

# STUDY OF THE OPTICAL PROPERTIES OF GELS

## Part II. Thorium Arsenate Gels

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IN a previous paper Prasad and Guruswamy<sup>1</sup> have investigated the changes in the intensity and depolarisation of the light transversely scattered by thorium molybdate gels during setting. In the present communication the intensity and depolarisation of the light transversely scattered by thorium arsenate gels during and after their formation have been studied. As in the case of thorium molybdate gels the density scattering and anisotropy scattering have been separately calculated from the total observed scattering and interpreted.

### *Experimental*

The gels were prepared by the method of Prasad and Desai<sup>2</sup> by mixing solutions of thorium nitrate and pyro-arsenic acid of suitable concentrations. The following solutions were employed for the preparation of the gels.

(A) *Thorium nitrate*  $Th(NO_3)_4 \cdot 4H_2O$  6% and (B) *Pyro-arsenic acid* 10%. Different volumes of (A) diluted to 25 c.c. were taken in one test-tube and in another were taken different volumes of (B) together with HCl or alcohol diluted to 25 c.c. The two solutions were mixed and the values of the intensity of scattered light and depolarisation factors were measured during the process of gel-formation, by the arrangement as described in the previous paper. The results obtained with gels prepared with different amounts of (A) and (B) are given in Tables I to VII in which T represents time in minutes. The amount of thorium arsenate in the gel has been calculated from the equation:



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

<sup>1</sup> *Proc. Ind. Acad. Sci.*, 1944, 19, 47.

<sup>2</sup> *J. Univ. Bom.*, 1938, 7, 132.

TABLE I

A = 25 c.c. = 1.21 g. of thorium nitrate  
 B = 5 c.c. = 0.5 g. of pyro-arsenic acid  
 The amount of thorium arsenate formed = 1.03 g.  
 The excess of pyro-arsenic acid present = 0.06 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
1	Opaque viscous sol .	..	..	11.0	1.4
2	Set to a gel ..	10.0	..	17.2	3.2
3	Opacity increases ..	13.2	..	23.6	4.2
4		17.5	..	29.5	4.8
5		19.8	89	33.0	5.0
6		..	..	35.5	5.2
8		23.0	..	40.0	5.4
10		..	81	43.8	5.5
12		26.5	..	47.2	5.7
15		28.3	70	49.1	5.8
20		30.7	70	49.1	5.8

TABLE II

A = 25 c.c. = 1.21 g. of thorium nitrate  
 B = 3.5 c.c. = 0.35 g. of pyro-arsenic acid  
 The amount of thorium arsenate formed = 0.83 g.  
 The excess of thorium nitrate present = 0.26 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
1		..	..	12.8	0.5
2	Opacity increases ..	5.8	..	16.3	1.4
3		..	..	18.0	2.2
4		..	89	20.2	2.9
5	Viscous ..	10.5	..	21.8	3.3
6		..	..	24.5	3.5
8	Set to a gel ..	12.5	76	30.7	3.8
12		..	..	33.3	4.1
15		16.3	..	36.1	4.2
20		17.5	76	36.1	4.2

TABLE III

A = 25 c.c. = 1.21 g. of thorium nitrate

B = 3 c.c. = 0.3 g. of pyro-arsenic acid

The amount of thorium arsenate formed = 0.71 g.

The excess of thorium nitrate present = 0.40 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
2		7.2	..	13.2	0.3
3		..	..	15.0	0.6
5		8.8	90	17.2	1.0
7		..	..	21.6	1.5
8	Viscous .. ..	..	..	23.8	1.8
10		11.9	..	27.0	2.1
12	Nearly set .. ..	..	..	29.5	2.4
15	Set to a gel .. ..	13.2	..	33.3	2.8
20		..	..	..	3.2
25	The gel is opaque and firm	14.7	81	38.0	3.3
30		14.7	81	38.0	3.4

TABLE IV

A = 25 c.c. = 1.21 g. of thorium nitrate

B = 2.5 c.c. = .25 g. of pyro-arsenic acid

The amount of thorium arsenate formed = 0.59 g.

The excess of thorium nitrate present = 0.48 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
2		..	..	7.0	0.1
5	Viscous .. ..	..	..	..	0.3
8	Opacity increases .. ..	..	..	9.0	0.5
15		5.8	..	10.6	1.0
20		7.2	85	11.5	1.6
25		9.9	..	12.5	2.3
30		12.5	..	14.0	2.8
35	Very viscous .. ..	13.2	..	16.3	3.1
40	Set to a gel .. ..	14.0	..	18.9	3.4
60		14.0	70	19.8	3.8

TABLE V

A = 20 c.c. = 0.91 g. of thorium nitrate  
 B = 3 c.c. = 0.3 g. of pyro-arsenic acid  
 The amount of thorium arsenate formed = 0.71 g.  
 The excess of thorium nitrate present = 0.10 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
2				4.5	0.3
5	Opacity increases .. ..	4.5	..	6.7	0.7
8		..	..	8.8	0.9
10		5.3	89	10.5	1.1
12	Very viscous .. ..	..	..	11.9	1.2
15	Nearly set .. ..	7.2	..	13.2	1.6
20	Set to a gel .. ..	9.3	..	14.0	2.0
25		10.5	..	14.7	2.4
30		10.5	..	15.5	2.8
40		10.5	75	15.5	3.0

TABLE VI

A = 25 c.c. = 1.21 g. of thorium nitrate  
 B = 5 c.c. = 0.5 g. of pyro-arsenic acid  
 HCl (1 N) = 2.0 c.c.  
 The amount of thorium arsenate formed (assuming  
 that HCl exercises no solvent action) = 1.03 g.  
 The excess of pyro-arsenic acid present = 0.06 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
1		..	..	..	0.3
2		..	..	7.0	0.8
3	Opacity increases .. ..	7.7	..	8.5	1.8
4		..	..	9.0	2.8
5		9.3	89	10.5	3.5
6		..	..	12.0	4.1
7		..	..	..	4.4
8	Viscous .. ..	11.9	..	13.5	4.7
10	Very viscous .. ..	..	..	18.0	5.0
12	Nearly set .. ..	14.7	..	..	5.2
15	Set to a gel .. ..	16.3	75	22.8	5.5
20		..	..	25.9	5.8
30		22.8	..	29.5	6.0
45		22.8	70	29.5	6.0

TABLE VII

A = 25 c.c. = 1.21 g. of thorium nitrate  
 B = 5 c.c. = 0.5 g. of pyro-arsenic acid  
 Ethyl alcohol = 5.0 c.c.  
 The amount of thorium arsenate formed = 1.03 g.  
 The excess of pyro-arsenic acid present = 0.06 g.

T	Observations	$\rho_v$	$\rho_h$	$\rho_u$	I in cm.
1		..	..	..	0.5
2		5.8	..	..	0.8
3	Opacity increases ..	..	..	4.5	1.1
4		..	..	..	1.5
5	Viscous ..	7.9	87	9.3	2.2
6		..	..	..	2.7
7		..	..	..	3.2
8		11.9	..	..	3.6
10	Nearly set ..	..	..	14.7	4.7
12		19.8	..	..	5.6
15	Set to a gel ..	23.8	75	21.8	6.8
20		27.1	..	32.0	8.6
25		29.5	..	40.6	10.0
45		30.7	68	45.5	..

#### Discussion of the Results

##### 1. Changes in the intensity and depolarisation of the scattered light during setting

The changes in the values of I and depolarisation factors during the gelation of thorium arsenate gels are shown in Tables I to VII. The values of  $\rho_v$  increase during gelation. This is contrary to what happens in the case of thorium molybdate gels. The values of  $\rho_v$  are very small when the solutions are mixed showing that the particles in the initial stages are nearly spherical. An increase in the value of  $\rho_v$  shows that during gelation they become anisotropic in shape or/and structure.

$\rho_h$  as in the case of thorium molybdate gels has a very high value in the beginning and it decreases during gelation. This shows that the particles grow in size during gel-formation. Further the high value of  $\rho_h$  shows that the size of the particles is not very large in comparison with the wavelength of light.

The values of  $\rho_u$  increase during the formation of the gel. This is due to an increase in the value of  $\rho_v$  and a decrease in the value of  $\rho_h$ .

The intensity of scattered light also increases during gelation. As observed in the case of thorium molybdate gels, the final values of I and

depolarisation factors in gels formed by mixing different amounts of A and B are different.

Unlike thorium molybdate gels, the values of  $I$ ,  $\rho_v$ ,  $\rho_h$  and  $\rho_u$  reach a constant value after or when the gel has set. In some cases, there are great changes in the values of  $I$  and depolarisation factors even after the gel has set. For example, the gel corresponding to Table I sets in about 2 minutes but large changes in the values of  $I$  and depolarisation factors continue to take place for about 20 mts.

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

It will be seen from Tables II, III and IV that the time of setting is increased by the presence of increasing amounts of thorium nitrate in the gel-forming mixture. Further, the rate of change of intensity of scattered light is decreased and the gel becomes more transparent, as the amount of thorium nitrate in the gel is increased. Increasing amounts of HCl also increase the time of setting. The gel particles formed in the presence of HCl are less anisotropic (*cf.* Tables I and VI). The opacity of the gels formed in the presence and absence of HCl is nearly the same. Thus the action of HCl on the formation of this gel appears to be different from that on thorium molybdate gel. The gel formed in the presence of alcohol is very firm. The addition of alcohol to the gel-forming mixture increases the time of setting (*cf.* Tables I and VII). Further, such an addition increases the final values of  $I$ ,  $\rho_v$  and  $\rho_u$ . The high final values of  $I$ ,  $\rho_v$  and  $\rho_u$  may be due to the unavoidable appearance of tiny air bubbles formed probably on account of the evaporation of alcohol.

3. *The size of the particles*

The high value of  $\rho_h$  during and after gel formation indicates that the gel particles are not very large in comparison with the wavelength of light.

An approximate idea of the magnitude of the size of scattering particles in this gel has been obtained by comparing the intensity of scattered light in the directions  $45^\circ$  and  $135^\circ$  to the direction of the incident light, for the least anisotropic thorium arsenate gel (gel corresponding to Table V,  $\rho_v = 10.5$ ). The experimental arrangement employed for this purpose was the same as that used in the study of thorium molybdate gel. The results show that  $I_{135}/I_{45}$  is not greater than 1.5. So, the size of the particles even after the gel has set is not greater than  $\frac{1}{4} \lambda$  (*cf.* Prasad and Guruswamy, *loc. cit.*). The particles of the gel are highly hydrated and so their actual size may be greater than  $\frac{1}{4} \lambda$ . This increase could not be measured by this method as

hydration cannot produce any direct change in the intensity of scattered light.

#### 4. Separation of the density scattering and anisotropy scattering

The separation of the density and anisotropy scattering from the total scattering observed has been done for the gel setting in a long time (gel corresponding to Table IV) by the same method as employed in the case of thorium molybdate gel (Prasad and Guruswamy, *loc. cit.*). The results obtained are shown in Table VIII.

TABLE VIII

Time in minutes	$\frac{6 + 6\rho}{6 - 7\rho}$	I in cm.	Density scattering	Anisotropy scattering	Volume of the particles in relation to the final volume
2	1.17	0.1	0.09	0.01	0.04
5	1.20	0.3	0.25	0.05	0.10
8	1.22	0.5	0.41	0.09	0.17
10	1.23	0.6	0.49	0.11	0.20
15	1.26	1.0	0.79	0.21	0.32
20	1.29	1.6	1.24	0.36	0.51
25	1.32	2.3	1.74	0.56	0.71
30	1.36	2.8	2.06	0.74	0.84
35	1.44	3.1	2.15	0.95	0.88
40	1.53	3.4	2.22	1.18	0.91
60	1.56	3.8	2.44	1.36	1.00

The gel corresponding to Table I is very interesting. This gel is prepared by mixing 25 c.c. of thorium nitrate and 5 c.c. of pyro-arsenic acid diluted to 25 c.c. It sets in about 2 minutes and there are great changes in the values of I and depolarisation factors after it has set and these changes continue for about 20 minutes. Therefore, for this gel also the intensities of scattering due to density and anisotropy have been separately calculated and shown in Table IX.

TABLE IX

Time in minutes	$\frac{6 + 6\rho}{6 - 7\rho}$	I in cm.	Density scattering	Anisotropy Scattering
1	1.27	1.4	1.10	0.30
2	1.47	3.2	2.18	1.02
3	1.73	4.2	2.43	1.77
4	1.97	4.8	2.43	2.37
5	2.16	5.0	2.31	2.69
6	2.31	5.2	2.25	2.95
7	2.35	5.3	2.25	3.05
8	2.62	5.4	2.06	3.34
10	2.94	5.5	1.87	3.63
12	3.28	5.7	1.74	3.96
15	3.49	5.8	1.66	4.14
20	3.49	5.8	1.66	4.14

(a) *Variation of the anisotropy scattering during gelation.*—Unlike the case of thorium molybdate gel, the scattering due to anisotropy in this case increases during gel-formation. In the initial stages of gel-formation the anisotropy scattering is small compared with the density scattering. During the process of gel-formation it increases and at the final stage of gel-formation it contributes in comparable measure to the total observed scattering. This shows that the particles in the early stages of gel-formation are nearly spherical and they become more anisotropic in shape or/and structure as gelation proceeds.

The density scattering for the gel corresponding to Table I is fairly constant soon after it sets. Later on, it decreases steadily by a small amount. The anisotropic scattering for this gel is less than the density scattering in the beginning. Later on it increases enormously after the gel has set and becomes about 2.5 times the density scattering, when the total intensity reaches a constant value. The enormous changes in the total scattering taking place after the gel has set are therefore due to the changes in anisotropy of shape or/and structure of the particles.

(b) *Variation of the density scattering during gelation.*—As in the case of thorium molybdate gels, the density scattering increases during gel-formation (*cf.* Table VIII, column 4). This behaviour points out to an increase in the volume and a decrease in the number of particles taking place during gelation, thus showing that gelation is analogous to coagulation.

(c) *Changes in the volume of the individual particles during gelation.*—As in the case of thorium molybdate gels, the values of  $V = I_D/I_F$ , that is, the volume of the particles during gelation in relation to the final volume are calculated and shown in the last column of Table VIII. It will be seen that the volume of the 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 25 times of that at the commencement of gel-formation.

(d) *Comparison of the final volume of the gel particles.*—The comparative volumes of the particles in gels formed by mixing different amounts of (A) and (B) are shown in column 5, Table X. These data have been obtained by dividing the final values of the density scattering  $I_D$  by the concentration of thorium arsenate in grams per litre (column 3, Table X) and expressing these values relative to the volume of the particles of the gel corresponding to Table III.



TABLE X

Gel corresponding to Table No.	Amount of thorium arsenate formed	Concentration of thorium arsenate	Final value of density scattering	Relative volumes of the gel particles	Excess of thorium nitrate
II	g. 0.83	16.6	1.79	1.11	g. 0.26
III	0.71	14.2	1.37	1.00	0.40
IV	0.59	11.8	2.44	2.14	0.48
V	0.71	14.2	2.11	1.55	0.10

It will be seen from the above table that the final volumes of the particles in the gel state change with a change in the values of (A) and (B), but the changes are not very great. The excess of thorium nitrate present which may contribute to changes in the volume of the particles is given in the last column of Table X. The effect of the presence of excess of thorium nitrate on the size is not very clear.

(e) *The mechanism of the formation of the gel.*—From the results obtained the following can be inferred as to the process of the formation of the gel. When the solutions of thorium nitrate and arsenic acid are mixed, a colloidal solution of thorium arsenate is immediately formed. The particles in the sol are nearly spherical (low value of  $\rho_p$ ). Later on, the sol gets coagulated; this is inferred from the increase in the size of the particles and a decrease in the number of particles during gelation. Unlike the behaviour of thorium molybdate gels, hydration also probably accompanies coagulation and the whole system sets to a gel by about the time taken for I and depolarisation factors to reach a constant value. The hydration of the particles cannot produce any change in the intensity of scattered light as there is no difference in refractive index between the water that is attached to the micelles and the "free" water. As the particles coagulate, they become more and more anisotropic (increase of anisotropic scattering during gelation). In this respect this gel is different from thorium molybdate, in which case, the anisotropy of the particles was found to decrease during gelation. From the above it can be seen that the time of setting is the time required for the coagulation of the sol of the gel-forming substance and the subsequent hydration of the gel particles. This time is increased by the presence of increasing amounts of thorium nitrate, HCl, and alcohol. This means that thorium nitrate, HCl and alcohol act as peptising agents hindering the coagulation and hydration.

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

The applicability of the relation theoretically deduced by R. S. Krishnan<sup>3</sup> has been examined for this gel by comparing the observed values of  $\rho_u$  with those calculated from the final observed values of  $\rho_v$  and  $\rho_h$  obtained at the completion of the gelation process. The results are shown in Table XI.

TABLE XI

Gel corresponding to Table No.	Final observed values of			$\rho_u$ (cal.)
	$\rho_h$	$\rho_v$	$\rho_u$ (obs.)	
I	72	30.7	49.1	56.1
II	76	17.5	36.1	34.4
III	81	14.7	38.0	28.7
IV	70	14.0	19.8	30.1
V	75	10.5	15.5	22.2

Considering the difficulties in the accurate determination of the high values of  $\rho_h$  by Cornu's method it can be inferred that Krishnan's relation holds good for the gel investigated, though the agreement between the calculated and the observed values is not so good as in the case of thorium molybdate gels. This point is being separately investigated.

*Summary and Conclusions*

The changes in the intensity and depolarisation of the light transversely scattered by gel-forming mixtures of thorium arsenate gels during and after setting have been investigated. The intensity of scattered light has been measured by a photoelectric arrangement and the depolarisation factors by the well-known Cornu's method.

It has been shown from the measurements of the value of  $\rho_u$  and a comparison of the backward and forward scatterings that the size of the gel particles is less than the wavelength of light. An approximate estimate of the size of the particles has been obtained by comparing the intensity of scattered light at 45° and 135° to 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 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 and anisotropy scattering have been separately calculated

<sup>3</sup> *Proc. Ind. Acad. Sci.*, 1935, 1, 717, 782.

from the total observed scattering and their changes during gelation studied. It has been found that the density scattering increases during gel-formation, showing thereby that gelation is analogous to coagulation.

Further, it has been found that the anisotropy scattering increases during gel-formation and it is smaller than the density scattering. In one case of thorium arsenate gel, the intensity of scattered light and the values of  $\rho_v$  and  $\rho_u$  increase enormously even after the gel has set. In this case also the density and the anisotropy scatterings have been separated. The results show that there are great changes in the anisotropy scattering after the gel has set and it is this scattering that contributes to the changes in the total intensity of scattered light taking place after the gel has set.

The volume of the gel-particles at different intervals of time during gelation has been expressed in relation to the final volume of the particles. The results show that the particles increase by about 25 times during gel-formation.

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

The applicability of the relation  $\rho_u = \left(1 + \frac{1}{\rho_h}\right) / \left(1 + \frac{1}{\rho_v}\right)$  has been examined for this gel. It has been inferred by comparing the final observed and calculated values of  $\rho_u$  that the above-mentioned equation is applicable to this gel to a fair extent.

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

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