

ON NON-SPHERICAL NATURE OF COLLOIDAL PARTICLES IN RELATION TO THE FORMATION OF JELLY STRUCTURE.

BY SATYA PRAKASH, D.Sc.

(From the Department of Chemistry, University of Allahabad.)

Received June 6, 1936.

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

1. Introduction.

THE non-spherical colloidal particles are known to orient themselves under the action of mechanical, electrical and magnetic strains. It was observed by Maxwell¹ that a viscous liquid during the course of flow exhibits birefringence and the extensive work of Vörlander and Walter² showed that this sort of mechanical or stream double refraction is observed in a large number of liquids possessing only a moderate viscosity. Kundt³ for the first time studied the Maxwell effect in the case of gelatine which forms a lyophilic suspension. Similar suspensoids were also investigated for the effect by Bernatzki⁴ and Bjornstahl,⁵ Quincke,⁶ Tiere,⁷ Freundlich and co-workers and also Graffi⁸ obtained a positive stream double refraction with an iron oxide sol. Bjornstahl obtained negative double refraction with gold sols Zocher¹⁰ investigated a number of dyestuffs like benzopurpurin, cotton yellow and aniline blue, and the vanadium pentoxide sol has been extensively studied by Freundlich, Zocher and others.¹¹

The phenomenon of electric birefringence in the case of colloids has not been investigated much. Chaudier¹² made only a few observations

¹ Maxwell, *Pogg. Ann.*, 1874, 151, 151.

² *Z. Phys. Chem.*, 1925, 118, 1.

³ *Wied. Ann.*, 1881, 13, 110.

⁴ *J. d. russ. Phys. Chem. Ges.*, 1905, T. 37, 39.

⁵ *Diss. Upsala*, 1924, 139.

⁶ *Ann. Physik.*, 1904, (4) 15, 28.

⁷ *Atti. Lincei*, 1910, (5) 19, 470.

⁸ *Elster-Geitai-Festschrift*, 1915, 453.

⁹ *Atti. Lincei*, 1926, (6) 3, 28.

¹⁰ *Z. Phys. Chem.*, 1921, 98, 293; 1923, 105, 119.

¹¹ *Ibid.*, 1924, 114, 161.

¹² *Compt. Rend.*, 137, 248.

with some suspensions, but Diesselhorst, Freundlich and Leonardt¹³ found that with the exception of vanadium pentoxide sol, no other colloidal solution exhibited this behaviour. Bergholm and Bjornstahl¹⁴ have, however, shown that the double refraction is also induced by an electric field in gold and silver sols.

Majorana¹⁵ was the first to observe that a solution of "Fer Bravis" when subjected to a magnetic field exhibited birefringence and Schumass¹⁶ suggested that the phenomenon is due to the orientation of colloidal particles. Cotton and Moutan¹⁷ inferred on the basis of their extensive investigations that ferric oxide and other iron colloids consisted of aelotropic particles. Freundlich and collaborators¹⁸ observed magnetic birefringence with vanadium pentoxide sols whilst Bjornstahl¹⁹ found a positive magnetic birefringence with gold, silver, platinum, 10-chloro-phenanthrene-6-sulphonic acid and antimony sulphide sols, and negative birefringence with congo red, mechanically prepared sulphur sol and chlorophyll sols. Recently, Heller²⁰ has published a detailed account of his studies on ferric hydroxide sols.

The author is interested in the study of hydrophilic colloids from the view-point of jelly formation. Up till now, only a few hydrophilic colloids have been examined from this point of view. Many substances show in colloidal solution, a double refraction of the same sign as in the amorphous solid state. Umlauf²¹ has found that the sols of cherry gum and tragacanth have positive and those of collodion, gelatine and gum arabic negative double refraction under high mechanical stress. Ambronn²² found that the dry gel of cherry gum shows under tension and compression a double refraction like that of glass, but if the gel is allowed to swell in alcohol, then under a quick pressure it shows the double refraction of the same sign, but this gradually passes into one of a reversed sign.

In the present paper, some results on the mercuri-sulphosalicylic acid sols have been given with respect to the magnetic birefringence. This sol is known to give jellies under various conditions. Some other sols have

¹³ *Elster-Geitel Festschrift*, 1915, 476.

¹⁴ *Phys. Zeit.*, 1920, 21, 137.

¹⁵ *Atti. Linc.*, 1902, 11, I, 374, 463, 531; II, 90, 139.

¹⁶ *Ann. Physik.*, 1903, (4) 10, 658; 12, 186.

¹⁷ *Ann. chim. et Physique*, 1907, (8) 11, 145, 289.

¹⁸ *Loc. cit.*

¹⁹ *Phil. Mag.*, 1921, 42, 352.

²⁰ *Z. Physik. Chem.*, 1933, 166, 365; *Kolloid-Beihefte*, 1933, 39, 1.

²¹ *Wied. Ann.*, 1892, 45, 544.

²² *Wied. Ann.*, 1889, 38, 159.

also been examined. Besides the concentration effect of the sol and the influence of electrolytes, which the author has reported in one of his previous publications,²³ the influence of a number of peptising and sensitising substances has also been studied.

2. Experimental.

The experimental arrangement adopted for the present investigations was that described by Chinchalkar²⁴ for the study of solutions. A point-o-lite lamp of 1,000 c.p. was used as a source, the light from which condensed and collimated before passing through the polariser of which the principal direction of vibration was inclined at 45° to the horizontal. The sol to be investigated was placed in 33 cm. long tubes between the two poles of an electromagnet, the poles being 33 cm. wide. A long glass strip under pressure or strain was used as a compensator. The strip bent in its own plane would produce different layers above and below the neutral axis which will behave like a series of uniaxial positive and negative crystals with their axes parallel to the neutral axis. The beam of plane polarised light, after being allowed to pass through this compensator strip is examined with a crossed Nicol and a telescope attached to an Adam-Hilger micrometer eyepiece. A current of about 2 to 3 amperes was passed throughout the electromagnet producing a field of 4,400 to 6,500 gauss. Nitrobenzene along with the same strained compensator was used as a standard for comparison, and the readings have been recorded in the terms of micrometer scale.

Influence of the field strength.—The field strength of the electromagnet was varied by changing the amount of current. 1.8% mercuri-sulphosalicylic acid sol was used. Mercuri-sulphosalicylic acid was prepared by dissolving freshly precipitated and well washed mercuric oxide in a concentrated solution of 5-sulphosalicylic acid, till a white gel was obtained. The gel was dried over water-bath and the white powder thus obtained was kept in well stoppered bottle, because the substance appears to absorb moisture from the atmosphere. A weighed amount of the substance was allowed to soak in distilled water for about 20 minutes and then shaken and diluted to the required volume. The sol thus obtained is almost clear with a few particles of suspension which are removed by filtration. It has been observed that the magnetic birefringent values markedly depend upon the mode of the preparation of the colloidal solution whereby the suspensions of different dispersity are obtained, and therefore, in one set of experiments, one and the same sol was used.

²³ *J. Indian Chem. Soc.*, 1934, 11, 449.

²⁴ *Indian J. Phys.*, 1931, 6, 165.

TABLE I.

Field strength in Gauss	Micrometer readings with	
	Nitrobenzene	1.8% Colloid
4,200	34	34
5,300	75	51
7,400	102	67
21,000	Beyond scale	118

From these readings, it would be seen that the variation in the field strength produces comparatively less change in the colloid than in nitrobenzene.

Influence of ageing.—A 2% of the mercuri-sulphosalicylic acid sol was kept for a number of days and the values for the magnetic birefringence were determined from day to day. The relative birefringence is given in the following table with 100 as the value for nitrobenzene.

TABLE II.

Days	Relative birefringence
0	100
1	83.33
2	66.16
4	66
6	65.30

The freshly prepared sample of the colloidal suspension is more birefringent but the value markedly diminishes within the next two days, after which a constant is attained.

Influence of concentration.—Mercuri-sulphosalicylic acid sol of 2% concentration was prepared and then it was diluted to different concentrations and the relative values of magnetic birefringence were determined.

TABLE III.

Concentration in per cent.	Relative birefringence (nitrobenzene = 100)
2.0	92.6
1.0	58.4
0.5	25.9
0.4	18.1

These results show that the birefringence is roughly proportional to the concentration of the sol. During the first few dilutions, the anomaly is more marked.

The influence of electrolytes.—The influence of potassium chloride, potassium bromide, potassium nitrate and barium nitrate has been investigated in a foregoing publication.²⁵ Some of the results are summarised below. 10 c.c. of 2% sol were mixed with varying concentrations of electrolytes as given in the table and the total volume was made 20 c.c. by adding the

TABLE IV.

Amount of electro- lyte added in c.c.	Relative birefringence with			
	N/10 KCl	N/35 KBr	N/20 KNO ₃	0.5% Ba(NO ₃) ₂
0.0 ..	58.4	43.5	43.5	43.5
0.5 ..	40.6	38
1.0 ..	29.6	32.4	53.7	43.5
2.0	44.3	65.7	44.4
3.0 ..	19.4	58.3	93.5	46.3
4.0	122	..
5.0	75.9
10.0	162.0

²⁵ *Loc. cit.*

The sugar is well known as an efficient peptiser of sols, and from the above results it will be seen that during the course of its action on the surface, it either disintegrates the anisotropic particles or in some other way makes them less non-spherical. The optical activity of sugar solutions causes difficulty in studying the influence of higher concentrations of this substance as a peptiser.

Influence of glycerol.—Experiments similar to those described above have been done with glycerol. Varying amounts of the substance have been added to 2% mercuri-sulphosalicylic acid sol, and the total volume was always made 20 c.c. The amount of sol taken was always 10 c.c. 2 amperes current was used.

TABLE VI.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	130	100
10 c.c. sol + 10 c.c. water	61	47
10 c.c. sol + 4 c.c. glycerol + 6 c.c. H ₂ O	53	41
10 c.c. sol + 6 c.c. glycerol + 4 c.c. H ₂ O	28	21
10 c.c. sol + 10 c.c. glycerol	22	17

The presence of glycerol along with a colloidal suspension brings about the dehydration of the hydrated particles, and also causes peptisation by forming a layer at the surface of the particle and our values show that it disintegrates the particles to a much smaller size and the particles thus obtained are more spherical than the former particles in the absence of glycerol.

Influence of urea.—Similar experiments with urea are described below. Varying amounts of 10% urea solution were added to 10 c.c. of 2% mercuri-sulphosalicylic acid sol and the total volume was made 20 c.c. 2½ amperes current was used.

TABLE VII.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	50	100
10 c.c. sol + 10 c.c. H ₂ O	23	46
10 c.c. sol + 5 c.c. urea + 5 c.c. H ₂ O	23	46
10 c.c. sol + 10 c.c. urea	24	48

The influence of urea does not appear to be marked on the magnetic birefringence of the sol. Urea is generally a well-known sensitiser. It appears that perhaps the results will be more marked by taking larger amounts of urea and the values for birefringence would slightly increase in its presence of which a slight tendency appears in the above table.

Influence of ethyl alcohol.—10 c.c. of the mercuri-sulphosalicylic acid sol were mixed with different concentrations of ethyl alcohol and the total volume was made 20 c.c. by adding water to it. $2\frac{1}{2}$ amperes current was used.

TABLE VIII.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	102	100
10 c.c. sol + 10 c.c. water	39.1	38.3
10 c.c. sol + 3 c.c. alcohol + 7 c.c. H_2O	39	38.3
10 c.c. sol + 5 c.c. alcohol + 5 c.c. H_2O	39	38.3
10 c.c. sol + 8 c.c. alcohol + 2 c.c. H_2O	37	36.2
10 c.c. sol + 10 c.c. alcohol	22	21.6

Small concentrations of alcohol appear to be without influence but the addition of a larger amount of alcohol beyond a certain limit causes at once a marked dehydration and disintegration of the colloidal particles with the result that the birefringent value falls down.

Influence of acetone.—The results exactly similar to those by alcohol have been obtained with acetone. To a 10% sol, varying amounts of acetone have been added, and the total volume was made upto 10 c.c. as before. $2\frac{1}{2}$ amperes current was used.

TABLE IX.

System	Micrometer shifts	Relative birefringence
Nitrobenzene	90	100
10 c.c. sol + 10 c.c. water	33	36.6
10 c.c. sol + 4 c.c. acetone + 6 c.c. water	34	37.7
10 c.c. sol + 6 c.c. acetone + 4 c.c. water	17	19
10 c.c. sol + 10 c.c. acetone	0	0

The results are interesting from the point of view that the mercuri-sulphosalicylic acid sol can be rendered non-birefringent by adding sufficient amount of acetone.

Fresh mercuri-sulphosalicylic acid.—In all the above experiments, the mercuri-sulphosalicylic acid used was the one obtained by dissolving mercuric oxide in sulphosalicylic acid, and drying out the gel. This dried powder formed a reversible sol when again dispersed along with water, and the colloidal solution thus formed was found to be magnetically birefringent. It was interesting to see whether the non-dried freshly prepared colloidal solution was also birefringent. A 5% suspension of well washed mercuric oxide was prepared in water and it was mixed with a 50% solution of 5-sulphosalicylic acid. The magnetic birefringence of the sulphosalicylic acid and also this freshly formed colloidal solution was determined. $2\frac{1}{2}$ amperes current was used in the magnet to give a field of 5,200 gauss.

TABLE X.

System				Micrometer shifts
Nitrobenzene	83
5-sulphosalicylic acid, 50% solution		15
20 c.c. of acid + 8 c.c. of HgO suspension	15
20 c.c. of acid + 12 c.c. of HgO suspension	16.5
The above suspension after 2 hours	16

These results show, that mercuri-sulphosalicylic acid sol, freshly prepared does not exhibit more birefringence than the sulphosalicylic acid itself, which being an aromatic compound would certainly exhibit some birefringence. This is only the reversible dried gel which is so highly birefringent. In the course of time, it has been shown by the author, that a concentrated freshly prepared sol gives a jelly, but slight separation of the solid phase causes inconvenience in measuring the magnetic birefringence at different stages at various times.

The non-birefringent jelly-forming systems.—It has been sometimes led to believe the hydration tendency is associated with the non-spherical nature of particles, and perhaps these non-spherical particles help in the formation of chains so essential for a jelly structure by providing a number of corners. The vanadium pentoxide sol exhibits high magnetic birefringence and is

also known to give excellent jellies. Mercuri-sulphosalicylic acid and also some dyestuffs show magnetic birefringence and give jellies. The following jelly-forming systems were tried for magnetic birefringence :

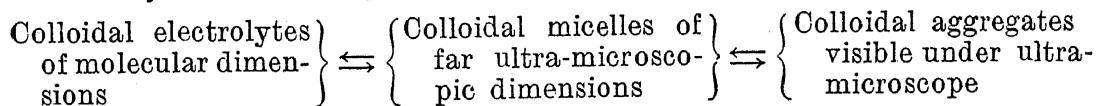
(1) Thorium phosphate and thorium molybdate systems obtained by adding potassium phosphate or molybdate solutions to thorium nitrate solution as described in previous papers. The optically clear sols did not exhibit any marked magnetic birefringence even with a very high magnetic field.

(2) Ferric arsenate and ferric phosphate sols obtained by adding potassium arsenate or potassium phosphate to ferric chloride in excess and dialysing the sols so as to give jellies. These sols when diluted did not exhibit any marked birefringence.

(3) Lithium urate sol freshly prepared by adding lithium carbonate to uric acid suspended in water. No birefringence was observed. The sol precipitates out during the course of some time and just before this, its particles show orientation in the magnetic field.

3. Discussion.

The exhibition of magnetic double refraction by colloidal particles is due to their non-spherical nature, or in other words, their asymmetry. According to Langevin's theory, the magnetic and optical anisotropies are both combined to give this effect. What is true for the case of molecules may be also true for the colloidal electrolytes, colloidal micelles and even bigger aggregates of colloids. In a heterogeneous colloidal system, all these states may simultaneously exist in equilibrium :



As the ageing of a sol proceeds, the tendency of the system is to transform itself to the colloidal aggregate system. It is very likely that the colloids of molecular dimensions may be isotropic but as the system tends towards the formation of bigger colloidal aggregates, the anisotropy might markedly develop. The growth of an aggregate from a colloidal bath is not just the same as the growth of a crystal from a saturated system, and therefore, in many cases, anisotropic aggregates have been obtained from the suspensions containing isotropic particles. Only the very aged ferric hydroxide colloids are anisotropic. A freshly prepared sol does not exhibit magnetic birefringence. The fresh vanadium pentoxide sol is also non-birefringent. In the case of mercuri-sulphosalicylic acid sol also, as is seen from the results recorded in this paper, the freshly formed system by dissolving mercuric oxide in sulphosalicylic acid is not birefringent. It is only the reversible sol obtained

by dispersing the dried powder which exhibits the anisotropy to such an extent. From all these observations, it is clear that in most of these cases, the sols do not possess their intrinsic molecular anisotropy ; it is only at some later stage that the isotropic particles assume rod or disc shapes and show rod or disc double refraction.

It appears to be very likely that the hydrophobic sols exhibit more anisotropy than the hydrated ones, as if the water layers around an asymmetric particle tend to smoothen the corners, and give more or less a symmetric spherical shape. Two sorts of hydration may be distinguished in this way : (i) Firstly, those hydrated viscous sols which show marked stream double refraction and also the electrical and magnetic birefringence,—these contain anisotropic particles of almost lyophobic nature, their hydration is essentially structural and not surficial, and they show mostly the structural viscosity. The structurally imbibed water is incapable of transforming the micellar anisotropy to a symmetrical spherical shape. (ii) Secondly, those lyophilic suspensions which do not show marked electric, stream or magnetic birefringence. In their case the surficially imbibed water layers have given rise to an isotropic spherical shape, they exhibit true viscosities. The water layers form the actual portion of the colloidal micelles.

The ageing effect on colloids may also be explained on this basis. It has been shown that ageing brings about the development of an anisotropic structure. This may be due to two reasons. In the case of hydrophilic substances, the surface energy decreases as the ageing proceeds, and some of the surficially adsorbed water is given out. This reverse process again makes the spherical particle a non-spherical one, and then on ageing, the system becomes more birefringent. In some cases, the agglomeration tendency of the particles also increases, and finer particles go to make bigger aggregates. In such cases also, it is likely that non-spherical particles may grow out from the spherical ones, as the aggregation phenomenon is not necessarily symmetrical. On account of these two reasons, we find that the hydrous ferric oxide and vanadium pentoxide sols show birefringence when they are aged.

Most of the jelly-forming sols, at least unless they are markedly aged, do not show birefringence. We also know that on ageing, the hydration tendency and hence the jelly-forming tendency gradually decreases. Thus, it appears that the non-spherical nature of particles cannot be associated with the jelly formation. In fact, when a water layer is allowed to envelop round a particle the surface forces are so symmetrical as to give a spherical covering. The anisotropic particle also thus becomes a spherical one.

In case of mercuri-sulphosalicylic acid, the sol has been obtained by a reverse way, and therefore, the aggregates are bigger in a freshly formed sol; and as the time proceeds, by the bombardment of the solvent over the solute, the aggregates become smaller and smaller, and during the course of disintegration they become less anisotropic also. This is why, the aged sol shows much less magnetic birefringence than the fresh one.

The influence of organic substances like sugar, glycerine, urea, alcohol and acetone throw some important light on the phenomenon of peptisation and sensitisation. In most of the cases, it has been found that the values for birefringence decrease. The peptising influence of organic substances may be due to the following reasons²⁷: (i) The aggregation tendency of the particles markedly diminish in their presence as they form an envelop round the particles. (ii) By forming a double layer similar to Helmholtz double layer, the particles are protected from the action of oppositely charged ions. (iii) By actually changing the dielectric, they modify the electrical properties of the system to a marked extent. In some cases, it might also happen that the organic substances may bring about the disintegration of the colloidal aggregates. At least in the case of sensitizers, this effect is more likely to be marked. The disintegration may be either due to the actual bombardment of the organic solvent against the colloidal aggregates, or it may be spontaneous when the dielectric has been changed. In case of peptisers like glycerine or sugar, the decrease in the birefringence may be due to the formation of an isotropic layer of the substances round the particles. In the case of alcohol, acetone, etc., it may be due to both the reasons but mainly due to the disintegrations to smaller isotropic particles. A slight decrease in the value may be simply due to the change in dielectric constant of the dispersion medium, and the particles experience difficulty in orienting themselves in the electromagnetic field. In fact, in case of colloids, all these factors go to contribute something,—sometimes in the same direction and sometimes oppositely.

The author wishes to express his indebtedness to Sir C. V. Raman and Dr. K. S. Krishnan for providing him the facilities to carry on the experimental work in the laboratory of the Indian Association for the Cultivation of Science, Calcutta, and to Dr. S. W. Chinchalkar for help in the experimental technique.

Abstract.

The magnetic birefringence of mercuri-sulphosalicylic acid sol has been studied in detail. The fresh sol directly obtained by dissolving mercuric

²⁷ Prakash, *Z. anorg. Chem.*, 1931, 201, 301.

oxide in sulphosalicylic acid is non-birefringent, but the reversible dried powder when dispersed in water gives birefringent sol. The birefringence increases as the magnetic field increases but not in the same proportion as in the case of nitrobenzene. The birefringence is also almost directly proportional to the concentration. In presence of dissolving ions, as chloride, the birefringence markedly diminishes, while in presence of nitrate ions or barium ions, it increases. The influence of peptisers and sensitisers as sugar, glycerine, ethyl alcohol, acetone and urea has also been investigated. With the exception of urea which does not produce any marked effect, in all other cases, the birefringence values decrease. With alcohol and acetone the fall is much marked. These results have been discussed and it has been shown that in their presence the anisotropy of the particles is decreased on account of disintegration of bigger aggregates to isotropic smaller ones and also due to the formation of spherical micelles by adsorbing layers of organic solutions round the originally anisotropic particles.

It has been shown that many of the well-known jelly-forming sols do not exhibit magnetic birefringence, and hence, it is not necessary to have non-spherical particles essential for jelly formation. On the contrary, it is also likely that the non-spherical lyophobic particles also become isotropic by becoming hydrated under favourable conditions.