $(90 - \alpha)$ according to equation 8. The agreement between the two is found to be quite satisfactory. From the curves the angles α at which $(\phi_2 - \phi_1) = \pi/2$ found to be $66 \cdot 5°$ and $58°$ for lemon oil and Bergamont

oil emulsions respectively, compare well with the values 67° and 57° obtained for α when $\theta = 45°$.

From Table I it can be seen that for emulsions, δ is sensibly constant irrespective of the angle of polarisation. The orientation θ of the elliptic vibration, however, changes as one rotates the polarising nicol from the vertical towards the horizontal. Furthermore it is seen that for both emulsions there is a very good agreement between the calculated values of δ and the average measured value of δ. Although the refractive index relative to water is small in both cases ($\sim 1 \cdot 15$) the large phase difference may be attributed to the large size of the particles in both the cases. It can also be seen that the angle α at which the orientation of the ellipse is 45° is such that $\cot^2 \alpha$ is nearly equal to ρ_u, the actual values of $\cot^2 \alpha$ being $\cdot 42$ and $\cdot 18$ for Bergamont oil and lemon oil emulsions respectively while the values of ρ_u are $\cdot 4$ and $\cdot 19$.

Coming next to the case of sulphur sols the behaviour is found to be quite similar to that of the emulsions. In the case of sol A which contains particles of the smallest size the constant phase difference is also the least and is negative. It is found that for sulphur sol A the value of $2\pi R/\lambda$ corresponding to the measured value of δ (Kastler, *loc. cit.*) leads to a particle radius R equal to $\cdot 19 \mu$. This agrees well with the value of $\cdot 18 \mu$ obtained from a measurement of the depolarisation factor ρ_u for incident unpolarised light, the mean wavelength of the incident radiation being taken as 5,400 Å.U. In the case of sols B and C which contained particles of large size, δ is also numerically larger but remains negative. No comparison could, however, be made with the theoretical values of δ calculated from Mie's theory as the values of A_ν, P_ν for such large particles were not available. In the case of sulphur sols also it is seen that the value of α at which $\theta = 45°$ is such that $\cot^2 \alpha$ is equal to the value of ρ_u measured directly. Thus for sol A $\cot^2 \alpha = 1 \cdot 15$ is identical with the measured value, while for sols B and C the measured values of namely $1 \cdot 34$ and $2 \cdot 04$ are also practically the same as the values of $\cot^2 \alpha$ *viz.*, $1 \cdot 32$ and $2 \cdot 04$.

It is clear from what has been said above that a complete study of the scattering of light by any colloidal medium should therefore include measurements of intensity, polarisation of the scattered light and also the phase relationship between the vertical and the horizontal components for incident linearly polarised light. In the present investigation we have restricted ourselves to the case of large spherical particles. An experimental study of the scattering of the light by large anisotropic particles with special reference to the ellipticity is in progress.

TABLE I

Emulsions

Bergamont oil emulsion			Lemon oil emulsion		
α	θ	δ''	α	θ	δ''
16	7	·48	16	5	·46
26	12·5	·47	26	8·6	·6
36	18·5	·49	36	13	·46
46	29	·46	46	19	·46·3
57	45	..	56	29	·43·5
66	59	·48	67	45	
76	73·5	·46	76	66	·49

Bergamont oil emulsion.—Average measured value of δ — ·50'; ρ_u — 0·4.
Lemon oil emulsion.—Average measured value of δ — ·48'; ρ_u — ·19.

TABLE II

Sulphur Sols

Sol A			Sol B			Sol C		
$\alpha°$	θ	δ''	α''	θ	δ''	α''	θ	δ''
16	14·5	—35·3	16	14·7	—42	16	14·5	—55·5
26	25	—34	28	28	—41·7	28	31	—58·4
36	36·5	—34·5	41	45	..	35	45	..
43	45	..	56	65·5	—41	56	73	—56·3
56	60	—33·2	76	80·75	—42·3	76	84·5	—57·3
66	70	—33·3	..	..	..	..	..	..
76	79	—34·7	..	..	..	..	..	..

Sol A.—ρ_u = 1·15; Average measured value of δ — —32'.
Sol B.—ρ_u = 1·342; Average measured value of δ — —41·5'.
Sol C.—ρ_u = 2·04; Average measured value of δ — —55'.

SUMMARY

By an analysis of the theoretical conclusions of Mie's theory concerning the elliptic polarisation of the scattered light when the incident light is plane polarised in an arbitrary azimuth, the significance of the phase difference between the vertical and the horizontal components has been pointed out. It has been shown how the experimental investigations so far carried out have failed to bring out clearly the implications of Mie's theory. Using suitable experimental methods to analyse the scattered radiation in some emulsions and monodisperse sulphur sols containing particles which were spherically symmetric and of uniform size, the constancy of the phase difference has been established by three different methods of measurement. The value of the phase difference calculated from the available Mie scattering functions for one sulphur sol agreed well with the measured value and the characteristics of the transversely scattered elliptically polarised light for different azimuths of polarisation of the plane polarised incident light, were in accordance with the predictions of Mie's theory.

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