DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part II. Silver Sols.

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1. *Introduction.*

In Part I (Krishnan, 1937) of this series, it has been pointed out by the author 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. A study of the dispersion of depolarisation of light-scattering in colloids is also important as it is connected with other well-known phenomena exhibited by colloidal solutions, namely, magnetic, electric and flow birefringence and their dispersion with wave-length. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h with gold sols indicated that in the region of characteristic absorption, the depolarisation factors and consequently the anisotropy of the particles assume rather high values. From a comparison of the observed depolarisation and absorption curves with the theoretical ones, it has been concluded that the particles in gold sols behave optically like prolate ellipsoids with axial ratio equal to 0·7. In view of the interesting results obtained with gold sols, it was thought desirable to extend these optical investigations to a series of other sols.

In this paper the results obtained with a series of six unprotected silver sols prepared according to different methods are given. The approximate form of the silver particles in the colloidal state has also been determined.

2. *Earlier Investigation.*

The property of exhibiting a wide variety of colours is probably the most outstanding characteristic of colloidal silver. This was pointed out for the first time by Siedentopf (1910). On the basis of Mie's theory of the colour of metallic turbid media, Muller (1911) and Feick (1925) calculated the absorption coefficient of silver sols containing particles assumed to be spheres of a given diameter. Feick had further deduced the alteration in colour that would occur with increase in the size of the particles. But it has been found by different observers that the colours of colloidal silver do not agree with these theoretical calculations. Gans (1915) has shown from theoretical considerations that the form of the particles in silver sols (as in gold sols) had a strong influence on the colour exhibited by them. From the observed absorption coefficients of collargol, he concluded that the silver particles were not spherical but were ellipsoidal in shape.

In a theoretical paper Gans (1921) has developed formulæ for the dispersion of refractive index and depolarisation of the light scattered by small colloidal silver particles of ellipsoidal shape. According to his theory the dispersion of refractive index of a sol containing spherical particles is normal while that of a sol containing ellipsoidal particles is anomalous. Some preliminary measurements of the depolarisation factor ρ_u of a silver sol were made by Gans (1921) and Isnardi (1921) for λ 5000 A.U., from which they concluded that the colloidal silver particles are prolate ellipsoids with the axial ratio slightly less than unity. But up till now, no detailed quantitative measurements have been made either of the dispersion of refractive index or the dispersion of depolarisation of light-scattering in silver sols.

3. *Preparation of the Sols.*

Six typical unprotected silver sols have been selected for the present investigation. Protected silver sols have been excluded because the results obtained with them will depend to a considerable extent on the nature of the protecting agent employed and consequently may not be easily amenable to theoretical interpretation.

Sol I was prepared by the well-known Bredig's method. An arc was struck between two pure silver electrodes immersed in double distilled conductivity water contained in a resistance glass beaker. The beaker was surrounded by ice. A current of about 5-6 amps. was passed just for a few seconds. The sol which resulted was allowed to stand for a day. After the heavy particles had settled down, the clear sol was decanted into a hard glass bottle which had previously been cleaned and well steamed. The sol is quite stable even after a month. The colour of the sol was greenish grey.

Sol II was a nuclear solution. This was prepared by adding 120 c.c. of double distilled water to 24 c.c. of a solution of pure silver oxide containing 0·001 per cent. silver. Two drops of an 0·18 N sodium carbonate solution were added to the silver solution followed by the addition of 1 c.c. of phosphorus solution prepared by diluting the saturated solution of phosphorus in ether twenty times with ether. The sol which resulted at once was slightly yellowish in colour. This sol was used as the nuclear sol for the preparation of sols III, IV and V.

Sol III was prepared as follows. To 50 c.c. of silver oxide solution containing 0·0005 per cent. silver were added 1 c.c. of 0·18 N sodium carbonate, 10 c.c. of silver nuclear solution and 0·2 c.c. of hydrogen peroxide solution diluted to 1 part in 1000. The reaction took place rapidly, giving a clear sol containing bluish particles.

Sol IV was prepared according to the method suggested by Voigt. To 50 c.c. of a solution of silver oxide containing 0·0005 per cent. silver were added 0·2 c.c. of 0·18 N sodium carbonate and 20 c.c. of silver nuclear solution. The mixture was heated to boiling and was then reduced by 0·5 c.c. of formaldehyde solution prepared by diluting 2 c.c. of commercial formalin with 100 c.c. of water. A bright yellow clear sol formed at once.

Sol V was prepared according to the method recommended by Voigt and Heumann (1928) for the preparation of uniform sol with particles of approximately the same size and colour. To 50 c.c. of a solution of pure silver oxide containing 0·0005 per cent. silver were added 0·4 c.c. of 0·18 N sodium carbonate solutior, 20 c.c. of nuclear solution and 2 c.c. of 0·0055 per cent. solution of hydrazine sulphate. Reduction took place at once with the formation of a light yellow clear sol.

It is well known that in the case of silver sols, most uniform sols result if a small amount of gold nuclear solution is used instead of silver nuclear sol. Sol VI was prepared according to this method. To 50 c.c. of a solution of silver oxide containing 0·0005 per cent. silver were added 0·3 c.c. of 0·18 N sodium carbonate solution and 0·5 c.c. of gold nuclear solution followed by the addition of 0·5 c.c. of hydrogen peroxide diluted to 1 part in 1000. An yellowish-brown sol resulted at once.

The sols were preserved in resistance glass bottles thoroughly cleaned and well steamed. The sols were not allowed to be unnecessarily exposed to light. Even after a month, the sols were quite stable.

4. *Depolarisation Measurements.*

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h for the ultra-violet region were made by the same method as was employed for the depolarisation measurements with gold sols. The experimental set up has already been described in Part I (Krishnan, 1937) of this series. From a series of photographs taken, the readings of the nicol in the path of the scattered light, corresponding to the equality of intensity of the two mutually perpendicular components of the scattered light for the following wavelengths, namely, 2967, 3650, 4046 and 4358 A.U. were read off and the depolarisation values were calculated therefrom. 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 correction for ρ_u was equal to 0·15 per cent. The correction for ρ_v was half of that for ρ_u.

The sols examined did not show any appreciable fluorescence. This was evidenced from the clear picture (without any background) obtained by photographing through the spectrograph the light scattered by these sols when they were illumined with the light from a mercury arc.

For the visible region the method adopted was slightly different from the one employed for gold sols. Since the scattering was more intense in silver sols than in gold sols, measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made visually using a monochromator. The experimental set up is shown in Fig. 1.

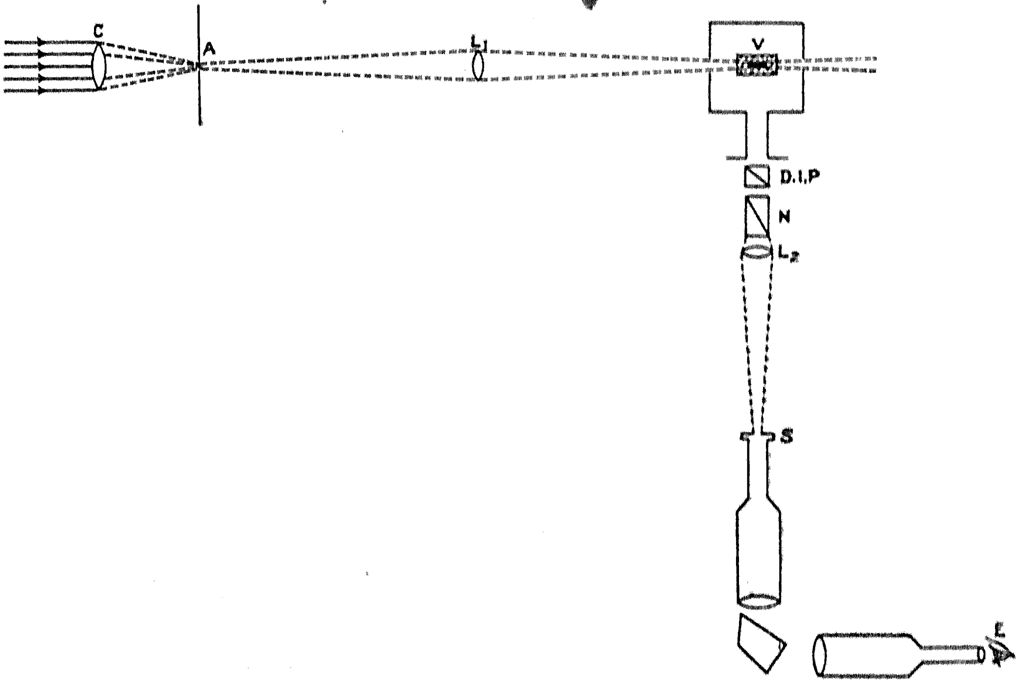

Fig. 1.

C = Condenser.
A = Square aperture (2 mm. square).
L_1 = Long focus photographic lens.
V = Cell containining the sol.
D.I.P. = Double-image prism.
N = Nicol (square ended).
L_2 = Lens.
S = Slit of a Hilger constant deviation spectroscope, which was used as a monochromator.
E = Eye of the observer.

A parallel beam of sunlight reflected by a single mirror (front silvered) Foucault Helistat was condensed by means of a long focus photographic lens C, on to the square aperture A. The axis of the collimator of the spectroscope was kept exactly normal to the incident beam. Before taking measurements the validity of the reciprocity theorem in silver colloids was tested out as follows. A double-image prism was placed in the path of the incident beam. The scattered light was viewed through another double prism. It was found that the middle two anisotropic components were exactly equal in intensity and colour, but they were more bluish than the outer two showing thereby that the depolarisation values would be greater for the blue region than for the yellow or red region. In sols IV and VI it was noticed that the fourth component was definitely brighter than the middle two.

The depolarisation factors were then measured as follows. The drum of the constant deviation spectroscope was set at readings corresponding to 4500, 5000, 5500, 6000 and 6500 A.U. Observing through the eye-piece, the nicol N was rotated and the rotation of the nicol was noted corresponding to the two adjacent positions of equality of intensity of the two components of the scattered light for each wave-length. The depolarisation factor was calculated from the mean value of the angle of rotation of the nicol. For polarising the incident beam a wide square-ended nicol was made use off. Thus ρ_u, ρ_v and ρ_h were determined experimentally for the sols I, III to VI for different wave-lengths.

As the intensity of scattering was very feeble in the nuclear sol, this method could not be applied. Using the point source mercury arc and the photographic method the values of ρ_u and ρ_v were determined for λ 2967, 3650, 4046, 4358, 5461 and 5790. The values of ρ_u and ρ_v corresponding to 4750, 5000 and 5500 were obtained by interpolation. The value of ρ_h was calculated from the observed values of ρ_u and ρ_v.

A correction arising from the finite angle of the incident beam was also applied to the observed values of ρ_u and ρ_v. The corrected values are given in Tables I and II.

TABLE I. *Dispersion of Depolarisation.*

Wave-length λ in A.U.	Silver Sol I (Bredig's sol)			Silver Sol II (Nuclear sol)			Silver Sol III (H_2O_2 reduction)		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	6·7	2·0	57	6·2	3·4	100	11·5	..	..
3650	12·5	4·9	93	7·2	4·2	100	14	4·9	49
4046	22·7	11	83	14	7·2	100	24·8	10	63
4358	30·7	17	100	12·5	6·2	100	27	11·2	68
4750	32	19·8	100	11	5·5	100	29·5	19·8	100
5000	33·3	20	100	10·5	5·2	100	29	19·8	100
5500	36	21·8	100	10	4·9	100	27·5	18	100
6000	38·3	23·8	100	..	..	..	26	16·3	100
6500	39	25·5	100	..	..	..	25·5	14	87

TABLE II. *Dispersion of Depolarisation.*

Wave-length λ in A.U.	Silver Sol IV (Formaldehyde reduction)			Silver Sol V (Hydrazine sulphate reduction)			Silver Sol VI (Au sol used as nuclear sol)		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	2·5	..	..	11·5	..	..	4·5	..	..
3650	6·2	2·2	63	18·9	7·2	78	8·8	3·1	61
4046	19	10·5	84	30·7	15·6	87	21·7	10·2	70
4358	22·8	12·5	95	34·7	17·2	100	27	13	75
4500	22·8	13·2	100	29·4	16·2	100	32	16·3	78
5000	16·3	6·4	100	24·8	14	100	42	21·4	81
5500	12·5	5·8	93	20·7	11·5	100	33·3	17·4	78
6000	10·2	4·9	87	18	10·5	100	30·7	17	90
6500	9·6	4·9	80	17	9·3	100	28·5	16·7	96·5

TABLE III.

Absorption Coefficient of Silver Sols.

Wave-length	Sol I	Sol II	Sol III	Sol IV	Sol V	Sol VI
2250	0·38	0·15	0·15	0·325	0·3	0·225
2500	0·23	0·12	0·135	0·24	0·21	0·22
2750	0·21	0·08	0·12	0·17	0·14	0·2
3000	0·275	0·05	0·1	0·11	0·07	0·15
3250	0·39	0·04	0·09	0·06	0·05	0·09
3500	0·55	0·13	0·12	0·19	0·22	0·19
3750	0·78	0·3	0·2	0·37	0·41	0·26
4000	0·98	0·52	0·28	0·6	0·6	0·32
4250	1·05	0·32	0·3	0·74	0·55	0·33
4500	1·05	0·18	0·275	0·6	0·4	0·3
5000	0·8	0·075	0·18	0·28	0·16	0·23
5500	0·625	0·05	0·12	0·15	0·08	0·14
6000	0·53	0·04	0·1	0·08	0·05	0·08
6500	0·45	0·02	0·08	0·045	0·03	0·07
7000	0·4	0·01	0·065	0·03	0·02	0·06

Sols I, III, IV and V were diluted three times and the measurement of ρ_u for two wave-lengths was repeated and it was found that no appreciable change in the value of ρ_u was produced by dilution showing thereby that the sols could be taken as optically infinitely dilute.

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

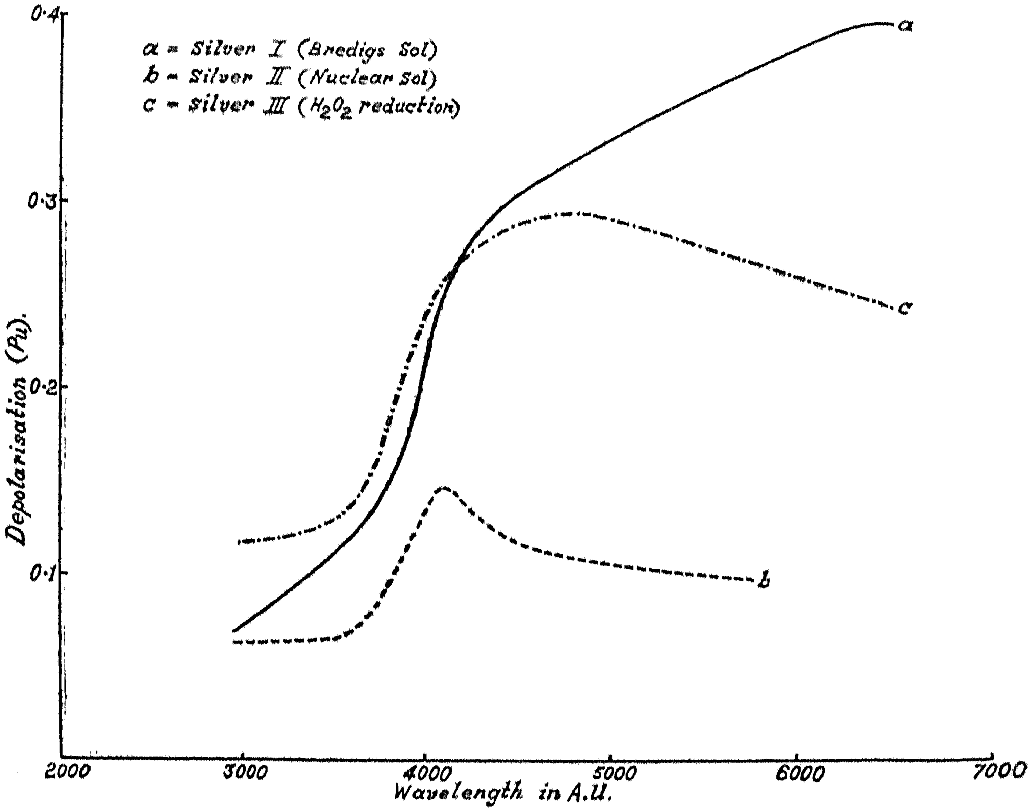
a = Silver I (Bredigs Sol)
b = Silver II (Nuclear Sol)
c = silver III (H_2O_2 reduction)
Depolarisation (ρ_u).
0·4
0·3
0·2
0·1
2000
3000
4000
5000
6000
7000
Wavelength in A.U.
a
b
c

FIG. 2.

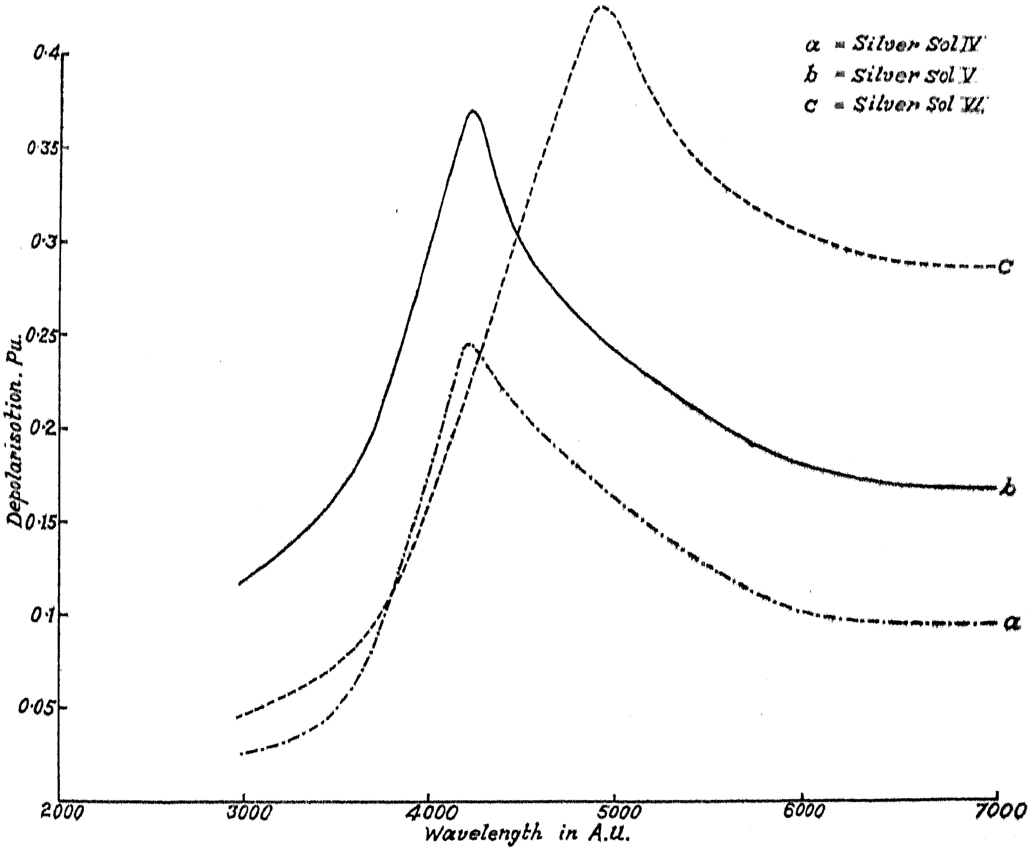
a = Silver Sol IV
b = Silver Sol V
c = Silver Sol VI
Depolarisation. Pu.
0·4
0·35
0·3
0·25
0·2
0·15
0·1
0·05
2000
3000
4000
5000
6000
7000
Wavelength in A.U.
a
b
c

FIG. 3.

5. *Absorption Measurements.*

The absorption measurements were made with a spekker ultra-violet photometer. The extinction coefficient per centimetre length of solution was determined for a series of wave-length from 2500 A.U. to 7000 A.U. The values are given in Tables III. The curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ.

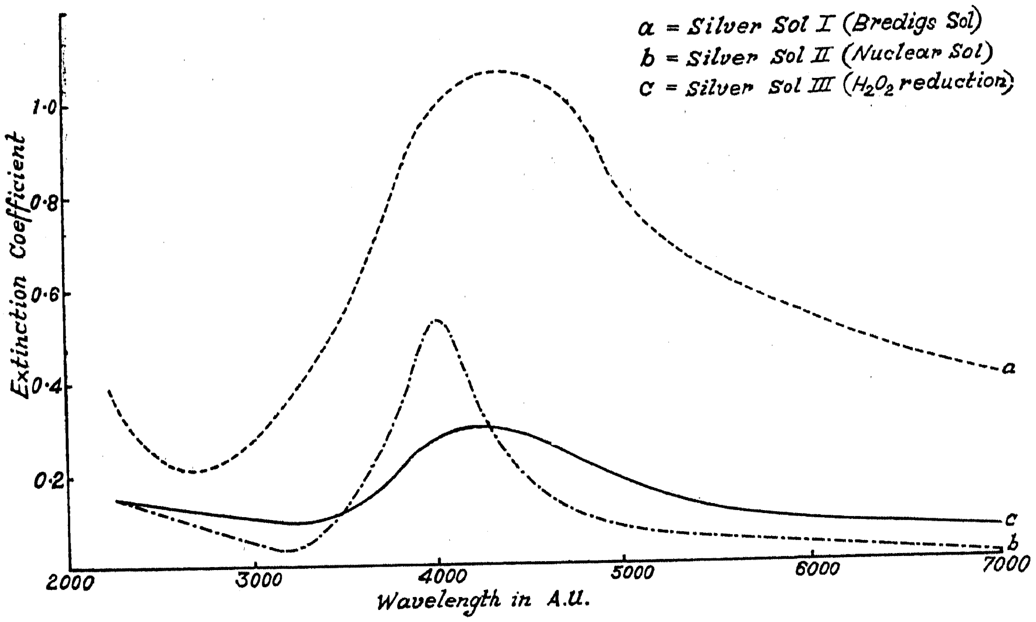

FIG. 4.

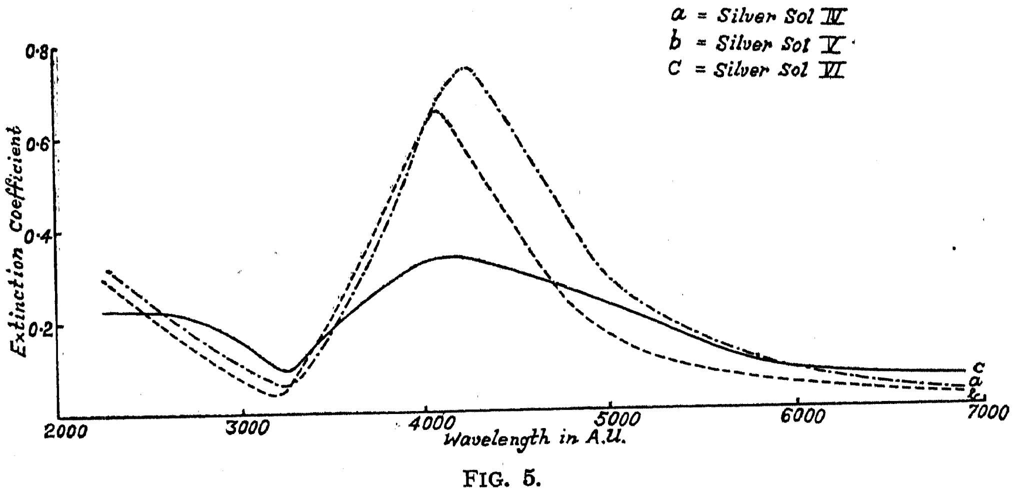

FIG. 5.

6. *Results.*

As in the case of gold sols, so also in silver sols ρ_u, ρ_v and ρ_h are markedly functions of wave-length. In all the sols studied except in Bredig's sol, *i.e.*, (sol I), starting from 3000 A.U. ρ_u goes on increasing, attains a maximum in the region of maximum absorption and diminishes with further increase of wave-length. In sol I ρ_u goes on increasing continuously with increase of wave-length. The depolarisation curves for all the sols show a pronounced asymmetry about the point of maximum depolarisation, the curves being steeper on the shorter wave-length side than on the longer wave-length side. This is also the case with the absorption curves. ρ_v follows the same course as ρ_u. In the region of the characteristic absorption there is an increase of the optical anisotropy as is evinced by the notable increase of ρ_v. For the nuclear sol ρ_h has its limiting value of 100 per cent. from $\lambda = 3000$ to $\lambda = 6000$ A.U. In sols I, III and V ρ_h is less than 100 per cent. in the ultra-violet region, whereas, in sol IV ρ_h is less than 100 per cent. throughout except in the region of the characteristic absorption where it attains its limiting value of 100 per cent. In sol VI ρ_h is less than 100 per cent. throughout and it increases or decreases with wave-length *pari passu* with ρ_u. A comparative study of the values of ρ_h for all the sols indicates that the nuclear sol contains particles of extremely small size, while in sols IV and VI the size of the particles becomes comparable with the wave-length of light. Sols I, III and V contain particles of intermediate sizes.

As has been observed previously, the curves of absorption show a pronounced maximum in the violet region, *i.e.*, at about 4200 A.U. for all the sols. There is a distinct minimum in the ultra-violet region at about 3200 A.U. for all the sols except for the Bredig's sol for which the minimum is shifted further towards the shorter wave-length side. Although the depolarisation curves show a maximum in the violet region where the absorption is maximum it is not possible to detect a minimum at about 3200 A.U. in the depolarisation curves corresponding to the point of minimum absorption using mercury arc as the source of ultra-violet radiation since it does not give rise to any intense line in this region. The maximum and minimum of the absorption curve for sol III are much flatter than for any other sol. This is because the sols obtained by reduction with hydrogen peroxide using silver nuclear sols contain particles of varied sizes. The points of maximum and minimum absorption are different for different particle sizes. It has often been remarked that this method of preparation of the sol is quite unsatisfactory. The maximum of the absorption curve for sol VI is also rather flat, although it contains particles of uniform size. According to Mie's theory as the size of colloidal metal (silver or gold) particles increases, the maximum value of the absorption curve increases and it shifts to the longer wave-length side, up to a certain critical value for the size of the particles. Any further increase in size of the particles, lowers the maximum value and consequently the curve becomes flatter and flatter. This fact has been beautifully illustrated in Figs. 4 and 5. From a comparison of the observed absorption curves for sols II, V, IV and VI and from what has been mentioned above it follows that $r_{II} < r_{V} < r_{IV} < r_{VI}$ where r_{II}, r_{V}, r_{IV} and r_{VI} are the diameters of the particles in sols II, V, IV and VI respectively. This is also in accordance with the depolarisation measurements of the author (see Tables I and II). In the Bredig's sol the absorption is relatively greater and the maximum extends over a wider range of wave-length than in any other sol. This is due to the presence of silver hydroxide in the sol and also due to the presence of particles of varied sizes.

7. *Theoretical Discussion.*

The values of the depolarisation factor ρ_u are evaluated from Gans' formula for very small particles of ellipsoidal shape. Table IV gives the comparative values of the depolarisation ρ_u for small elongated and flattened rotation ellipsoids.

Table IV.

Values of ρ_u *(calculated).*

B/A / λ in A.U.	Elongated rotation ellipsoid					Sphere	Flattened rotation ellipsoid		
	0·00 %	0·23 %	0·57 %	0·77 %	1 %	1·60 %	2·63 %	10 %	∞ %
3500	22·9	18·4	8·1	2·8	0·0	32·9	64·9	70·2	52·4
4000	74·7	51·3	54·7	38·0	0·0	31·8	38	49·8	41·9
4200	69·7	73·5	70·2	27·7	0·0	18·6	29·9	38·7	40·7
4500	81·7	83·2	47·4	11·1	0·0	11·5	22·1	33·7	35·7
5500	83·8	75·1	24·7	5·1	0·0	7·4	16·5	26·5	30·9
6500	71·5	50·3	11·7	2·4	0·0	4·6	11·6	22·4	25·9
7500	62·8	44·4	9·9	2·1	0·0	4·1	10·5	21·1	24·7

According to Gans' theory for a flattened rotation ellipsoid the maximum of the depolarisation curve should lie in the ultra-violet region, *i.e.*, below 3500 A.U. whereas for an elongated ellipsoid or a prolate spheroid it is shifted towards the longer wave-length side of the region of characteristic absorption maximum. The latter corresponds to the experimentally observed data. Comparing the theoretical values of ρ_u with the experimental values it is seen that the particles in silver sols are more like elongated rotation ellipsoids with the axial ratio equal to 0·75. The theoretical curves of the dispersion of ρ_u for elongated ellipsoidal particles having an axial ratio = 0·75 shows also an asymmetery about the point of maximum depolarisation. The observed values of ρ_u for regions of the spectrum far away from the region of characteristic absorption and on either side of it are higher than the calculated values of ρ_u for prolate ellipsoids having an axial ratio 0·75. This is because in these regions the anisotropy of the particles is smaller and hence the finite size of the particles enhances the observed depolarisation. Gans' theory is true only for particles of molecular dimensions. In the region of characteristic absorption the agreement is more perfect because the anisotropy is much greater and consequently the size effect is completely subdued.

The following table gives the absorption constant $k \times 10^{-3}$ for different wave-lengths calculated according to Gans, for very small particles of ellipsoidal shape. The values are taken from Gans' paper. The values of k given in the table below for an elongated rotation ellipsoid with the axial ratio B/A = 0·8 are obtained by interpolation.

TABLE V.

Absorption Coefficient (calculated).

B/A λ in A.U.	Elongated rotation ellipsoid					Sphere	Flattened rotation ellipsoid			
	0·00	0·23	0·57	0·77	0·8	1·0	1·61	2·63	10	∞
3500	86·9	61·2	35·4	29·8	29	27·9	41·6	100·3	13·6	8·1
3750	75	127·6	258·2	194·9	189	152·3	101·1	30·5	9·7	6·6
4000	18·8	27·5	81·0	199·1	218	353·7	185·4	49·5	11·3	7·0
4200	11·2	16·5	77·2	202·9	188	93·5	343·4	114·9	13·5	7·5
4500	7·8	13·6	240·1	45·1	38	27·5	68·8	464·6	182·3	8·4
5000	6·7	19·1	34·8	11·5	11	9·1	15·3	63·4	34·2	10·4
5500	7·5	97·8	11·1	5·5	5·3	4·8	6·9	18·9	76·7	13·0
6000	8·4	24·9	5·6	3·2	3·2	2·8	3·9	9·0	224·9	16
6500	9·8	10·8	3·3	2·1	2·0	1·9	2·5	5·2	817·5	18·6
7000	10·4	6·1	2·2	1·5	1·4	1·3	1·7	3·4	405·1	20·1

A comparative study of the Tables III and V shows that the experimentally determined curves are similar to the theoretical curves calculated according to Gans' theory for elongated rotation ellipsoids of axial ratio equal to 0·8, It is clear from the above considerations that the particles of silver in the colloidal state are not spherical in shape but behave optically as elongated ellipsoids with an axial ratio of 0·75 or 0·8.

It will be of interest to study the dispersion of refractive index of these silver sols and to correlate the results with the shape of the particles. This will be taken up as early as possible.

8. *Other Experimental Evidence.*

The double refraction in silver sols produced by mechanical flow has been investigated by Bjornstahl (1924). He observed negative streaming double refraction in some silver sols. The protected silver sol prepared according to Gutbier showed a positive effect. This is because the sol is really a silver oxide sol. Let us suppose that the particles can be represented as ellipsoids of revolution. The direction of flow is parallel to Z-axis in a co-ordinate system X, Y, Z, while the light is passed along the axis Y. If we consider the simple case of complete orientation, all the particles will be oriented in such a way that the greatest axis of the ellipsoid is parallel to the Z-axis, *i.e.*, to the direction of flow. The expression for the phase difference between the vibrations parallel to the Z-axis and to the X-axis respectively as derived by Bjornstahl (1924), is given by

$$\frac{n_z - n_x}{n_0} = \frac{N \pi v}{n_0^2} \left\{ h' - h \right\}^{\text{Real}}$$

where N = number of particles per unit volume ;

n_0 = refractive index of the dispersion medium ;

$\frac{n}{n_0}$ = refractive index of colloid ;

v = volume of the ellipsoid ;

$h = n_0^2 \dfrac{m'^2 - 1}{4\pi + (m'^2 - 1)\,P}$;

$h' = n_0^2 \dfrac{m'^2 - 1}{4\pi + (m'^2 - 1)\,P'}$;

$m' = \dfrac{m}{n_0}$;

m = complex refractive index for the disperse phase and

$P = 4\pi \dfrac{1 - e^2}{e^2} \left[\dfrac{1}{2e} \log \dfrac{1 + e}{1 - e} - 1 \right]$ for a prolate spheroid ;

$P = \dfrac{4\pi}{e^2} \left(1 - \dfrac{\sqrt{1 - e^2}}{e} \arcsin e \right)$ for an oblate spheroid ;

$P + 2P' = 4\pi.$

$\frac{3P}{4\pi}$ is less than unity for an elongated rotation ellipsoid, while it is greater than unity for a flattened rotation ellipsoid. $\frac{3P'}{4\pi}$ is greater than unity for an elongated one and less than unity for a flattened one.

In the case of silver for $\lambda = 6000$ A.U. $(h' - h)^{\text{real}}$ is negative for an elongated rotation ellipsoid. This gives rise to a negative flow birefringence $(h' - h)^{\text{real}}$ is positive for a flattened rotation ellipsoid. The negative effect at 6000 A.U. observed by Bjornstahl in silver sols indicates, therefore, that the particles are not spherical in shape but are elongated. The dispersion of flow birefringence in silver sols has not yet been studied. A large dependence of flow double refraction on wave-length should be expected from consideration of the dispersion of refractive index and anisotropy of colloidal silver particles.

Bergholm and Bjornstahl (1920) have shown that silver sols exhibit distinct negative double refraction in an electrical field. The electric double refraction is attributed to an orientation of silver particles of asymmetric shape. In the electric field the largest axis of the ellipsoid has a tendency to place itself parallel to the lines of force. Since the particles are charged cataphoresis takes place owing to the influence of the field. A body of asymmetric shape moving in a liquid tries to place its greatest axis at right angles to the direction of movement. These two opposing forces act on the particles. By comparison with the experiment on mechanical double refraction a negative electric double refraction indicates a resultant orientation along the direction of the field and an elongated ellipsoidal shape for the silver particles.

Silver sols should not, in general, exhibit any magnetic double refraction since silver, just like 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 silver in mass. This is in accordance with the observations of Bjornstahl (1924) and also with the recent observations of Nilakantan (1937). Only silver sols prepared according to Carey-Lea showed a strong negative effect. This is due to the contamination of the sol with iron to the extent of 0·3 to 1 per cent. of the silver quantity.

When silver sols are examined under a Cardioid ultra-microscope, scintillations are observed. Spherical particles scatter light symmetrically, while non-spherical ones scintillate because the scattered light is more intense when the particle, in the course of Brownian Movement lies with its long axis in the plane of the microscope and at right angles to the illuminating light.

It has been found by Levi and Tabet (1933) that when silver is deposited electrolytically growth takes place in a direction perpendicular to the octahedral faces. Since X-ray analysis discloses that the particles in silver sols consist of crystals similar to those of silver in mass, the primary units are probably minute octahedra. The volume of an octahedron of side a, is equal to $\frac{\sqrt{2}}{3} a^3$, *i.e.*, $0 \cdot 47\ a^3$. The volume of the sphere circumscribed round the octahedron is equal to $\frac{\sqrt{2}}{3}\pi a^3$, *i.e.*, $1 \cdot 5\ a^3$. A prolate spheroid of axial ratio $0 \cdot 8$ can be inscribed inside the octahedron touching the four square edges. The semi-minor axis of such a spheroid would be equal to half the side of the octahedron, *i.e.*, $\frac{a}{2}$ and its volume is equal to $\frac{\pi}{4 \cdot 8}a^3 = 0 \cdot 65a^3$ which does not differ so greatly from that of the octahedron as the volume of the circumscribed sphere. It is thus permissible to consider the colloidal silver particles which are minute octahedra as optically equivalent to prolate spheroids of axial ratio $0 \cdot 8$ and not as spheres.

In conclusion, the author takes this opportunity to thank Prof. Sir C. V. Raman for his kind and helpful interest in the work.

9. *Summary.*

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and the extinction coefficient of a series of six silver sols are made for different wave-lengths from 2500 A.U. to 7000 A.U. As in the case of gold sols, so also in silver sols in the region of the characteristic absorption the depolarisation factors show an enormous increase. The optical anisotropy of the silver particles in the colloidal state is rather low in the ultra-violet and the red regions, whereas it assumes rather high values in the violet region where the absorption is maximum. Compared with the sols prepared according to other methods Bredig's sol behaves anomalously. Depolarisation measurements indicate that the nuclear sol contains particles of very small size, while the sols prepared by using formalin as reducing agent and that got by employing gold nuclear solution and hydrogen peroxide as reducing agent contain particles of size comparable with the wave-length of light. In the other sols the particles are of intermediate sizes. The observed values of the extinction coefficient and the depolarisation factor ρ_u are compared with the values calculated according to Gans' theory. From both these considerations it is inferred that the particles in silver sols behave optically like elongated ellipsoids with the axial ratio equal to $0 \cdot 75$. It is further suggested that the colloidal particles of silver may be in the form of minute octahedra which can be considered as optically equivalent to a prolate spheroid of the axial ratio stated above. The negative streaming double refraction and the negative electric double refraction observed by the earlier investigators are explained on the basis of the elongated ellipsoidal shape of the silver particles.

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