SCATTERING OF POLARISED LIGHT BY COLLOIDS CONTAINING ANISOTROPIC PARTICLES

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1. INTRODUCTION

WHEN a beam of light traverses any colloidal medium a part of it is scattered in all directions. The light scattered in any particular direction is characterised by two parameters namely intensity and state of polarisation. These factors vary with the size, shape and distribution of the particles and with the angle of scattering. If the incident light is plane polarised the scattered light is also plane polarised as long as the particles are spherical and small compared with the wavelength of light. If the particles are small but anisotropic the scattered light will be partially polarised or depolarised but not elliptically polarised. If the particles are of a size comparable with the wavelength of light, the scattering is multipolar in character and in general has an elliptically polarised part. Under such circumstances the depolarisation factor ρ_h for incident light polarised in the horizontal plane has a value less than unity. The finite size of the particle can, therefore, be detected and estimated either by the extent to which ρ_h is less than unity or by the existence of ellipticity in the scattered light. Perrin (1939, 1942) showed theoretically that the existence of ellipticity in the scattered light would be a more sure test of the multipolar character of the scattering of light by any colloid.

The experiments carried out by the earlier workers on the ellipticity of the scattered light were not designed to bring out clearly the implications of Mie's theory (1908). Using the Babinet compensator method the light scattered by certain heterogeneous media was shown to be elliptically polarised by Darbara Singh (1942), Hariharan (1942), Krishnan and Venkata Rao (1944) and 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 beam over which they were able to detect any elliptic polarisation in the light scattered in the horizontal transverse direction. It is only recently that the theoretical implications of Mie's theory regarding ellipticity have been clearly brought out by the work of LaMer

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and Kerker (1950), Kastler (1952), Krishnan, Narayanan and Sivarajan (1954). From Mie's theory one can deduce that when the incident light is plane polarised in any azimuth, there exists a phase difference between the vertical and horizontal components of the light transversely scattered by large spherical particles, which is independent of the azimuth of polarisation, α, of the incident beam. This phase difference δ is a function of the size and the relative refractive index of the particles. Krishnan, Narayanan and Sivarajan (1954) recently carried out experiments specially designed to bring out these facts. They gave a satisfactory explanation for the qualitative results of the earlier workers on ellipticity, which showed apparent variation of ellipticity with the angle of polarisation of the incident beam. In the case of identical particles possessing spherical symmetry, δ will be the same for the individual particles of the medium and consequently the scattered light by the medium as a whole will be completely polarised. In the case of non-spherical particles, however, in addition to the polarised scattering arising from the finite size, there will be some depolarised scattering arising from varying orientations of the anisotropic particles. Using the method suggested by Krishnan, Narayanan and Sivarajan (1954) an experimental study has therefore been made on the ellipticity of the transversely scattered light in the case of carefully prepared aqueous colloidal sols containing anisotropic particles and these results are reported in this paper.

2. Experimental

Preparation of the Sols

The following sols which are known to contain anisotropic particles were prepared: Graphite sol, arsenic trisulphide sol, gelatine sol, gold and silver sols. The details of preparation have already been given in the earlier papers of Krishnan (1937). The sols were prepared in dust-free double distilled water and care was taken to ensure the absence of dust from the solutions.

Optical Set-up

Since the object of the experiment was to measure the phase difference δ that existed between the vertical and horizontal components of the scattered light, the Babinet compensator had to be set with its axes vertical and horizontal. Under such conditions, when the incident beam was linearly polarised, the elliptic polarisation in the transversely scattered light would be exhibited in the field of view of the compensator-analyser combination as a shift of the fringes with respect to the crosswire. This shift is a measure of the phase difference δ. If, however, the compensator was set with its axes at 45° to the vertical, one no longer measured the phase difference δ, but some phase difference of the resolved components along the axes of the compensator which were at 45° to the vertical. One would therefore, observe a continuous shift of the fringes past the crosswire as one varies the azimuth of polarisation α of the incident beam, α being the inclination of the plane of polarisation with respect to the vertical. This procedure was employed by the earlier workers and consequently their qualitative results could not satisfactorily be correlated with the implications of Mie's theory.

Both methods of observation were used in our experiments. The source of light was sunlight reflected by means of a Foucault heliostat into a darkened room through an aperture in one wall. The light was condensed by means of a long focus Dallmeyer lens and rendered nearly parallel with the aid of a second lens. It was then allowed to fall on the rectangular glass cell containing the colloid. Filters were used in the path of the incident beam to give a narrow band of wavelengths. Observations were made in the transverse horizontal direction, suitable precautions being taken to avoid errors due to stray light, etc. By using a Fuess polarising microscope kept with its axis horizontal in conjunction with a Babinet compensator analyser combination, the compensator could be rotated and the position of its axes accurately measured. With the compensator axes set vertical and horizontal, measurements were made of δ for various values of α. The depolarisation factors ρ_u, ρ_v and ρ_h were also measured for the colloids investigated.

3. RESULTS AND DISCUSSION

It was found that the phase difference δ was independent of the azimuth of polarisation α, of the incident beam. Variations observed if any in the value of δ were within the limits of experimental error. The average values of the phase difference δ for α from 0–90° for the different colloids were determined and are given in Table I together with the values for the depolarisation factors ρ_u, ρ_v and ρ_h. From the observed values of ρ_v and ρ_h it is evident that we are here dealing with large anisotropic particles ($\rho_v \neq 0$, $\rho_h < 100\%$).

It was also found that in all the cases, when the axes of the ellipse were inclined at 45° to the vertical, the corresponding values of α were such that $\rho_\alpha = 100\%$. The same result was observed with spherical particles also. Thus, an extremely interesting fact emerges from this study, namely that even in the case of large anisotropic particles, the scattered radiation exhibits elliptic polarisation with a constant phase difference between the vertical and horizontal components which is independent of the azimuth of polarisation of the incident beam. This is what is to be expected theoretically in the case of a colloidal medium containing large anisotropic particles which are randomly

TABLE I

Sol	ρ_u%	ρ_v%	ρ_h%	Average value of δ
Graphite	19	6	36	60°
Gelatine	6·8	2·5	57	59°
Arsenic trisulphide ..	33	3·4	11	7·5°
Silver sol A	32	12·3	52	96°
Silver sol B	15	3·0	57	19°
Gold sol	18·4	4·4	82	78°

oriented. Such a scattering medium can be considered as symmetrical. The Stokes parameters of the light transversely scattered by a symmetrical scattering medium are given by the following set of equations which are the same as 47 A in Perrin's (1942) paper.

$$\begin{aligned} I' &= a_1 I + b_1 M \\ M' &= b_1 I + a_2 M \\ C' &= a_3 C + b_2 S \\ S' &= -b_2 C + a_4 S \end{aligned} \qquad (1)$$

The phase difference δ of the scattered light is given by the relation

$$\tan \delta = \frac{S'}{C'} \qquad (2)$$

If the incident light is plane polarised in a direction making an angle α with the perpendicular to the scattering plane, *i.e.*, vertical, $I = 1$, $M = -\cos 2\alpha$, $C = \sin 2\alpha$ and $S = 0$. Substituting these values in (2) and (1) we get

$$\tan \delta = -\frac{b_2}{a_3}$$

It follows therefore, that the phase difference δ for the scattered light is independent of the azimuth of polarisation of the incident beam. This is what has been observed experimentally.

SUMMARY

It is only recently that the theoretical significance of the elliptic polarisation of light scattered by colloids containing particles of large size has been

pointed out and an analysis made of the theoretical conclusions regarding ellipticity from Mie's theory for spherical particles. The earlier qualitative measurements on ellipticity of the scattered light have been explained on the basis of these new ideas and the implications of Mie's theory brought out more clearly. New experiments have been devised and used for measuring the constant phase difference δ that exists between the vertical and horizontal components of the transversely scattered light when the incident light is polarised in any azimuth. Measurements have been made both for systems of spherical particles and anisotropic particles. It is found that even in the case of large anisotropic particles δ is a constant. It follows therefore, that in the most general case of large anisotropic colloidal particles the polarised scattering due to finite size is elliptic in nature and is superposed on the depolarised part due to anisotropy.

REFERENCES

1. Darbara Singh .. *Proc. Ind. Acad. Sci.*, 1942, **15 A**, 406.
2. George, A. .. *Curr. Sci.*, 1950, **19**, 239.
3. Hariharan, P. S. .. *Proc. Ind. Acad. Sci.*, 1942, **16 A**, 278.
4. Kastler, A. .. " La diffusion de las lumiere par les milieux troubles, " 1952.
5. Kerker and LaMer .. *J. Am. Chem. Soc.*, 1951, **72**, 3516.
6. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1937, **5**, 94, 305 and 499.
7. ——— Narayanan, P. S. and Sivarajan, S. R. *Ibid.*, 1954, **40 A**, 140.
8. ——— and Venkata Rao, P. *Ibid.*, 1944, **20 A**, 109.
9. Mie, G. .. *Ann. d. Physik*, 1908, **25**, 377.
10. Perrin, F. .. *J. de. Chim. Physique*, 1939, **36**, 239.
11. ——— .. *J. Chem. Phys.*, **10**, 415.