DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part I. Gold Sols.

By R. S. Krishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received January 25, 1937.

(Communicated by Sir. C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

The problem of the diffraction of light by spherical conducting particles was dealt with rigorously on the basis of the electromagnetic theory by G. Mie[1] in a well-known paper. He developed formulæ for the scattering and absorption of light by colloidal solutions under the assumption that the refractive index and the absorption coefficient of the colloidal particles possess the same values as those of the metal in bulk. In this theoretical paper the colour phenomena of metals in the colloidal state, especially of gold sols, have been beautifully explained by him. According to this theory small gold particles give ruby red solutions whereas large ones give blue solutions. This accords well with the experimental observations. Further, Mie's theory indicates regarding the state of polarisation of the scattered light that when the beam incident horizontally is unpolarised, the light scattered in the transverse horizontal direction by the particles in the colloidal state will be perfectly polarised with vibrations vertical if the size of the particles is the order of molecular dimensions, and will be imperfectly polarised only if the size is comparable with the wave-length of light. Moreover, if the incident beam is polarised with vibrations vertical or horizontal, the light scattered transversely in the horizontal direction should be completely polarised with its vibrations vertical or horizontal respectively. Steubing[2] has, however, shown experimentally that in gold sols the transversely scattered light is not completely polarised even when the incident light is plane polarised. This fact of observation does not find an explanation in Mie's theory.

---

[1] G. Mie, *Ann. der Phys.*, 1908, **25**, 377.

[2] Steubing, *Ann. der Phys.*, 1908, **26**, 329.

R. Gans[3] has considered the problem of the scattering of light by very small ellipsoidal particles. In a theoretical paper he has extended the calculations of the absorption and the scattering of light in gold sols by generalising the shape of the particles into an ellipsoid of rotation, which may be either prolate or oblate, the size of the particles being assumed to be small compared with the wave-length of light. He has shown that as soon as the spherical shape is departed from appreciably, the curve of absorption moves towards the less refrangible end of the spectrum, whether the sphere is flattened or elongated. He has derived expressions for ρ_u and ρ_v for ellipsoidal particles possessing rotation symmetry, where ρ_u and ρ_v are the so-called depolarisations or the measures of the imperfection of polarisation of the light scattered in the transverse horizontal direction when the incident beam is unpolarised and polarised with vibrations vertical respectively. The quantities ρ_n and ρ_u are connected by the following relation :

$$\rho_u = \frac{2\,\rho_v}{1+\rho_v} \qquad (1)$$

From the considerations of Gans, it follows that the light scattered by very small ellipsoidal particles in the transverse horizontal direction when the incident beam is polarised with vibrations horizontal should be unpolarised, *i.e.*, ρ_h is equal to unity. If the restriction regarding the size of the particles is not satisfied, the relation (1) is no longer valid. The author[4] has already shown in an earlier paper both experimentally and theoretically that there is a more general relation connecting ρ_u, ρ_v and ρ_h which is valid also for particles of larger size, namely :—

$$\rho_u = \frac{1 + 1/\rho_h}{1 + 1/\rho_v} \qquad (2)$$

Relation (2) reduces to (1) when ρ_h = unity. The values of the three quantities both absolutely and relative to each other are a measure of the size, shape and structure of colloidal particles. D. S. Subbaramaiya[5] has measured the values of ρ_u, ρ_v and ρ_h for a series of six gold sols using incident white light. He has shown that in the case of Zsigmondy's blue sol, relation (2) but not relation (1) is satisfied, ρ_h being as small as 54%. No definite conclusions can, however, be derived as regards the size and shape of the gold particles from a measurement of the depolarisation values, ρ_u, ρ_v and ρ_h with incident white light alone ; for, the optical constants of gold, indeed also of any metal, depend very much on the wave-length of

[3] R. Gans, *Ann. der Phys.*, 1912, 37, 883.

[4] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 1, 782.

[5] D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, (A), 1935, 2, 358.

light, and measurements of depolarisation made with white light are therefore inadequate.

In some unpublished investigations, Mr. D. S. Subbaramaiya used sunlight filtered through coloured glasses and found in gold sols a marked dependence of the degree of depolarisation on wave-length. Lange[6] had earlier made a careful study of the depolarisation and light absorption of colloidal gold solutions over the wave-length range from 4250 A.U. to 7000 A.U. He has measured the depolarisation factor ρ_u but not the other two quantities ρ_v and ρ_h. From a measurement of ρ_u alone, no definite conclusions can be arrived at regarding the size and shape of the particles, since ρ_v and not ρ_u is the indicator of the optical anisotropy of the particles. Considering the inadequateness of the experimental data even in the classical case of gold sols, it was thought desirable to determine the dispersion of the depolarisation factors ρ_u, ρ_v and ρ_h of the light scattered by the gold sols corresponding to the three states of polarisation of the incident light, over a wide range of wave-length, say from 2500 A.U. to 7000 A.U. In order to make the investigation complete, the absorption of light by the same gold sols has also been measured.

The study of the dispersion of depolarisation of light scattering in colloids is very important since it is connected not only with the size and shape of the particles, but also with other well-known phenomena, such as magnetic, electric and flow birefringence and their dispersion with wave-length exhibited by the colloidal solutions.

2. *Preparation of the Gold Sols.*

The gold sols were prepared by Mr. D. S. Subbaramaiya to whom the author's thanks are due. The details of the preparation of the six gold sols are described by him in his paper.[7] The sols I and II were nuclear sols containing particles of extremely small size. The sols III, IV and V were prepared by the addition of nuclear sol to chlorauric acid solution and reduction by hydrogen peroxide. These sols were red in colour. The sol VI was a blue sol prepared according to the method suggested by Zsigmondy. The sols were preserved in resistance glass bottles thoroughly cleaned and well steamed. The sols were taken as optically infinitely dilute, for on further dilution the colour of the sols remained unchanged.

3. *Depolarisation Measurements.*

Measurements of depolarisation were made separately for the ultra-violet and for the visible regions. For the ultra-violet region a point-light

[6] B. Lange, *Zeits. f. Phys. Chemie*, 1928, 132, 27.

[7] D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, (A), 1935, 2, 358.

quartz mercury arc lamp was used as the source of light, the scattered light being analysed through a Hilger quartz spectrograph. The experimental set up is shown in the accompanying Fig. 1.

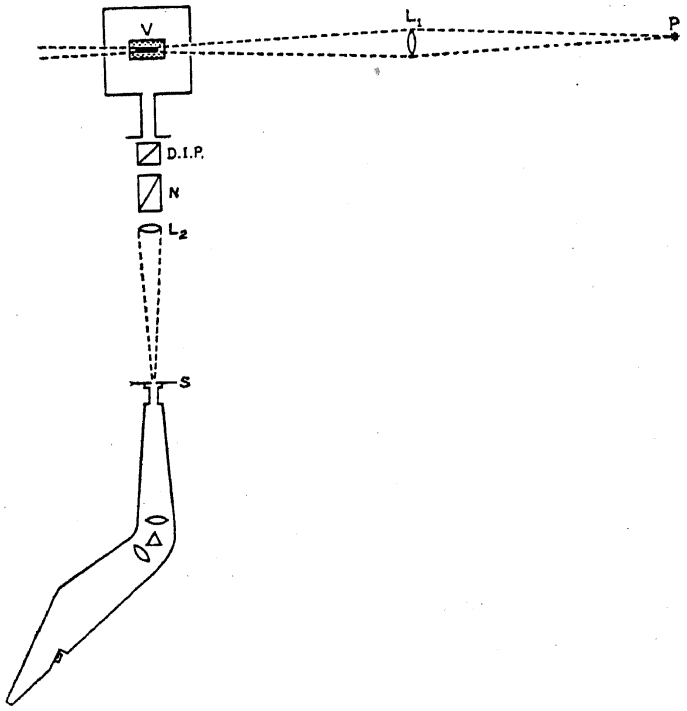

FIG. 1.

P =Point-light mercury arc.
L_1 and L_2=Long focus quartz lens.
D.I.P. =Double-image prism.
N =Nicol which transmits the ultra-violet region also.
V =Quartz cell containing the sol under investigation.

The details of the experiments have already been described in one of the earlier papers of the author.[8] From a series of photographs taken the readings of the nicol corresponding to the equality of intensity of the two components of the scattered light for the two wave-lengths, 2967 and 3650 A.U. were read off and the depolarisation values were calculated therefrom.

For the visible region, the method adopted was slightly different. The light from a 500 c.p. pointolite lamp was condensed on a square aperture (2 mm. square). The illuminated aperture was used as the source of light

[8] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1936, 3, 566.

instead of the point-light mercury arc. The rest of the experimental arrangement was similar to that shown in Fig. 1. A Fuess glass spectrograph of large dispersion was used instead of the quartz spectrograph. The slit of the spectrograph was kept rather wide. The orientation of the nicol was adjusted so that the two components of the scattered light as seen through the spectrograph were almost of equal intensity for a particular wave-length. One photograph was taken for this position of the nicol. In this manner, for each sol two photographs, one corresponding to incident light unpolarised and the other corresponding to incident light polarised with vibrations vertical, were taken on the same plate along with an iron arc spectrum. Ilford hypersensitive panchromatic plates were used throughout. A series of graded intensity marks was obtained on another plate by photographing the spectrum of a tungsten straight filament lamp with different slit widths, but keeping the time of exposure constant. With the aid of a Moll microphotometer the density log intensity curves were plotted for the following wave-lengths, 4000, 4500, 5000, 5500, 6000, 6500 and 7000 A.U. All the negatives were microphotographed. The ratio of the intensities of the horizontal and the vertical components of the scattered light for each individual wave-length was calculated from the density log intensity curve. From a knowledge of this ratio and the corresponding orientation of the nicol the depolarisation for any particular wave-length could be calculated. Thus the values of ρ_u and ρ_v were calculated.

A correction arising from the finite angle of convergence of the incident beam had to be applied to the observed values of the depolarisation. The angle of convergence ω was 1/7 of a radian. Consequently, the convergence correction for ρ_u is $\omega^2/8 = 0{\cdot}25\%$. The correction for ρ_v is half of that for ρ_u. The corrected values of ρ_u and ρ_v are given in Tables I and II. ρ_h was calculated from the observed values of ρ_u and ρ_v using the relation (2). In a few cases owing to a small experimental error in the determination of either ρ_u or ρ_v the calculated value of ρ_h was found to be slightly greater than 100%. In such cases ρ_h was put equal to 100%.

TABLE I. *Dispersion of Depolarisation.*

Wave-length	Gold sol I			Gold sol II			Gold sol III		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	3·8	2·2	100	4	2·1	100	3·4	1·6	86
3650	4	2·2	100	3·8	2	100	3·4	1·6	86
4000	4·6	2·4	100	3	1·59	100	4·6	2·4	100
4500	4·6	2·5	100	3·9	1·76	83	4·75	2·4	98
5000	6·2	3·1	100	4·5	2·2	92	7·2	3·9	100
5500	8	4·4	100	12·3	6·4	100	18	10·6	100
6000	14	8	100	13	6·6	100	29·5	16	100
6500	16	9·2	100	16·3	9	100	16	9	100
7000	..	..	..	10·9	6	100	16	9	100

TABLE II. *Dispersion of Depolarisation.*

Wave-length	Gold sol IV			Gold sol V			Gold sol VI		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	3·1	1·5	91	3	1·3	75	..	..	..
3650	3·1	1·6	100	3	1·4	85	5·5	2·1	60
4000	3·6	1·7	86	2·4	0·9	59	5·0	1·7	50
4500	3·2	1·75	100	2·5	1·5	100	4·6	1·6	52
5000	3·8	2·2	100	6	3·2	100	5·2	1·9	65
5500	14·3	7·85	100	13	7	100	12·7	6	80
6000	16·3	9	100	13·6	7·8	100	17	8·4	84
6500	16·5	9·3	100	14·6	8	100	18·8	10	94
7000	16·8	9·7	100	15·3	8·2	100	22·7	12·7	97

The values of ρ_u were plotted against wave-length. The curves are reproduced in Figs. 2 and 3.

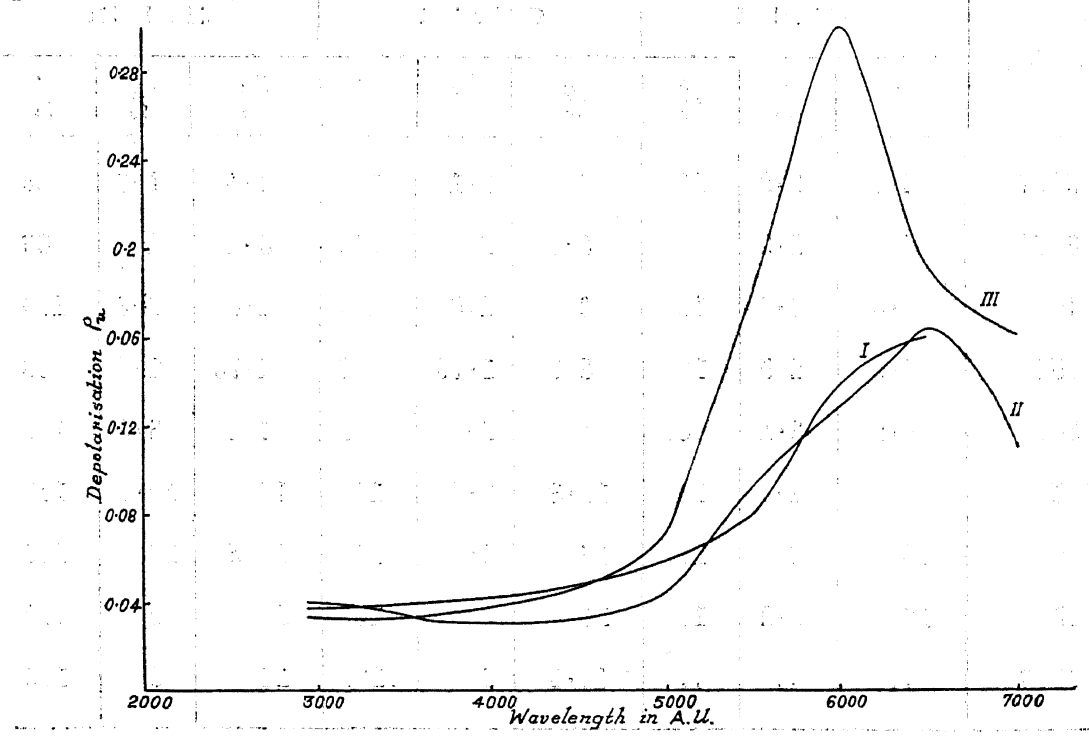

FIG. 2.

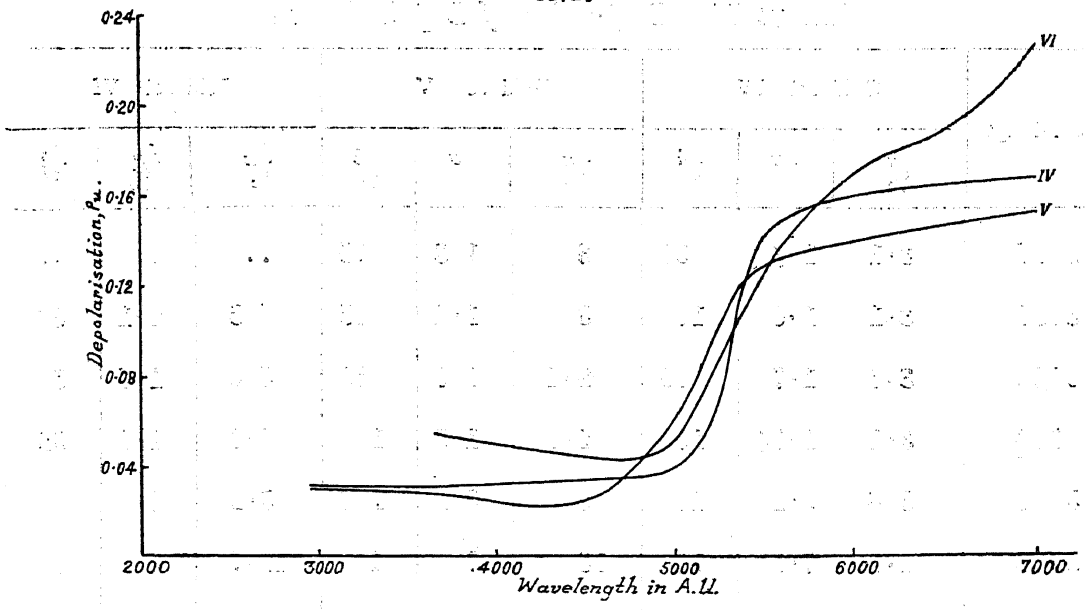

FIG. 3.

4. *Absorption Measurements.*

The absorption measurements were made with a Spekker ultra-violet photometer and a quartz spectrograph. The source of ultra-violet radiation

was the condenser spark between two tungsten steel electrodes. To correct for the reflections of the end plates of the tube containing the sol under examination, a similar tube was used in the second light path of the photometer, this tube being filled with pure double-distilled water. The extinction coefficient $\left(\log \frac{I'}{I}\right)\Big/D$ was determined for a series of wave-lengths from 2500 A.U. to 7000 A.U. D is the thickness of the cell in centimetres. The values of the extinction coefficients are given in Table III.

TABLE III.

Extinction Coefficient of Gold Sols.

λ	I	II	III	IV	V	VI
2250	0·75	0·57	0·9	0·575	0·575	>3
2500	0·7	0·55	0·9	0·575	0·575	>3
2750	0·65	0·5	0·8	0·53	0·49	>3
3000	0·6	0·42	0·65	0·5	0·425	>3
3250	0·525	0·37	0·55	0·45	0·35	1·3
3500	0·4	0·35	0·525	0·4	0·3	0·75
3750	0·4	0·32	0·47	0·37	0·29	0·6
4000	0·375	0·30	0·45	0·35	0·275	0·475
4250	0·35	0·29	0·425	0·35	0·275	0·45
4500	0·3	0·3	0·4	0·325	0·26	0·425
5000	0·35	0·32	0·575	0·46	0·4	0·45
5250	0·4	0·42	0·84	0·76	0·55	0·52
5500	0·35	0·38	0·56	0·575	0·55	0·525
6000	0·25	0·2	0·225	0·35	0·2	0·5
6500	0·15	0·125	0·125	0·15	0·125	0·475
7000	0·1	0·1	0·09	0·09	0·062	0·45

The curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ.

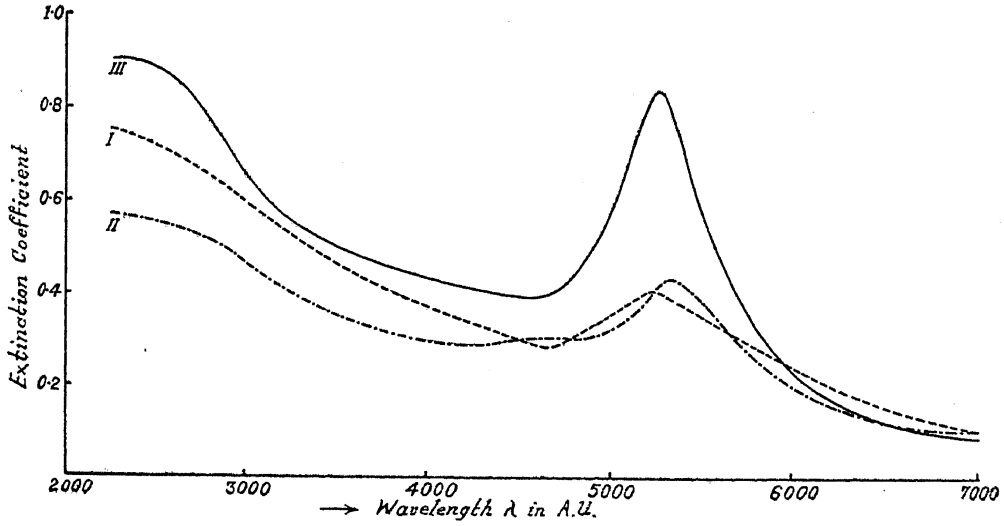

FIG. 4

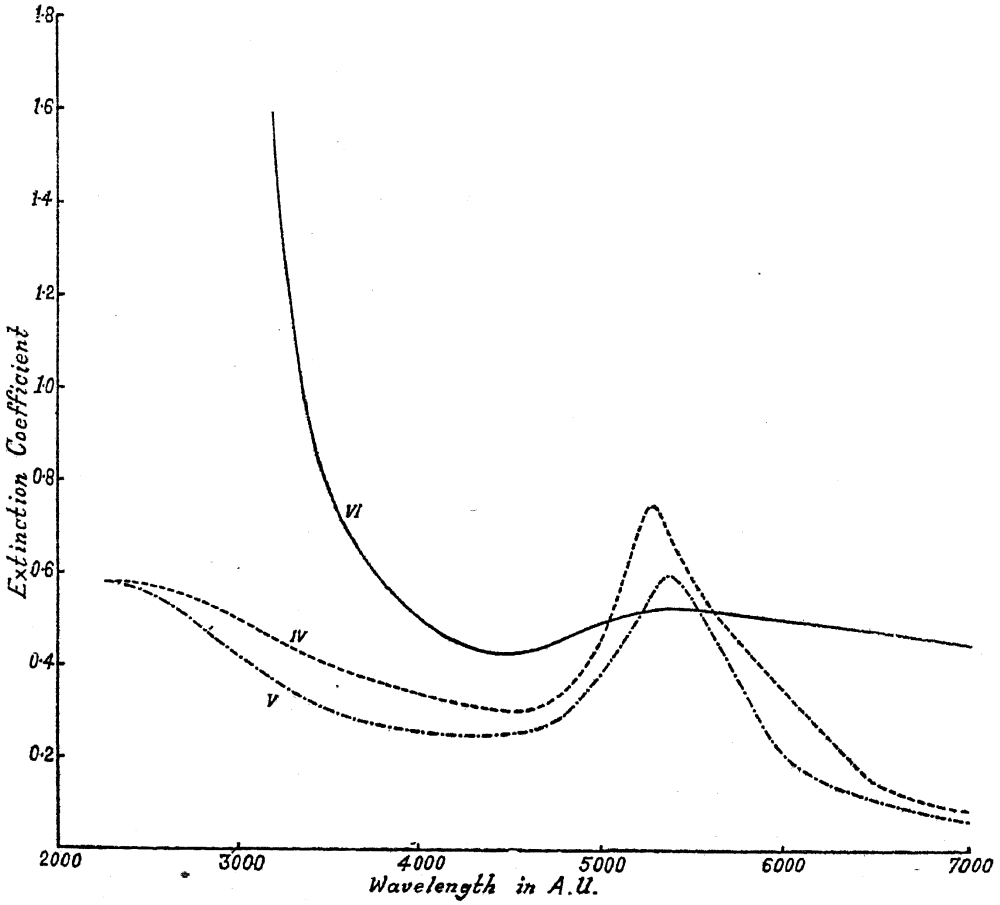

FIG. 5.

5. *Results.*

In all the sols studied it is found that ρ_u is markedly a function of wave-length. In the case of sols II and III after attaining a maximum in the region of the characteristic absorption, ρ_u diminishes with further increase of wave-length. In the case of the last two sols the value of ρ_u goes on diminishing at first and then it increases. ρ_v follows the same course as ρ_u. For the first three sols ρ_h has its limiting value of 100% from λ 2500 to 7000 A.U. For the sols IV and V ρ_h is definitely less than 100% in the ultra-violet region. In the blue sol ρ_h is less than 100% throughout, and increases or decreases with wave-length *pari passu* with ρ_u. In the region of the characteristic absorption there is an increase of the optical anisotropy as is shown by the notable increase of ρ_v. A comparative study of the values of ρ_h for all the sols shows that sols I, II and III contain particles whose size is of the order of molecular dimensions, while, in sol VI the size of the particle is comparable with the wave-length of light. The sols IV and V contain particles of intermediate sizes. The fact that ρ_u has the same low value for almost all the sols at about 3000 A.U. indicates that the anisotropy of shape of the particles is small and is independent of the method of preparation of the sol and also of the particle size, provided the latter is small compared with the wave-length of light. This is not surprising, for the sols III to VI are prepared using the nuclear sol I, and consequently it is natural to expect the general shape of the particles in the nuclear sol to be retained in the other sols also. The small increase in the value of ρ_u below 4000 A.U. evinced by the sols V and VI is a size effect.

As has been observed previously, the curves of absorption show a pronounced maximum in the green region, *i.e.*, at about 5250 A.U., for all the sols except for the blue sol. The actual value of the extinction coefficient goes on increasing from sol I to sol IV, while, it goes on decreasing from sol IV to sol VI. It is found that the maximum of the absorption curve is shifted towards the longer wave-length side as one goes from sol I to sol VI. In all the sols studied the absorption increases again in the ultra-violet region.

6. *Theoretical Discussion.*

According to Gans's theory, for a flattened rotation ellipsoid the maximum of the depolarisation curve should lie in the green region, *i.e.*, at about 5250 A.U., whereas for an elongated ellipsoid or a prolate spheroid the maximum is shifted towards the longer wave-length side. The latter corresponds to the experimentally observed data. Table IV gives the comparative values of the depolarisation ρ_u calculated according to Gans's

formula for very small particles of ellipsoidal shape. The values are taken from Lange's paper.[9] The values of ρ_u for an elongated rotation ellipsoid with axial ratio B/A = 0·7 have been obtained by interpolation.

TABLE IV.

Values of ρ_u (calculated).

	Elongated rotation ellipsoid				Sphere	Flattened rotation ellipsoid			
B/A / λ in A. U.	0·00 %	0·57 %	0·70 %	0·82 %	1·00 %	1·28 %	2·63 %	6·25 %	∞ %
4200	35·8	4·7	2	0·49	0·0	8·84	9·3	20·5	30·6
4500	37·9	4·4	1·9	0·49	0·0	0·86	9·4	20·5	30·5
5000	76·6	32·3	10	1·48	0·0	2·06	19·1	36·1	19·1
5250	40·3	28·2	10·5	3·12	0·0	3·51	26·3	44·2	55·9
5500	47·8	51·8	21	4·6	0·0	2·36	28·1	37·9	56·1
6000	87·4	17·1	6	2·0	0·0	1·79	6·5	37·4	48·1
6500	2·2	10·5	4·5	1·2	0·0	0·98	5·6	32·0	41·6

Comparing the theoretical values of the depolarisation ρ_u witn the experimental values, it is seen that the particles in the gold sol are more like elongated rotation ellipsoids with the axes ratio B/A = 0·7. In the case of the sols IV, V and VI the observed value of ρ_u goes on increasing continuously with wave-length. This may be due to the finite size of the particles. The theory of Gans is only true for particles of extremely small size.

It is not difficult to explain the observed values of the extinction coefficient provided it is assumed that the particles are prolate ellipsoids and that the deviation from spherical shape is small. The following table gives the absorption constant $k \times 10^{-3}$ for different wave-lengths caclulated according to Gans, for very small particles of ellipsoidal shape. k is defined given by the equation $I = I_o\, e^{-kcx}$, where x is the thickness of the layer in millimetres. For a sol containing one millimetre cube of gold by volume per litre of the sol, c is equal to 10^{-6}. The values are taken from Gans's paper.[10]

[9] B. Lange, *Loc. cit.*

[10] R. Gans, *Loc. cit.*

The values of k given in the table below for an elongated rotation ellipsoid with the axes ratio B/A = 0·7 are obtained by interpolation. A comparative study of the Tables III and V shows at once that although the experimentally determined absorption curves are similar to the theoretical curves calculated according to Mie's theory for spherical particles, there is better agreement between the observed curves and the curves calculated according to the theory of Gans for elongated rotation ellipsoidal particles having an axial ratio equal to 0·75. From the above discussion it can be said with certainty that the particles in the gold sols studied are not spherical in shape but behave as elongated ellipsoids with the axial ratio B/A of the order of magnitude stated.

TABLE V.

Absorption Coefficient.

	Elongated rotation ellipsoid				Sphere	Flattened rotation ellipsoid			
B/A / λ in A. U.	0·00	0·57	0·70	0·77	1·00	1·61	2·63	45	∞
4200	36·7	41·8	41·3	41·0	40·6	42·4	46·4	48·3	44·9
4500	34·5	38·8	38·1	37·8	37·4	39·1	43·6	45·7	43·3
5000	30·9	57·3	58·7	59·4	59·2	62·2	64·0	60·0	29·5
5250	24·5	68·6	71·0	72·3	69·1	82·7	87·4	75·8	22·2
5500	18·7	83·0	71·5	67·3	55·2	89·0	131·5	102·9	16·6
6000	8·7	68·7	33·5	21·6	16·4	29·5	126·9	262·5	12·0
6500	8·5	18·0	9·5	8·3	6·92	10·5	31·0	77·2	14·2

7. *Other Experimental Evidence.*

The double refraction in gold sols produced by mechanical flow has been investigated by Bjornstahl[11] and S. Berkman, J. Boehm and H. Zocher.[12] According to them all the gold sols except the sol prepared by Zsigmondy's formaline method show a negative streaming double refraction indicating thereby that the particles are not spherical in shape, but are elongated. The influence of the wave-length is very pronounced; the effect can be scarcely observed in the violet region whereas it is great in the red region.

[11] Y. Bjornstahl, *Inaugural Dissertation*, Upsala, 1924.

[12] S. Berkman, J. Boehm and H. Zocher, *Zeits. f. Phys. Chemie*, 1926, **124**, 83.

This type of dispersion of flow birefringence is generally anomalous. But in the light of the present investigation it finds an easy explanation. Depolarisation measurements indicate that the optical anisotropy is much greater in the red region than in the violet region. Since the intensity of scattering is also great in this region of the spectrum, the refraction should necessarily increase with wave-length. In consequence of this the double refraction produced by mechanical flow should also exhibit a similar dispersion. This is actually the case. From a knowledge of the dispersion of refractive index of the colloidal solution and the anisotropy of shape calculated from the depolarisation measurements, it should be possible to calculate the magnitude of the streaming double refraction in these colloidal solutions and also its dispersion with wave-length.

Gold sols should not exhibit any appreciable magnetic double refraction since gold is diamagnetically isotropic, and since X-ray analysis discloses that the particles in the colloidal state exhibit a crystal structure similar to that of gold in mass. This is in accordance with recent observations with gold sols which fail to exhibit magnetic double refraction made by Mr. P. Nilakantan[13] in this laboratory. It is difficult to understand how Bjornstahl[14] observed a considerable magnetic double refraction in gold sols prepared by the nuclear method using hydrogen peroxide as the reducing agent. Assuming for the present that the observed magnetic anisotropy in his experiments was due to the presence of a small trace of some impurity (say iron), the large dispersion of magnetic double refraction observed by him finds an easy explanation on the same lines as indicated in the previous paragraph.

8. *Summary.*

The earlier investigations (theoretical as well as experimental) on the light scattering and absorption of gold sols have been briefly reviewed. It is pointed out that in order to determine the size and shape of colloidal particles, it is important to make comparative studies of the dispersion of depolarisation of the transversely scattered light with the incident light in three different states of polarisation, namely, unpolarised, vertically polarised and horizontally polarised. Measurements of the depolarisation factors ρ_u and ρ_v and the extinction coefficient of a series of six gold sols are made for different wave-lengths from 2500 A.U. to 7000 A.U. The value of ρ_h is calculated from the observed values of ρ_u and ρ_v using the reciprocity relation. In the region of the characteristic absorption the

[13] P. Nilakantan, *Unpublished work.*

[14] Bjornstahl, *Loc. cit.*

depolarisation factors show an enormous increase. The optical anisotropy of the gold particles in the colloidal state is rather low in the shorter wave-length region, whereas it assumes rather high values in the green region where the absorption is maximum. The observed values of the extinction coefficient and the depolarisation factor ρ_u are compared with the values calculated according to Gans's theory. From both of these considerations, it is inferred that the particles in the gold sols behave optically like elongated ellipsoids with the axial ratio equal to about 0·75. The values of ρ_h indicate that the size of the particles in the nuclear sols is small compared with the wave-length of light, while the blue sol contains particles of size comparable with the wave-length of light. The negative streaming double refraction and its dispersion with wave-length observed by the earlier investigators are explained on the basis of the elongated ellipsoidal shape of the particles and the dispersion of their optical anisotropy.

In conclusion the author takes this opportunity to thank Prof. Sir C. V. Raman for his keen interest and helpful criticism during the progress of this investigation.

1735-36—Printed at the Bangalore Press, Bengalore City, by G Srinivasa Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.