

THE DEPOLARISATION OF LIGHT SCATTERED BY SOLS

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1. INTRODUCTION

OF the various optical properties of colloids one of the most important and the most widely studied is the Tyndall Effect. According to Rayleigh's theory of light scattering, it is to be expected that light scattered in a direction normal to the incident beam is completely polarised. On account of the various assumptions made in the theory, the law cannot be expected to hold in the case of colloids. In fact, it is found that the light scattered in a direction normal to the incident beam is not completely polarised. The degree of depolarisation of scattered light depends on the size, shape and anisotropy of the colloidal particles. So, the colloid-optic method is potentially of great value in enabling one to ascertain the particle size, shape and anisotropy.

The degree of depolarisation is expressed as the ratio of the weaker component to the stronger component§ in the scattered beam and is referred to as the "Depolarisation factor". Mie's theory¹ indicates that the degree of depolarisation using unpolarised incident light, *i.e.*, ρ_u becomes equal to zero if the particles are spherical, isotropic and small ($d \ll \lambda$). ρ_u attains a finite value as the size of the particles increases. Further Gans² has shown that ρ_u also increases with anisometry and intrinsic anisotropy.

An important advance in this field of colloid-optics has been made in the laboratories of Sir C. V. Raman in employing incident polarised light.³ By this technique it is possible to determine ρ_v and ρ_h separately which, being simpler quantities, may be expected to be more easily correlated with the characteristics of the scattering particles. A finite value of ρ_v indicates shape, anisometry and structural anisotropy. The deviation of ρ_h from unity

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§ To avoid ambiguity it would be better to define P_h as the ratio of the vertical to the horizontal component. It is no doubt true that Krishnan effect (*Proc. Indian Acad. Sci.*, 1941, 14, 230) holds normally. It has been found by us that when the multiple scattering is large and the observation is by the "Limited Background" method, the Krishnan effect is not obeyed [Table I, 1st value]. Moreover, it is well known that Krishnan effect may not hold for systems in which particles are subjected to an orientating field.

indicates finite size. This deviation also indicates deviations from sphericity and isotropy. Krishnan⁴ has derived from theoretical considerations, the relation :

$$\rho_u = \frac{1 + \frac{1}{\rho_h}}{1 + \frac{1}{\rho_v}} \quad (1)$$

This is known as the reciprocity theorem and is sometimes referred to as the Krishnan effect. The equation holds for systems in which the particles are distributed at random, and has been confirmed experimentally by a large number of workers in the field, of whom mention may be made of Krishnan,⁴ Boutaric and Breton⁵ Hoover, Putnam and Wittenberg.⁶

An attempt is made in the present work to study the depolarisation of light scattered by a few sols of known shape and size.

2. EXPERIMENTAL

Preparation of Sols.—The silver iodide and stearic acid sols used in this work were prepared by the methods described previously.⁷ The size of the particles in the sols was determined by the ultramicroscope.⁷

An examination of the sol with regard to (a) Schlierung, (b) twinkling under the ultramicroscope, (c) electric double refraction, (d) stream double refraction and (e) changes in Tyndall intensity brought about by the electric field and the flow, showed that the silver iodide sol consists of particles which are practically isometric whereas the stearic acid sol contains anisometric particles. The adoption of the Langmuir pipette technique⁸ has revealed that the stearic acid particles are disc-shaped.⁷

Optical Apparatus.—The arrangement of the apparatus is diagrammatically shown in Fig. 1.

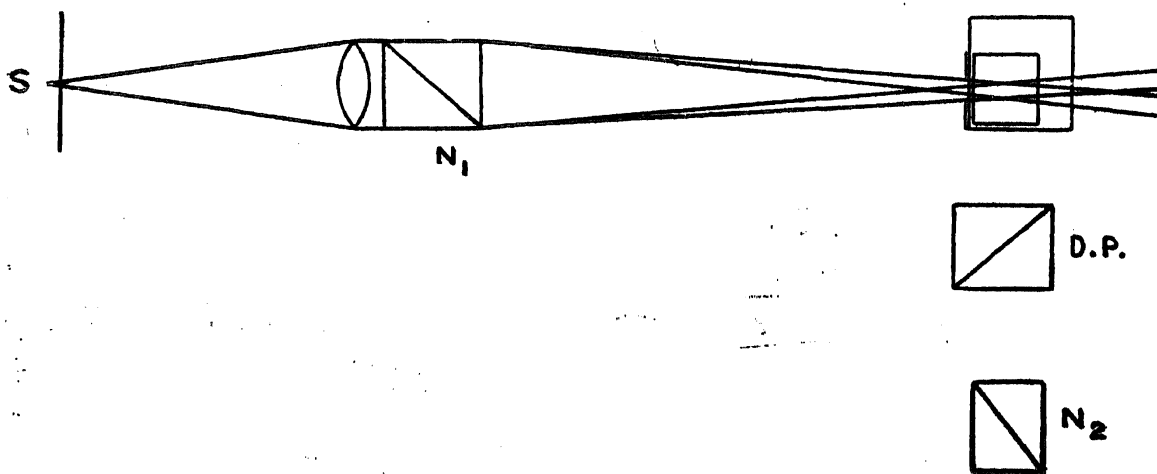


FIG. 1

S, the source of light, is a 500 C.P. point-o-lite lamp housed in a chamber having an aperture for the beam to pass. The beam was condensed by means of a lens and defined by an Ehrlich stop placed before the cell. The cell itself is placed inside a bigger cell filled with water. The outer cell is darkened by means of black paper. The polarisation of the incident light could be adjusted by rotating the nicol NI. The scattered light was studied by employing the two methods (a) having the natural background (*i.e.*, viewing the entire beam of the incident light transversely) and (b) having a limited background (*i.e.*, viewing the scattered light through an Erlich stop 2 m.m. square). This was done with a view to see if any correlation exists between the two methods of study. The depolarisation was determined employing the Cornu method. The scattering was observed exactly at 90° to the incident beam. It was found that the two images as seen in the Cornu apparatus were of slightly different colours so that matching was difficult. The precision in matching was greatly improved by using a red filter. Eight readings at least were taken of the angle corresponding to each of the depolarisation values and the mean used in the calculations. The average error in the matching did not exceed $\pm 0.2^\circ$.

3. RESULTS

The depolarisation factors for silver iodide sol B got by using the natural background, and limited background are given in Table I. The dilution of the sol in the experiments, was always done maintaining the concentration of the peptising ion constant.

TABLE I

Effect of nature of the background on the depolarisation values and the dilution effect

Sol used : Silver iodide sol B.

C = Concentration of the undiluted sol : 0.25 g of silver iodide per 100 c.c. of solution.

Average size of the particles = 104.8 m. μ

Number of particles per c.c. in undiluted sol = 7.32×10^{11} .

Concentration of the sol	Natural background			Limited background
	ρ_{μ}	ρ_{ν}	$\rho_{\frac{1}{2}}$ (cal.)	ρ_{μ}
C ..	0.133	0.065	0.85	0.305
C/2 ..	0.085	0.034	0.64	0.175
C/4 ..	0.066	0.021	0.44	0.137
C/8 ..	0.052	0.016	0.46	0.123
C/16 ..	0.052	0.016	0.46	0.125
C/32 ..	0.052	0.017	0.49	..

With a view to finding out whether the reciprocity theorem holds for limited background, the values of ρ_u , ρ_v and ρ_h were determined for sol A employing the limited background, for various dilutions. The results are given in Table II. In order to investigate the effect of size on the depolarisation values at different dilutions, the particles of the silver iodide sol B were

TABLE II
Krishnan effect and limited background

Sol used : Silver iodide sol A

$$\theta_h = \log \sin^{-1} \left\{ \begin{array}{l} \text{Conc. } 0.5\% \\ \log \sin \theta_v - \log \tan \theta_h \end{array} \right\}$$

Concentration of the sol.	θ_u	θ_v	θ_h (obs.)	θ_h (calc.)
C ..	36.4°	33.0°	45.8°	47.6°
C/2 ..	32.0°	25.5°	43.2°	43.5°
C/4 ..	27.0°	19.05°	40.1°	39.8°
C/8 ..	24.25°	16.1°	38.1°	37.9°
C/16 ..	21.6°	13.7°	36.6°	36.7°
C/32 ..	19.15°	11.6°	..	35.4°
C/64 ..	19.45°	11.6°	..	34.7°
C/128 ..	19.3°	11.6°	..	35.2°

made to grow by the addition of 10 c.c. of 0.1 N potassium iodide to 10 c.c. of the sol. Measurements of ρ_u of the resulting sol BB were made at different dilutions. The size of the particles in sol BB was determined by using the ultramicroscope as described previously.⁷ The results are given in Table III.

TABLE III
Effect of aggregation on depolarisation: Natural background

C = 0.25 g of silver iodide per 100 c.c. of the sol.

Number of particles per c.c. in sol of concentration C/2 in sol B = 3.66×10^{11} .

Number of particles per c.c. in sol of concentration C/2 in sol BB = 2.6×10^{10} .

Concentration	ρ_u of original sol. 'B' (size 104.8 m. μ)	ρ_u of aggregated sol. BB (size 254 m. μ)
C/2 ..	0.085	0.124
C/4 ..	0.066	0.099
C/8 ..	0.052	0.089
C/16 ..	0.052	0.079
C/32 ..	0.052	8.080
C/64 ..	0.052	0.081

The effect of temperature on depolarisation was next investigated. The results obtained with silver iodide (sol B), are given in Table IV. Effect of the width of the slit on the values of depolarisation is given in Table V. The effect of dilution on the depolarisation of stearic acid sol is given in Table VI.

TABLE IV

Effect of temperature on depolarisation

Sol used : silver iodide sol B.
Natural background.

ρ_{μ} at 23° C.	ρ_{μ} at 60° C.
0.068	0.070

TABLE V

Effect of width of slit on depolarisation

Sol used : Silver iodide sol B.
Natural background.

Concentration	ρ_{μ} with a slit of 2 mm. square	ρ_{μ} with a slit of 1 mm. square
C ..	0.133	0.092
C/32 ..	0.052	0.052

TABLE VI

Depolarisation of stearic acid sol

Natural background.

C = concentration of the original sol = 0.085%.

Size = 390.8.

Concentration	ρ_{μ}	ρ_{ν}	ρ_h (obs.)	ρ_h (Calc.)
C	0.087	0.030	0.57	0.52
C/2	0.066	0.026	*	0.68
C/4	0.048	0.022	*	0.82
C/8	0.034	*	*	..
C/16	0.034	*	*	..

* These values could not be taken on account of the low intensity of scattering of Tyndal light.

4. DISCUSSION

1. *Effect of nature of the background on depolarisation.*—An examination of Table I shows that the values of depolarisation differ according as the background is natural or limited. With the natural background, the effect of the depolarisation of the light from the background gets cancelled out and so the true values of depolarisation are obtained. With the limited background, only apparent and not true values

are got. It was also found that the depolarisation value as determined by the limited background method was found to be affected by distance travelled by the incident and the scattered beams through the colloid during observation. No such effect was noticed by the natural background technique. It is however of interest to note that the change of depolarisation with dilution is similar in the two modes of observation. An examination of Table I shows that the depolarisation decreases with dilution in both the cases. Moreover the final constant value is reached in either case, at a concentration of $C/8$.

It is of interest to examine as to whether the reciprocity theorem is applicable to the data on the apparent depolarisation values got by the limited background method. A slight deviation from the normal procedure has been adopted in the present work in examining the reciprocity theorem. On the basis of the reciprocity theorem it can be easily shown that

$$\log \sin \theta_h = \log \sin \theta_v - \log \tan \theta_u \quad (2)$$

where

$$\theta_v, \theta_h \text{ and } \theta_u \text{ are related to } \rho_v, \rho_h \text{ and } \rho_u$$

by the equation $\tan^2 \theta = \rho$. The value of θ_h calculated by the equation (2) is compared with the value of θ_h actually observed in the Cornu apparatus. These values are given in Table II. An examination of the Table shows that the reciprocity theorem holds very well indeed even for the observation with the limited background. At the highest concentration however, there is a deviation both from the Krishnan effect (in that $\theta_h > 45^\circ$) and the reciprocity theorem. This deviation is not due to any increased influence of the experimental error in this region. For, it can be shown by an application of the theory of errors that, the error $\delta\theta_h$ in the calculation of θ_h from the errors in the values of θ_u and θ_v is given by the equation

$$\frac{\rho_h \rho_u \sin 2\theta_h}{\rho_u} \left\{ \frac{\delta\theta_v}{\sin 2\theta_v} - \rho_v \cdot \frac{\delta\theta_u}{\sin 2\theta_u} \cdot \frac{1}{\sin^3 \theta_v} \right\}$$

An application of this equation to the present case, shows that the error introduced in the final result is of the same order throughout the range of the experimental data used in the calculation. This deviation from the reciprocity theorem is real as also is the deviation from the Krishnan effect. Both of these effects are probably due to high multiple scattering that occurs in the highly concentrated colloidal solution, which introduces a high and complex background effect in the limited background method of observation.

2. *Effect of concentration on depolarisation.*—An examination of Tables I, II, III and VI shows that, on diluting the sols, the depolarisation

at first exhibits a change and then remains constant with both the Sols investigated in the present paper. This is in agreement with the observation of G. Sharada Bai, Doss and Rao,⁹ on clay sols and by Hoover and others⁶ on bentonite sols.

The change is exhibited by all the three depolarisation factors alike as can be seen from the Table I. The values reach the constant value at a concentration of $C/8$ in all the three cases. $\rho_{\frac{1}{2}}$ (Table II) no doubt, attains the final value a little earlier but this is due to the fact that the variation in the values of $\rho_{\frac{1}{2}}$ with concentration is comparatively small. In general, the depolarisation factors decrease with dilution. But with stearic acid sol, $\rho_{\frac{1}{2}}$ definitely increases with dilution. This exceptional behaviour which is probably connected with disc-shaped particles possessed by the particles, needs elucidation.

The change of depolarisation is not due to any change in particle size since it is not likely to occur in our system wherein the ion environment has been maintained constant during dilution. The change of depolarisation with change in concentration is therefore to be ascribed to the other factors: (a) Molecular field effect of Gans¹¹ and (b) multiple scattering.¹⁰ We shall first discuss the former. The field effect may be considered to a first approximation, as due to a close mutual approach of the particles so that the group would have different scattering properties as compared with what it would be if the particles acted independently. The probability of occurrence of such proximity can be computed by adopting statistical methods. Let us assume that the molecular field effect becomes appreciable only when two or more particles are contained within a sphere of diameter d . The volume of such a sphere is $0.52 d^3$. The probabilities P_1 and P_2 of finding singles and pairs respectively in that volume is given by (12):

$$P_1 : P_2 :: 1 : \nu/2$$

where ν is the average number of particles contained in that sphere.

Let us apply this idea to silver iodide sol B. A noticeable effect of concentration on depolarisation begins at a concentration of $C/4$ which corresponds to 1.8×10^{11} particles per c.c.

$$\begin{aligned} \therefore \nu &= 1.8 \times 10^{11} \times 0.52 d^3 \\ &= 9.36 \times 10^{10} d^3. \end{aligned}$$

If we assume that the particles are to be within a distance of about 4000 \AA , in order to get the required interaction, we should have,

$$\begin{aligned} \text{for Ag I sol B, } \nu/2 &= \frac{9.4 \times 10^{11}}{2} \times (4 \times 10^{-5}) \\ &= 3 \times 10^{-3}. \end{aligned}$$

Similarly, the $\nu/2$ for Ag I sol BB, and steric acid sol work out to be 1.1×10^{-4} and 1.3×10^{-4} respectively. From these calculations we come to the conclusion, that the effect of this interaction may vary enormously in the different cases. Whereas with silver iodide sol B, the pairs should occur to the extent of 0.3% to bring about a certain amount of interaction, it is sufficient to have only 0.01% of the pairs to produce a similar effect in silver iodide sol BB and stearic sol. Moreover, the idea that 0.01% of the pairs would upset the value of depolarisation is itself not plausible. We have no doubt neglected the occurrence of higher order clusters; but their probability of occurrence is much smaller and need not be taken into account. We have no doubt assumed a value of 4000 \AA for d . Assumption of any other plausible value does not remove the difficulty.

The above considerations lead us to the conclusion that the effect due to molecular field is small and any observed large changes in depolarisation should be due to the other factor multiple scattering. The fact that the concentration effect becomes more considerable as the particle size increases also points to the same conclusion. Larger the particle size, larger the scattering and larger would be the influence of multiple scattering. In fact, the ferric oxide sol which contains very fine particles scatters light to a very small extent, shows no change of depolarisation with increase in concentration.⁶ The existence of multiple scattering was confirmed by the fact that the depolarisation value depended upon the width of the incident beam, in the more concentrated solutions as can be seen from Table V. We agree with Hoover and co-workers⁶ in emphasising on the importance of finding out the value of depolarisation at infinite dilution for use in any theoretical considerations.

The value of the concentration at which the constancy of ρ occurs is very sensitive to changes in particle size. It appears possible to take advantage of it in the determination of average size of the particles. Since ρ_u shows the effect as well as the other factors, and the effect can also be observed with the limited background, the size can easily be determined by measuring ρ_u using the limited background method. It is necessary, of course, to find out the empirical relation between the particle size and the concentration at which a definite percentage deviation of ρ_u occurs (from the limiting value).

3. *Effect of temperature on depolarisation.*—Table IV shows that in the case of Ag I sol, temperature has very little effect on the depolarisation of light.

The function $\frac{10\rho_u}{6-7\rho_u}$ is suggested to be a measure of the anisotropy of the scattering centres. That this cannot be true with systems such as

those worked by us, becomes obvious by the fact that the value of the function for stearic acid sol is smaller than that for silver iodide sol, though the former contains particles which are highly anisotropic and the latter have no sensible anisotropy as conclusively shown by other data. A similar anomaly occurs even if the corresponding ρ_v function is considered. This made us suspect that the observed phenomenon may be connected with the small difference in refractive index between the disperse and the continuous phases. In order to test out this idea, the refractive index of the medium was changed by the addition of glycerine maintaining ionic strength constant. Even when the refractive index was made almost equal to that of stearic acid, as could be seen by the enormous fall in the intensity of scattering, the ρ_u was not detectably affected. Again the value of ρ_h for the stearic acid sol is larger than the same for the silver iodide sol, though the latter has smaller and anisotropic particles. These observations have to be taken into account in any theory proposed for explaining the depolarisation of light scattered by colloids.

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6. SUMMARY

1. Measurements of ρ_u , ρ_v and ρ_h have been carried out with stearic acid sol (anisometric particles) and silver iodide sol (isometric particles), containing particles of known size.
2. That the limited background technique yields only apparent depolarisation values, has been confirmed.
3. The reciprocity theorem is found to hold exactly even with the limited background observations, except at the highest concentrations (0.5%).
4. It is shown that molecular field effect of Gans cannot account for the variation of depolarisation with concentration. Multiple scattering adequately accounts for the phenomenon.
5. The possible application of depolarisation studies at the different concentrations for the determination of particle size is indicated.
6. Temperature is found to have no sensible effect on depolarisation of silver iodide sol.
7. Difficulties in correlating ρ_u , ρ_v and ρ_h with size and anisotropy have been pointed out.

7. REFERENCES

1. Mie .. *Ann. Phys.*, 1908, **25**, 377.
2. Gans, R. .. *Ann. Physik*, 1912, **37**, 881; 1915, **47**, 270; 1920, **62**, 330, 1921, **65**, 97.
3. C. V. Raman .. *Proc. Ind. Acad. Sci.*, 1941, **14**, 228.
4. Krishnan .. *Ibid.*, 1 A, 1935, 782.
5. Boutaric and Breton .. *J. Chim. Phys.*, 1939, **36**, 193.
6. Hoover and Co-workers .. *J. Phy. Chem.*, 1942, **46**, 81.
7. R. S. Subrahmanya, .. *Proc. Ind. Acad. Sci.*, 19 A, 1944, 405.
K. S. G. Doss & B. S. Rao
8. Langmuir .. *J. Chem. Phys.*, 1938, **6**, 873.
9. Sharada Bai and Co-workers, *M.Sc., thesis, Mys. Uni.*, 1942.
10. Lotmar .. *Helv. Chim. Acta*, 1938, **21**, 792.
11. Gans .. *Ann. Physik.*, 1920, **62**, 331.
12. Taylor .. *Treatise on Physical Chemistry*, **2**, Second edition, 1578.
13. Krishnan .. *Proc. Indian Acad. Sci.*, 7 A, 91-97, 1938.