INFLUENCE OF SECONDARY SCATTERING ON DEPOLARISATION MEASUREMENTS

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1. Introduction

As is well known, one of the most useful methods for the determination of the size, shape and structure of particles in colloidal suspensions is that based on the study of the Tyndall scattering in the solutions. Such a study includes the measurement of the intensity and state of polarisation of the light scattered by the colloidal solution in a direction perpendicular to the incident beam. Using incident unpolarised light as also light polarised with vibrations respectively vertical and horizontal three different measures of the state of polarisation or the so-called depolarisation of the transversely scattered light are obtained, namely, ρ_u, ρ_v and ρ_h. These three quantities are related to the size, shape and structure of the particles contained on the solution and hence from a knowledge of their magnitudes it is possible to estimate the size, shape and structure of the scattering particles. This is true so long as the individual particles scatter quite independently of one another and the *macroscopic* depolarisation factor, *i.e.*, the depolarisation of the light scattered by the solution in bulk is equal to the *microscopic* depolarisation factor characteristic of the light scattered by any individual particle under the action of the incident light. But in most cases the conditions stated above are not satisfied as is evident from the fact that the values of ρ_u, ρ_v and ρ_h are influenced to a marked extent by the concentration of the colloidal solution. It is found that the values of ρ_u, ρ_v and ρ_h decrease progressively with increasing dilution and reach limiting values equal to the corresponding values of the individual particles. This dependence on concentration arises from two causes :—(1) the existence of a molecular field surrounding the particles and (2) the presence of secondary scattering. Gans (1920) considered the effect of molecular field on any particle inside the scattering medium arising from the dipoles induced in the neighbouring particles under the action of the incident electric vector and derived an expression for the macroscopic depolarisation factor in terms of the concentration, for colloidal solutions containing small ellipsoidal particles. Gans' formula indicates

that this effect due to the molecular field could be neglected if the concentration of the colloidal solution is small and the refractive index of the dispersed phase is not far different from that of the dispersing medium.

The second and more important cause for the dependence of the macroscopic depolarisation on concentration is the existence of what is known as secondary scattering. Rousset (1936) emphasised the importance of considering the effect of secondary scattering in depolarisation measurements. Each individual colloidal particle under the influence of the intense primary scattering from all the particles which are illuminated by the incident beam becomes a luminous source and scatters radiation in all directions. This process is called secondary scattering. In the case of colloidal solutions of low scattering power the secondary scattering is quite negligible, whereas in the case of emulsions and protein solutions where the scattering is very intense the secondary scattering becomes comparable in intensity. The presence of secondary scattering in such solutions can be easily demonstrated by passing a narrow beam of light through the solution. If one observes the scattered track in the transverse direction one finds the whole volume of the solution luminescent. The scattered track is superposed on an intense background the intensity of which is maximum along the track and fades off as one moves away from it on either side. The depolarisation of this background illumination which is due to secondary scattering is different at different points in the scattering medium (Krishnan, 1937 and Lotmar, 1938), and is always greater than that of the scattered track (primary scattering). In such cases, therefore, the observed depolarisation is the resultant effect of the depolarisations of the primary scattering and of the secondary scattering in the region of observation. The secondary scattering in a small element of volume is proportional to the number of particles contained in it and also to the total intensity of primary scattering which itself is proportional to the concentration. The intensity of secondary scattering is therefore proportional to the square of the concentration. This explains why the dependence of depolarisation on concentration is very marked in emulsions which are so dilute that the molecular field does not come into play.

In the case of simple dipole oscillators the intensity of secondary scattering and the depolarisation arising thereform, can be calculated by applying Rousset's theory (Rousset, 1936). For the most general case of large ellipsoidal particles the theory of secondary scattering is rather complicated and has not been fully worked out. It was, however, thought desirable to investigate this problem experimentally and to suggest ways and means of eliminating the errors in depolarisation measurements arising from secondary scattering.

2. Some Experimental Observations

In order to eliminate the effect of secondary scattering one has to employ the proper optical arrangement for the measurement of the depolarisation. The correct way of measuring the depolarisation factor is to observe the two components of the scattered track that are separated by the double image prism, in the same background and then to compare their intensities. This method has been designated by Lotmar (1938) as the Cornu method. The defective method of measurement consists in inserting a diaphragm on the observation side, with a very small aperture and thus viewing a portion of the scattered track in a dark background. This method is called the diaphragm method. In this method one measures the combined depolarisation of the primary scattering and of the secondary scattering. Consequently abnormally high values are obtained for ρ_u, ρ_v, and ρ_h. The high value of ρ_h obtained by Mookerjee (1938) for phenol-water mixture and the abnormal values of ρ_u, ρ_v and ρ_h obtained by Rao and Muthuswamy (1936) for some emulsions are partly due to the defective method of measurement employed by these investigators. Lotmar (1938) has made a comparative study of the different methods of measuring the depolarisation factors and has shown that the diaphragm method and the photographic method of measurement always give enhanced values for the depolarisation factors.

As has already been pointed out the intensity of secondary scattering per unit volume of the solution depends on the intensity of primary scattering which in turn depends on the number of particles illuminated by the incident beam. Therefore, in order to reduce the effect of secondary scattering it is necessary to reduce the number of particles illuminated by the incident beam. This can be achieved without diluting the colloidal solution, by using a small cell as container and also a narrow pencil of light for measuring the depolarisation factors. In the ideal case one should illuminate a single colloidal particle and measure the depolarisation of the light scattered by it. But in practice this is not possible. Moreover the following observations will show that this is unnecessary. Table I gives the values of ρ_u, ρ_v and ρ_h obtained with a dilute solution of milk for different sizes of the illuminated volume. Since the vertical depth of track inside the medium was large in those cases which are marked with an asterisk the depolarisation measurements were made with a diaphragm on the observation side. The dimensions of the illuminated volume were varied by inserting a diaphragm with variable aperture in the path of the incident beam. A critical study of the figures given in Table I shows that as one reduces the volume of the milk solution, which is directly illuminated by the incident beam the depolarisation factors ρ_u, ρ_v and ρ_h decrease in value progressively. They attain steady values for

TABLE I

a in cm.	b in cm.	c in cm.	V in c.c.	ρ_u %	ρ_v %	ρ_h %
*4	1·5	1·5	9	19·45	6	35·3
*4	1	1	4	18·2	4·95	30·
*4	0·5	0·5	1	15·5	3·64	25·3
*1	1·5	1·5	2·25	17·3	4·8	43·8
*1	1	1	1	15·4	4·2	39·
*1	0·5	0·5	0·25	15·2	3·6	30·
4	0·25	0·25	0·25	8·5	0·28	3·9
4	0·15	0·15	0·09	6·9	0·2	3·4
1	0·25	0·25	0·0625	6·2	0·19	3·4
1	0·15	0·15	0·0225	7·3	0·19	3·1

[a = the length of the track inside the colloidal solution, *i.e.*, the width of the containing vessel. b and c are respectively the horizontal width and vertical depth of track inside the medium. V is the volume of the solution actually illuminated by the incident beam. $V = a \times b \times c$.]

V = about 0·1 c.c. Any further reduction in the volume of the solution illuminated does not appreciably affect the values of ρ_u, ρ_v and ρ_h showing thereby that the secondary scattering has little or no influence on the depolarisation factors. The microscopic depolarisation factors, *i.e.*, the depolarisation factors of the primary scattering are given by the limiting values of ρ_u, ρ_v and ρ_h obtained above.

3. Conclusion

From what has been said above it is clear that in order to eliminate the effect of secondary scattering on depolarisation measurements one has to take the following precautions:—(1) The incident beam of light should be as narrow as possible so as to reduce the volume of the colloidal solution illuminated to a minimum and (2) Cornu method should be employed for the measurement of the depolarisation factors.

The conclusions detailed above are also applicable to the case of liquid mixtures very near the critical solution temperature at which the scattering

becomes very intense. Table II gives the values of ρ_u, ρ_v and ρ_h obtained with a phenol-water mixture which was kept very near the critical solution temperature, for various values of the volume of the mixture illuminated. It is seen that even after eliminating the effect of secondary scattering by using a very narrow pencil of light for illumination and measuring the depolarisation factors by the Cornu method the value of ρ_h is definitely less than unity showing thereby that real clusters of molecules of size not small compared with the wave-length of the incident light exist in liquid mixtures in the neighbourhood of the critical solution temperature.

TABLE II

a in cm.	b in cm.	c in cm.	V in c.c.	ρ_u %	ρ_v %	ρ_h %
*.4	2	2	16	7·5	3·3	81·6
*.4	1·5	1·5	9	6·9	2·8	74·
*.4	1	1	4	4·5	1·4	53
*.4	0·5	0·5	1	2·0	0·37	53
·4	0·3	0·3	0·48	0·77	0·12	22
·4	0·2	0·2	0·16	0·62	0·09	16
·4	0·15	0·15	0·09	0·62	0·1	18
·4	0·07	0·07	0·02	0·6	0·09	16

In all the previous measurements of ρ_u, ρ_v and ρ_h in liquid mixtures, which were reported in the *Proceedings of the Indian Academy of Sciences* (Krishnan, 1935, 1937) the author had consistently used a very narrow beam of light (of cross-section about 2 mm./2 mm.) and hence the values of ρ_u, ρ_v and ρ_h were not vitiated by the existence of secondary scattering.

Mookerjee (1938) made some measurements of ρ_h in a phenol-water mixture by the diaphragm method employing a wide beam for illuminating the mixture. In such circumstances the secondary scattering will have a preponderating influence and abnormally high values would be obtained not only for ρ_h but also for ρ_u and ρ_v.

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4. Summary

It is pointed out that in emulsions and protein solutions in which scattering is very intense, the secondary scattering has a marked influ on the depolarisation factors. The values of ρ_u, ρ_v and ρ_h are in gen enhanced, due to the presence of secondary scattering in the solution. effect of secondary scattering on the depolarisation factors could be el nated by illuminating the colloidal solution by means of a very nai pencil of light and then measuring the depolarisation factors by the Cc method.

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