STUDY OF THE OPTICAL PROPERTIES OF GELS

Part I. Thorium Molybdate Gels

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TYNDALL[1] seems to have been the first to take note of the blue colour and the polarised character of the light scattered by gold sol. Lord Rayleigh[2] developed the theory of the scattering of light by colloidal solutions and his equation is of considerable importance for the study of colloidal particles. Mardles[3] has studied the changes with temperature of the Tyndall-number (*i.e.*, the ratio of the intensity of the light scattered by sols and gels to that of some standard) of sols and gels of cellulose acetate in benzyl alcohol during the reversible sol-gel transformation by visual photometry. His results show that the Tyndall-number depends on the mechanical treatment and the rate of gelation. Further it varies with temperature and the concentration of cellulose acetate. The Tyndall-number—temperature curves reveal the existence of a maximum which decreases with the rise of temperature.

Kraemer and co-workers[4] made a detailed quantitative study of the Tyndall intensity of gelatin solutions and found that the intensity of scattered light increased enormously within a narrow range of pH near the isoelectric point. The influence of pH on the intensity of the light scattered by casein solutions has been studied by Holweda[5].

Krishnamurthi[6] has measured the intensity and depolarisation of the scattered light during the sol-gel transition of agar-agar and gelatin, using unpolarised incident light. His results point to the existence of a maximum gelation temperature. Further he finds that there is practically no change in Tyndall-number with time at or above 40° C., but at or below 35° C., it increases with time until a constant value is reached, and that the particles in the gel state are bigger and/or greater than in the sol state. It has been remarked in his paper that the variations in the intensity of scattered light are due to changes in the particle size and number alone, while the changes in the depolarisation factors are due to changes in the shape of the particles. He has not made any calculations from the observed total intensity of scattering, the scattering due to anisotropy, size and number separately.

D. S. Subba Ramiah[7] and R. S. Krishnan[8] have shown that in order to obtain information regarding the size and shape of the particles in the colloidal state it is not sufficient to measure the intensity and depolarisation of the scattered light, using unpolarised light alone. They suggest that it is necessary to obtain the values of depolarisation factors for the light scattered transversely by a colloidal system with incident light unpolarised, (ρ_u) vertically polarised (ρ_v), and horizontally polarised (ρ_h).

Accordingly D. S. Subba Ramiah[7] has measured the values of ρ_v, ρ_h, and ρ_u for (1) sulphur suspensions in water, (2) castor oil emulsions in water, (3) arsenic sulphide sol in water, and (4) casein solutions in water, at various pH values, and has shown how the inter-comparison of the values of these three quantities furnishes more information regarding the size and anisotropy of shape and/or structure of the particles than the measurement of only one of the three quantities.

The application of the measurements of ρ_v, ρ_h and ρ_u has been extended by K. Subba Ramiah[9] to the study of protein solutions. He has also studied the changes in intensity and ρ_v, ρ_h and ρ_u during the setting of silicic acid, stearic acid and sodium stearate gels.[10] He finds that in the case of silicic acid gels (1) there is a continuous increase in the micellar size during gelation and this increase continues even after the gel has set, though at a small rate; (2) the micelles have almost complete spherical symmetry at a stage prior to gel-formation; and (3) in the case of rapidly setting systems the micelles show greater departure from sphericity. As judged from the high polarisation of the transversely scattered light when the electric vector of the incident polarised light is along the direction of propagation of the incident light, the particles in these gels have a large size even at the earliest stage of formation. This result makes the correlation of the scattering data obtained by him with the particle constants, in the course of gel-formation, very complicated.

Recently Prasad and Gogate[11] have investigated the opacity changes during the setting of inorganic gels by an improved apparatus designed by them. Desai and Guruswamy[12] have continued this investigation to more inorganic gels using Prasad and Gogate's apparatus. It has been pointed out by the above-mentioned authors that the changes in number, size, distribution, arrangement, etc., of the micelles of the gel, contribute to the observed changes in opacity. In the present investigation, the intensity and depolarisation factors (ρ_v, ρ_h and ρ_u) of the light scattered transversely by thorium molybdate gels have been studied and an attempt has been made to separate the scattering due to anisotropy and size.

Experimental

1. *Intensity measurements*

The intensity of light scattered transversely by the gel-forming mixture was studied by allowing the scattered light to fall on a photocell. The current from the photocell was amplified by a valve bridge circuit and measured by a suitably shunted Moll galvanometer. The circuit employed for amplification is essentially the same as that developed by Ananthakrishnan.[13] The principle of working consists in bringing the bridge to balance with the photocell in the dark. When light falls on the photocell, the photoelectric current flowing across the grid leak produces a small change in the grid potential of one valve and the balance is disturbed. The resultant current is a measure of the light falling on the photocell.

Testing the linearity of the photocell unit.—To test the linearity of the photocell unit the following method was employed. The photocell was completely covered with a black paper and a slit (8 × 8 mm.) was cut on the paper in front of the vane of the photocell. A Hefner's standard lamp was placed at different distances (d) from the photocell and the corresponding deflections of the galvanometer (D) were noted. Care was taken to place the lamp such that the slit on the photocell and the flame were in the horizontal plane and the rays falling on the photocell were normal to its surface. The results obtained are shown in Table I. The constant value of $D \times d^2$ excepting at higher intensities shows that the response by the photocell unit is linear within the range of intensity of scattering investigated. Even the deviations from linearity at higher intensities are not great and a correction has been applied to the deflections obtained at these intensities from the $D—1/d^2$ graph.

TABLE I

Distance of the lamp from the photocell (d)	Deflections of the galvanometer (D)	$D \times d^2$
cm.	cm.	
100	4·3	$4 \cdot 30 \times 10^4$
90	5·5	$4 \cdot 45 \times 10^4$
80	6·9	$4 \cdot 42 \times 10^4$
70	8·7	$4 \cdot 26 \times 10^4$
60	12·0	$4 \cdot 32 \times 10^4$
50	16·7	$4 \cdot 17 \times 10^4$
40	23·6	$3 \cdot 78 \times 10^4$

The optical arrangement.—Light from a pointolite lamp A (Fig. 1) was condensed on the gel-forming mixture contained in a rectangular glass cell C (4″ × 2·5″ × 0·9″) by means of a long focal length lens L ($f = 30$ cm.).

the intensity of scattering is large and hence the accuracy of measurements is greater.

Convergence error.—There has been considerable divergence of views regarding the existence of this error. The convergence error is of very great importance only when we are dealing with depolarisation factors which are relatively small as are met with in gases (*cf.* Ananthakrishnan[15]).

3. *Preparation of gels*

Thorium molybdate gels were prepared by the method of Prakash and Dhar,[16] and the following solutions were employed:—(1) 6% solution of thorium nitrate Th (NO_3) $4{\cdot}4_4H_2O$. (A); (2) 10% solution of potassium molybdate (B). It was found that if the two solutions were mixed a precipitate is obtained which disappears in a few seconds and results in an opaque mixture which clears up during setting and after some time sets to a nearly transparent gel.

In order to prepare the gels different volumes of (A) and (B) were taken in two different test-tubes and the volume in each of the test-tubes was made to 25 c.c. by the addition of distilled water; thus the total volume of the gel-forming mixture was 50 c.c. The two solutions were mixed and the changes in the intensity and depolarisation factors with time were measured.

The course of gelation is greatly modified by the presence of non-electrolytes (*cf.* Prasad, Mehta and Desai).[17] Hence the influence of the non-electrolytes on gelation was also investigated.

4. *Results*

The results obtained with gels prepared by mixing different amounts of A and B are shown in Tables II to VIII, in which T represents the time in minutes. The amount of thorium molybdate in the gel has been calculated from the equation:

$$\mathrm{Th}\,(NO_3)_4 + 2K_2MoO_4 \rightarrow \mathrm{Th}\,(MoO_4)_2 + 4\,KNO_3$$

and is given on the top of the tables. The amount of thorium nitrate remaining unreacted is shown as excess of thorium nitrate in the tables.

TABLE II

A = 25 c.c. = 1·21 g. of thorium nitrate

B = 5 c.c. = 0·5 g. of potassium molybdate

The amount of thorium molybdate formed = 0·58 g.

The excess of thorium nitrate present = 0·71 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	An opaque sol. The scattered light is red in colour ..	..	..	..	26·5
2		..	..	..	25·0
3	Opacity decreases	84·0	..	84·0	23·5
4		..	..	..	22·0
5		..	89	..	17·2
6	Scattered light is white in colour	76·0	..	..	12·4
7		..	..	78·0	9·5
8		66·0	..	..	7·3
10		32·0	73	63·0	6·4
12		..	..	..	6·0
15	Viscous	28·3	..	52·8	5·9
20	Nearly set	25·9	67	52·8	5·9
30	Set to a gel	25·9	67	52·8	5·9

TABLE III

A = 25 c.c. = 1·21 g. of thorium nitrate

B = 4 c.c. = 0·4 g. of potassium molybdate

The amount of thorium molybdate formed = 0·52 g.

The excess of thorium nitrate present = 0·76 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1		..	..	..	21·5
2	An opaque sol	74·0	..	..	18·9
3		..	..	..	15·6
4		..	..	73·0	9·8
5		..	89	..	4·8
6		..	..	..	3·6
7		33·3	..	49·0	3·4
8		..	..	..	3·2
10		18·9	78	33·3	2·9
15		12·6	..	..	2·8
20		..	..	29·5	2·7
30	Very viscous	11·9	..	29·5	2·6
45	Set to a gel	11·9	78	29·5	2·6

TABLE IV

A = 25 c.c. = 1·21 g. of thorium nitrate
B = 3 c.c. = 0·3 g. of potassium molybdate
The amount of thorium molybdate formed = 0·35 g.
The excess of thorium nitrate present = 0·91 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	Opaque sol	..	..	..	17·3
2		..	..	..	14·4
3		66·0	..	..	7·4
4		..	..	30·7	2·9
5		23·8	90	..	2·2
6		..	..	18·0	2·0
8		10·6	..	..	1·9
10		8·2	..	16·3	1·8
15		7·2	80	14·7	1·8
40		7·2	80	14·0	1·8
90	Set to a gel	7·2	70	14·0	1·8

TABLE V

A = 20 c.c. = 0·91 g. of thorium nitrate
B = 3 c.c. = 0·3 g. of potassium molybdate
The amount of thorium molybdate formed = 0·35 g.
The excess of thorium nitrate present = 0·61 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	An opaque sol	..	..	..	17·7
2		..	..	..	15·5
3		68·0	..	..	14·5
4		..	..	84·0	13·0
5		61·0	87	..	10·8
6		..	..	..	7·0
7		40·6	..	76·0	3·3
8		..	..	..	2·0
10		19·6	79	49·0	1·8
15		10·6	..	20·8	1·8
20	Viscous	..	..	20·8	1·8
90		9·9	67	20·8	1·8
The gel sets in about three hours ..		9·9	67	20·8	1·8

TABLE VI

A = 25 c.c. = 1·21 g. of thorium nitrate

B = 5 c.c. = 0·5 g. of potassium molybdate

HCl (1N) = 1·0 c.c.

The amount of thorium molybdate formed (assuming that HCl exercises no solvent action) = 0·58 g.

The excess of thorium nitrate present = 0·71 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	An opaque sol	..	..	..	17·4
2		..	..	..	9·9
3	Opacity decreases	51·0	..	68·0	6·7
4		30·7	..	58·9	5·6
5		..	85	..	5·2
6		23·8	..	49·0	4·7
8		..	..	..	4·4
10		20·8	..	45·5	4·2
15	Set to a gel	19·8	..	40·6	4·0
20		19·8	..	37·6	3·5
30		19·8	70	37·6	3·5

TABLE VII

A = 25 c.c. = 1·21 g. of thorium nitrate

B = 5 c.c. = 0·5 g. of potassium molybdate

HCl (1 N) = 3·0 c.c.

The amount of thorium molybdate formed (assuming that HCl exercises no solvent action) = 0·58 g.

The excess of thorium nitrate present = 0·71 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	An opaque sol. The opacity decreases rapidly ..	..	..	..	1·7
3		23·8	..	45·5	0·9
5		12·5	85	30·7	0·8
7	Set to a gel	9·9	..	23·8	..
10		9·3	..	21·8	..
15		9·3	..	20·8	0·7
30		9·3	78	20·8	0·7

TABLE VIII

A = 25 c.c. = 1·21 g. of thorium nitrate
B = 3 c.c. = 0·3 g. of potassium molybdate
Ethyl alcohol = 10·0 c.c.
The amount of thorium molybdate formed = 0·35 g.
The excess of thorium nitrate present = 0·91 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	Opaque sol	..	..	..	14·8
2	Opacity decreases	..	..	..	13·0
3		51·0	..	49·0	10·2
4		..	..	..	6·6
5		18·9	89	29·5	3·7
7		..	..	..	2·4
8		13·3	..	13·3	1·9
10		12·5	..	11·2	1·5
20	The sol is viscous	11·9	..	9·9	1·4
45	Nearly set	11·9	70	9·9	1·4
90	Set to a gel	11·9	..	9·9	1·4

Discussion of the Results

1. *Changes of the intensity and the depolarisation factors during setting*

It will be seen from Tables II to VIII that the values of ρ_v are very high and they decrease during setting and then reach a constant value ; in some cases these values are very small (*cf.* Table IV). Any deviation from zero value of ρ_v shows that the particles are anisotropic. Since the values of ρ_v are very high it shows that the particles are highly anisotropic in shape or/and structure. During gel-formation the anisotropy in shape or/and structure decreases and the gel becomes less and less anisotropic.

The values of ρ_h are also very high. They decrease during gelation and reach a constant value when the gel sets. The high value of ρ_h indicates that the particles are not very large in comparison with the wavelength of light and a decrease in its value shows that the particles grow in size during gel-formation. Since the values of ρ_h are very high they could not be accurately determined by Cornu's method.

The values of ρ_u also decrease during the formation of gels. ρ_u is related to ρ_v and ρ_h by the relation $\rho_u = (1 + \frac{1}{\rho_h})/(1 + \frac{1}{\rho_v})$. (R. S. Krishnan.[8]) The decrease in the value of ρ_u is due to the decrease in the value of ρ_v.

The intensity of scattered light decreases rapidly during gel-formation, and reaches a constant value after some time. It is interesting to note that the values of I and the depolarisation factors reach a constant value much before the gels set. For example, in the case of the gel prepared by mixing 20 c.c. of thorium nitrate and 3 c.c. of potassium molybdate (Table V) the values of I and depolarisation factors reach a constant value in about 20 minutes, whereas the gel sets in about three hours.

2. *The effect of different constituents of the gel-forming mixture on the rate of change of intensity and on the values of ρ_v*

The effect of thorium nitrate on the formation of the gel can be seen from Tables II, III and IV. Increasing amounts of thorium nitrate increase the rate of change of the intensity of scattering and make the gel more transparent and less anisotropic. The time of setting is also increased by the addition of increasing amounts of thorium nitrate to the gel-forming mixture. Increasing amounts of HCl make the gel more transparent and less anisotropic, cause it to set earlier, and increase the rate of change of intensity of scattered light (Tables II, VI and VII). The gel formed in the presence of ethyl alcohol is more transparent and anisotropic (*cf.* Tables IV and VIII).

3. *Size of the particles*

The very high values of ρ_v in the initial stages of gel-formation suggest that at this stage the particles are highly anisotropic. Therefore an attempt was made to separate the density and orientation scatterings and to study their changes during gel-formation. In order to do that it is essential to get an idea of the magnitude of the size of the gel-particles.

The high values of ρ_h indicate that the particles are not very large compared to the wavelength of light. An approximate idea of the magnitude of the size of the particles was obtained by comparing the scatterings in the forward and backward directions. The intensity of light scattered at 45° and 135° to the incident beam by the least anisotropic thorium molybdate gel (*cf.* Table IV, $\rho_v = 7 \cdot 2$) was compared. The following apparatus was employed for this purpose. The gel was prepared in a cylinder of diameter 2·5 cm. A thin beam of light was admitted through the centre of the cylinder. The whole cylinder was blackened excepting for 4 slits, two for the incident light to pass through, one at 45° and another 135° to the track of light. The slits at 45° and 135° were equal in area (8 × 4 mm.). The cylinder was kept in a small rectangular tank containing water to avoid errors due to the spherical nature of the cylinder. The tank was suitably blackened so that the track at 45° and 135° could be clearly observed without parasitic light. There was not much deviation of the track. The other experimental details were the same as those employed for the measurement of the intensity of light scattered transversely. Visual measurements showed that there was no great difference in the intensity of the two scattered beams. A quantitative measurement of the intensity was then made by keeping the photocell unit at equal distances from the two slits. All parasitic lights were cut off by suitable screening. A number of readings were taken and it was found that the ratio of the intensities of scattering at 135° and at 45° was not greater than 1·5.

If the scattering particles are very small compared with the wavelength of light, the scattered energy is distributed symmetrically around the scattering particle, and it is represented by Rayleigh's formula. Shoulejkin[18] has calculated the intensity of scattered light for particles of size comparable with the wavelength of light and his results show that if the diameter of the particle exceeds 1/3 λ, the distribution of the scattered light is no longer symmetrical. At $2\rho \simeq \lambda/3$, one notices a definite asymmetry of scattering, the brightness of the scattered light in the direction of the incident rays being 2·5 times greater than in the opposite direction (the relative value of m', that is, relative refractive index of the particles to that of the medium, used for calculation was 1·32).

Blumer[19] has studied theoretically the intensity of scattered light at different angles to the incident light, by particles of different sizes having different relative refractive indices. In the following table (Table IX) is given the intensities of scattered light ($i_1 + i_2$) at 45° and 135° by particles of different sizes. These values have been taken from his paper,[19] for the relative refractive index of the particles and the medium equal to 1·25, which probably corresponds to the case of gels under investigation. The values of I_{135}/I_{45} are given in the last column of Table IX.

TABLE IX

$\alpha = \frac{2\pi p}{\lambda}$	$(i_1 + i_2)$ for 45° (I_1)	$(i_1 + i_2)$ for 135° (I_2)	I_2/I_1
0·01	$\cdot 3769 \times 10^{-13}$	$\cdot 3769 \times 10^{-13}$	1·00
0·1	$\cdot 3730 \times 10^{-7}$	$\cdot 3749 \times 10^{-7}$	1·00
0·2	$\cdot 2400 \times 10^{-5}$	$\cdot 2400 \times 10^{-5}$	1·00
0·3	$\cdot 2727 \times 10^{-4}$	$\cdot 2727 \times 10^{-4}$	1·00
0·5	$\cdot 6460 \times 10^{-3}$	$\cdot 9010 \times 10^{-3}$	1·39
0·6	$\cdot 1900 \times 10^{-2}$	$\cdot 2704 \times 10^{-2}$	1·42
1·0	·022	·1177	5·10
1·2	·0373	·2763	7·4
2·0	·0100	1·9874	198·00

It will be seen from the above table that the value of the intensity at 135°/the intensity at 45° is one for the particles whose value of α does not exceed 0·3, that is, the diameter of the particles is not greater than about $\cdot 3/\pi\ \lambda = 0\cdot 1\lambda$. If the diameter of the particles is greater than this, a definite asymmetry of scattering sets in, and I_{135} becomes many times greater than I_{45}. The values of I_{135}/I_{45} obtained in this experiment was not greater than 1·5. It has to be remembered that no special precautions were taken to remove dust particles, etc., from the different solutions used and so this may contribute to more backward scattering. Even if the value of I_{135}/I_{45} for this gel is taken as 1·5, it can be seen from Table IX that the diameter of the particles is much less than $\cdot 8/\pi\ \lambda$, that is, about $\frac{1}{4}\ \lambda$. The gel particles are highly hydrated and therefore the actual size of the particles may be greater than $\frac{1}{4}\ \lambda$. But this increase in size cannot be determined by the above method as hydration cannot produce any direct change in the intensity of scattered light because there is no difference in refractive index between the water that is attached to the micelles and the "free" water.

Thus it will appear both from the values of ρ_h and from the comparison of intensities in the backward and forward directions that the size of the particles even after the gel has set is less than the wavelength of light.

Another evidence for the smallness of the size of the particles is obtained from the microscopic examination of the gel. The smallest particles that can be seen through a microscope[22] at its best magnification have a diameter of about I/2000 mm. or 5000×10^{-8} cm. Since the microscopic examination does not reveal the identity of individual gel particles, this can be taken as a further evidence to show that the diameter of the gel particles is less than the wavelength of light.

For the purpose of discussion of results it has been presumed that all the gel particles are of the same size and shape.

4. *Separation of the density scattering and orientation scattering*

The total intensity of light scattered by a transparent "homogeneous" medium consisting of optically anisotropic particles whose linear dimensions are small in comparison with the wavelength of light is the sum of two types of scattering, namely, (*i*) density scattering I_D and (*ii*) Orientation or anisotropy scattering I_A.

The density scattering I_D is due to local inhomogeneities that are produced in the medium by the thermal agitation of the particles in it. It will be greater, the larger the compressibility of the medium and can therefore assume very large values in the neighbourhood of the critical temperature where the compressibility becomes very large.

The anisotropy or orientation scattering I_A arises from the fact that the moment induced by the incident electric vector in an anisotropic particle is not in general parallel to the direction of the electric vector. Detailed calculations have been made by Cabannes[20] and Ramanathan[21] on the intensity of scattering due to orientation of anisotropic particles in homogeneous transparent media and they find that the effect of fluctuations in orientation would be to increase the total scattering to $\frac{6+6\rho}{6-7\rho}$ times the density scattering alone. In this expression ρ denotes the ratio of the weak component to the strong component in the partially polarized light that would be scattered in a direction transverse to the direction of propagation of the incident light in the medium, the incident light being unpolarised.

The foregoing discussions refer to a stationary medium at constant temperature. In the case of gels the number, size and shape of the particles vary with time during the process of gel-formation. Therefore a detailed study of the orientation and density scattering at various stages of gel-formation will enable one to follow closely the progressive changes in the number, size and shape of the particles.

From the measurement of the total intensity and depolarisation factor of the scattered light using unpolarised incident light, the component of scattering due to fluctuations in density and that due to fluctuations in the orientation of the scattering particles can be separately calculated as follows:

Let I be the total scattering observed. It is equal to $I_D + I_A$ where I_D is given by the relation $I_D = I/\frac{6+6\rho}{6-7\rho}$ or $I \times \frac{6-7\rho}{6+6\rho}$.

Hence, $I_A = I - (I \times \frac{6-7\rho}{6+6\rho}) = I \times \frac{13\rho}{6+6\rho}$.

The changes in the orientation scattering indicate the changes in the shape and structure of the particles taking place during gelation.

The density scattering is directly proportional to the number of particles and the square of the volume of the particles, provided the size of the particles is less than the wavelength of light (Rayleigh[2]). Under standard and fixed conditions I_D is given by

$I_D = KNV^2$........(*i*) where all the constants are included in K.

If C is the amount of matter in the colloidal state, then $C = NV\sigma$ where σ is the density of the substance in the colloidal state and is a constant.

Eliminating N between the two equations, we obtain

$$I_D = KCV/\sigma \quad \ldots\ldots\ldots \qquad (ii)$$

Therefore if the changes in I_D are measured in the case of a system undergoing gelation, they would represent the changes in the volume of the individual particles taking place during this process, provided the condition regarding the size of the particles in the Rayleigh's equation is satisfied by the system at all stages of gel-formation. It has been established already that the size of the particles even after the gel has set, is less than the wavelength of light.

On eliminating V between the first two equations we obtain:

$$I_D = C^2K/N\sigma^2 \ \ldots\ldots\ldots \qquad (iii)$$

Therefore the reciprocal of the changes in the value of I_D during gelation would represent the changes in the number of the scattering particles taking place during gel-formation.

The values of I_D were calculated in the case of a gel system containing A = 25 and B = 5·0 (*cf.* Table II). This choice was made because, in this case, the rate of change of I with time is the slowest. This would avoid any errors creeping in on account of the rapid changes of I with time. Further for the sake of accuracy the values of I and $\frac{6+6\rho}{6-7\rho}$ have not been taken from the data in Table II but from the smoothened curve drawn between I and $\frac{6+6\rho}{6-7\rho}$ against time; the values of these factors are given in Table X. The calculated values of $I_D = I \times \frac{6-7\rho}{6+6\rho}$ and $I_A = I \times \frac{13\rho}{6+6\rho}$ are shown in columns 4 and 5 of Table X.

TABLE X

Time in minutes	$\frac{6+6\rho}{6-7\rho}$	I in cm.	Density scattering I_D	Anisotropy scattering I_A	Volume of the particles in relation to the volume after gelation
3	92·0	23·5	0·26	23·2	0·18
4	50·0	22·0	0·44	21·6	0·30
5	32·0	17·2	0·54	16·7	0·37
7	13·7	9·5	0·69	8·8	0·47
10	6·2	6·4	1·03	5·4	0·70
12	5·0	6·0	1·20	4·8	0·81
15	4·0	5·9	1·48	4·4	1·00
20	4·0	5·9	1·48	4·4	1·00

(*a*) *Changes in the anisotropy scattering during gelation.*—It will be seen from Table X that in the early stages of gel-formation I_A predominates over

I_D. The anisotropy scattering decreases rapidly during gelation and it is this scattering that decides the final observed changes of the total intensity of scattering which also decreases during gel-formation.

(*b*) *Changes in the density scattering during gelation.*—It is very interesting to note that although the total scattering decreases during gelation, the density scattering I_D increases during gel-formation. The increase of I_D during gelation points out that an increase in volume and a decrease in the number of particles take place during gel-formation. This is analogous to coagulation. Hence this gives an independent evidence to support the view that gelation is a special type of coagulation.

(*c*) *Changes in the volume of the individual particles during gel-formation.*—If I_f is the density scattering at the final stage of gelation and I_D at any other stage, then from equation (*ii*) $I_D/I_f = V/V_f$, where V and V_f are the corresponding volumes at the two stages. If V_f is assumed to be unity then $V = I_D/I_f$.

These values of V at different stages of gelation have been calculated in the case of gels corresponding to Table II and the data obtained are shown in the last column of Table X. It will be seen that the volume of the individual particles increases during gelation and reaches a constant value when the gel is set. The volume of the particles in the gel state is about six times of that at the commencement of the gelation process.

(*d*) *Comparative volume of the gel particles, in gels under different conditions of formation.*—An attempt has been made to compare the final volume of the gel particles, in the gels formed under different conditions. The results are shown in Table XI. The third column gives the concentration of the gel (the amount of thorium molybdate per litre) corresponding to table numbers given in column 1 of Table XI. The final values of the density scattering which is proportional to CV is shown in column 4.

TABLE XI

Gel corresponding to table No.	Amount of thorium molybdate formed	Concentration of thorium molybdate	Final values of I_D	Relative volume of the particles	The amount of excess of thorium nitrate
	g.				g.
II	0·58	11·6	1·48	1·00	0·71
III	0·52	10·4	1·32	1·00	0·76
IV	0·35	7·0	1·32	1·48	0·91
V	0·35	7·0	1·13	1·26	0·61

The numbers in column 5 is a measure of the comparative volume of the particles obtained by dividing the numbers in column 4 by the concentration of thorium molybdate expressed in grams per litre and expressing these values relative to the volume of the particles of the gel corresponding to Table II. In the last column is given the excess of thorium nitrate, etc., present which may exert an influence on the volume of the particles.

The results show that there are only little changes in the final volumes of the particles in the gels formed under different conditions. The relation between size and the excess of thorium nitrate present are not marked, due probably to other factors like the amount of potassium nitrate, etc., present in the gel-forming system.

(*e*) *The mechanism of the formation of the gel.*—From the results obtained the following can be inferred regarding the process of the formation of thorium molybdate gel. When thorium nitrate and potassium molybdate solutions are mixed, a precipitate of thorium molybdate is formed which is peptised in a few seconds by thorium nitrate (an excess of thorium nitrate is always necessary for gel-formation in this case) to a highly anisotropic (high ρ_v) opaque thorium molybdate sol. This opaque sol can be prepared if necessary by diluting the product obtained by mixing the two solutions. The high value of ρ_v and ρ_u may be due to the high anisotropy in shape or/and structure of the sol particles. The sol then gets coagulated and so there is an increase in the volume and a decrease in the number of scattering particles during gel-formation. The volume of the coagulated particles is less than the wavelength of light. During gelation the anisotropy scattering decreases and this is due to the decrease in shape or/and structure of the particles taking place during the formation of the gel. The gel is not set when the coagulation is complete, that is, when the values of I become constant. The coagulum now takes up plenty of water and the gel particles become heavily hydrated. This process does not produce any change in the intensity of scattered light for reasons explained before. Probably at this stage great changes in viscosity take place and after a time the whole system sets to a gel.

5. *Applicability of the relation* $\rho_u = \left(1+\frac{1}{\rho_h}\right)\Big/\left(1+\frac{1}{\rho_v}\right)$

The applicability of the relation connecting ρ_v, ρ_h and ρ_u theoretically deduced by R. S. Krishnan[8] has been examined in the case of the gels studied in this investigation by comparing the observed values of ρ_u with those calculated from the above relation using the final values of ρ_v and ρ_h, that is, the values at the completion of the gelation process. The results are given in Table XII.

TABLE XII

Gel corresponding to table No.	Final observed values of			
	ρ_h	ρ_v	ρ_u (obs.)	ρ_u (cal.)
II	67	25·9	52·8	51·2
III	78	11·9	29·5	24·3
IV	70	7·2	14·0	16·3
V	67	9·9	20·8	22·5
VI	70	19·8	37·6	40·1
VII	78	9·3	20·8	19·4

Considering the difficulties in the accurate determination of the high values of ρ_h by Cornu's method, it can be inferred that Krishnan's relation holds good for the gel investigated.

Summary and Conclusions

The changes in the intensity and depolarisation factors of the light transversely scattered by thorium molybdate gels have been investigated. The intensity of scattered light has been measured by a photoelectric arrangement with an amplifying unit. The depolarisation factors (ρ_v, ρ_h and ρ_u) have been measured by the well-known Cornu's method using a double image prism and Nicol.

It has been shown from the measurements of ρ_h and a comparison of the backward and forward scatterings that the size of the particles even after the gel has set is smaller than the wavelength of light. An approximate estimate of the size of the particles of thorium molybdate gels has been made by comparing the light scattered at 45° and 135° to the direction of the incident light. It has been shown that the size of the particles is about $\frac{1}{4}\lambda$. It has been pointed out that hydration produces no change in scattering and so the actual size of the gel particles may be greater than $\frac{1}{4}\lambda$.

Since the size of the particles is smaller than the wavelength of light, the density scattering I_D and the anisotropy scattering I_A have been separately calculated from the total intensity of scattering and their changes during gelation studied. It has been found that the density scattering increases during gel-formation. This increase is due to an increase in the volume and a decrease in the number of particles during gel-formation. This is analogous to coagulation. It has therefore been inferred that gelation is a coagulation and hydration phenomenon.

The study of the anisotropy scattering has led to interesting results. In the early stages of gel-formation, the anisotropy scattering is very many times greater than the density scattering, in other words, it dominates over the density scattering. The anisotropy scattering decreases rapidly during gelation and it is this scattering that decides the final observed changes in the intensity of scattered light. Thus the total intensity of scattered light decreases although the density scattering increases during the formation of the gel.

A comparison of the final volume of the gel particles of the same gel formed by mixing different amounts of the gel-forming constitutents shows that there are no great changes in the final volumes of the gel particles in the gels formed under different conditions of gel-formation.

It has been found that the relation connecting ρ_v, ρ_h and ρ_u theoretically deduced by R. S. Krishnan holds good for the gel investigated.

The process of formation and the effect of different constituents of the gel-forming mixture on the course of gel-formation have been discussed in detail.

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