

STUDY OF THE OPTICAL PROPERTIES OF GELS

Part III. Silicic Acid Gels

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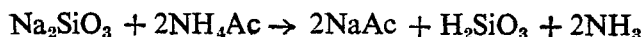
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IN previous communications Prasad and Guruswamy¹ have studied the changes in the intensity and depolarization of the light scattered transversely by thorium molybdate and thorium arsenate gels during and after setting. The present communication deals with the study of the intensity and depolarization of light transversely scattered by silicic acid gels during and after their formation. The effects of the constituents of the gel-forming mixture and of the addition of HCl and ethyl alcohol on these factors have also been studied.

Experimental

Silicic acid gel is the earliest known inorganic gel and this has been prepared by several workers usually by the action of acids, organic and inorganic, upon sodium silicate solutions. In the present investigation these gels were prepared by the method of Bhatnagar and Mathur² by mixing solutions of sodium silicate and ammonium acetate of suitable concentrations. The following solutions were used:

(A) *Sodium silicate solution 6% and (B) Ammonium acetate 20%.*—Different volumes of (A) diluted to 25 c.c. were taken in one test-tube. In another were taken different volumes of (B) together with HCl, alcohol, etc., diluted to 25 c.c. The two solutions were mixed and the intensity and depolarization factors were measured at different intervals of time during and after setting. The experimental arrangements were the same as that described in earlier publications. The results are given in Tables I to IX in which T represents time in minutes. The amount of silicic acid in the gel has been calculated from the equation:



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

¹ *Proc. Ind. Acad. Sci.*, 1944, 19, Parts I and II.

² *Koll. Zeit.*, 1922, 30, 368.

TABLE I

A = 25 c.c. = 1.5 g. of sodium silicate
 B = 5 c.c. = 1.0 g. of ammonium acetate
 The amount of silicic acid formed = 0.51 g.
 The excess of sodium silicate present = 0.71 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1					0.5
2	Opacity increases	2.5	81	2.2	1.1
3		2.1
4		2.8	3.1
5		3.4	76	3.8	4.1
6		5.8	4.6
7		5.2
8		Set to a gel	5.8	..	13.3
9	5.8
10	7.2		71	14.7	6.0
15	..		68	15.5	6.3
20	8.2		..	15.5	6.3

TABLE II

A = 25 c.c. = 1.5 g. of sodium silicate
 B = 4.5 c.c. = 0.9 g. of ammonium acetate
 The amount of silicic acid formed = 0.46 g.
 The excess of sodium silicate present = 0.79 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.	
1					0.2	
2	Opacity increases	2.0	..	3.1	0.8	
3		1.1	
4		1.5	1.4	
5		2.5	84	1.6	2.1	
6		Viscosity increases	2.6
7			3.0
8			4.1	3.3
10	4.1	81	4.9	4.0		
12	Set to a gel	4.6	
15		6.2	76	9.3	5.3	
20		7.7	..	11.9	5.9	
25		8.3	..	13.3	6.1	
35		8.4	70	15.5	6.2	

TABLE III

A = 25 c.c. = 1.5 g. of sodium silicate

B = 4 c.c. = 0.8 g. of ammonium acetate

The amount of silicic acid formed = 0.41 g.

The excess of sodium silicate present = 0.87 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
3	Opacity increases	0.8	..	4.9	0.3
8		1.4	..	2.9	1.0
10		1.6	80	2.0	1.6
15		2.2	..	3.1	2.4
20	Viscous	3.5	..	4.1	3.0
25		4.9	70	5.3	3.6
30	Nearly set	5.9	..	7.0	4.2
35	Set to a gel	6.7	..	7.5	4.6
60		8.2	70	13.3	5.2

TABLE IV

A = 20 c.c. = 1.2 g. of sodium silicate

B = 4 c.c. = 0.8 g. of ammonium acetate

The amount of silicic acid formed = 0.41 g.

The excess of sodium silicate present = 0.57 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1	Opacity increases	0.6
2		0.9
5		2.0	90	2.0	1.1
8		1.7	1.3
10		2.5	..	2.5	1.7
15		3.8	..	4.7	2.9
18		3.4
20		4.9	..	6.2	3.8
25	Nearly set	6.2	87	7.2	4.1
30		Set to a gel	8.2
45		4.9
60		8.2	..	12.5	4.9
180		8.3	78	14.7	..

TABLE V

A = 15 c.c. = 0.9 g. of sodium silicate

B = 4 c.c. = 0.8 g. of ammonium acetate

The amount of silicic acid formed = 0.41 g.

The excess of sodium silicate present = 0.27 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
2		0.6
3		0.9
5	Opacity increases	2.8	90	2.0	1.0
7		1.5
8		3.2	..	2.2	1.8
10		3.5	..	3.8	2.1
12		2.5
15	Viscous	4.5	..	5.8	3.3
18		3.6
20	Nearly set	5.8	75	7.7	3.8
30	Set to a gel	8.2	..	11.2	3.9
45		9.3	..	13.3	4.1
70		9.3	66	14.7	..

TABLE VI

A = 25 c.c. = 1.5 g. of sodium silicate

B = 4 c.c. = 0.8 g. of ammonium acetate

HCl (1 N) = 1.0 c.c.

The amount of silicic acid formed = 0.41 g.

The excess of sodium silicate present = 0.87 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
2		2.0	..	2.6	1.0
3		1.2
5	Opacity increases	2.8	90	2.2	1.6
6		2.0
8	Viscous	3.4	..	3.4	2.9
10		4.5	..	4.1	3.6
12	Nearly set	5.3	..	4.9	4.0
15	Set to a gel	6.7	..	7.7	4.6
18		5.0
20		7.7	..	11.9	5.2
25		8.2	75	13.2	..
30		5.4
45		8.2	70	14.3	5.5

TABLE VII

A = 25 c.c. = 1.5 g. of sodium silicate
 B = 4 c.c. = 0.8 g. of ammonium acetate
 HCl (1 N) = 2.0 c.c.
 The amount of silicic acid formed = 0.41 g.
 The excess of sodium silicate present = 0.87 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
1		2.2	..	3.4	1.0
2		1.5
3		2.3
4		3.1
5	Opacity increases	4.1	90	4.9	3.7
6		4.4
8	Viscous	6.2	..	9.6	5.0
10	Nearly set	5.4
12	Set to a gel	8.2	5.7
15		8.8	80	13.3	5.8
20		9.3	..	14.7	5.9
40		9.6	70	15.5	5.9

TABLE VIII

A = 25 c.c. = 1.5 g. of sodium silicate
 B = 4 c.c. = 0.8 g. of ammonium acetate
 Ethyl alcohol = 2.0 c.c.
 The amount of silicic acid formed = 0.41 g.
 The excess of sodium silicate present = 0.87 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
2		2.8	..	4.5	0.2
3		0.4
4		0.6
5	Opacity increases	3.1	90	5.3	1.0
6		1.5
7		2.0
8		4.4	..	6.2	2.4
9		2.9
10	Viscous	7.2	3.3
12		5.3	..	8.8	4.2
15	Set to a gel	6.7	..	10.6	4.7
20		8.8	..	13.3	5.6
25		9.4	..	14.7	5.9
30		9.4	74	15.5	6.0

TABLE IX

A = 25 c.c. = 1.5 g. of sodium silicate
 B = 4 c.c. = 0.8 g. of ammonium acetate
 Ethyl alcohol = 5.0 c.c.
 The amount of silicic acid formed = 0.81 g.
 The excess of sodium silicate present = 0.23 g.

T	Observations	ρ_v	ρ_h	ρ_u	I in cm.
2		2.2
3	Opacity increases ..	2.8	90	4.5	3.5
4		4.5
5		5.3	5.1
6		3.1	5.5
8		4.4	..	6.2	5.8
10	Viscous	7.2	6.0
12	Nearly set ..	5.3	..	8.8	..
15	Set to a gel ..	6.7	75	10.6	6.2
20		8.8	..	13.3	6.4
30		9.3	..	16.3	..
40		9.3	65	16.3	6.4

Discussion of the Results

1. Changes in the intensity and depolarization factors during gel-formation

The changes in the values of I and depolarization factors with time are shown in Tables I to IX. The values of ρ_v are very small in the beginning, that is when the solutions are mixed, showing the nearly spherical nature of the micelles in the initial stages of gel-formation. During gelation, these values increase indicating that the particles become more and more anisotropic in shape or/and structure.

ρ_h has a very high value. It decreases during gelation showing thereby that particles grow in size with time. High values of ρ_h indicate that the particles are not very large in comparison with the wavelength of light.

The changes in the value of ρ_u with time are interesting. It increases during gel-formation at first slowly and afterwards rapidly and reaches a constant value. In the case of the gel which sets in a comparatively long time, ρ_u has a high value in the beginning; later on, it decreases at first, passes through a minimum and then increases to a constant value (Table II). The changes in the value of ρ_u may be due to the increase in the value of ρ_v and a decrease in the value of ρ_h .

The intensity of scattered light also increases during setting. Further, it has been observed that the values of I and depolarization factors increase

even after the gel has set. This observation is similar to the one made in the case of thorium arsenate gels (Prasad and Guruswamy, *loc. cit.*). The silicic acid prepared by Subba Ramiah³ by mixing an acid and sodium silicate solutions seem to contain particles of size much greater (a comparatively low value of ρ_h) than the gels prepared by mixing sodium silicate and ammonium acetate solutions. The gels prepared by mixing an acid and sodium silicate solutions take a long time to set, whereas, the gels prepared by the method used in this investigation, set in a very much shorter time.

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

Increasing amounts of sodium silicate in the gel-forming mixture increase the time of setting and decrease the rate of change of intensity of scattered light (*cf.* Tables I, II and III). On the other hand, increasing amounts of HCl decrease the time of setting and increase the rate of change of scattered light (*cf.* Tables III, VI and VII). Ethyl alcohol acts as a coagulating agent, for in the presence of ethyl alcohol, the gel is formed in a much shorter time (*cf.* Tables III and IX). It is interesting to note that the anisotropy of the gel particles in the various gels prepared from different amounts of the gel-forming constituents, is nearly the same as shown by the nearly same values of ρ_v .

3. *Size of the Particles*

The high value of ρ_h during and after gel-formation indicates that the size of the particles is small in comparison with the wavelength of light. As in the case of other gels an approximate idea of the magnitude of the size of the particles of silicic acid gels has been obtained by comparing the intensity of light scattered in the directions 45° and 135° to the incident light for the least anisotropic gel (gel corresponding to Table I, $\rho_v=8.2$). The results show that I_{135}/I_{45} is not greater than 1.5 and therefore the size of the particles is not greater than $\frac{1}{4} \lambda$ (*cf.* Prasad and Guruswamy, *loc. cit.*).

4. *Separation of the density and anisotropy scattering*

As in the case of thorium molybdate and thorium arsenate gels (Prasad and Guruswamy, *loc. cit.*) the density and anisotropy scatterings have been separately calculated from the total scattering and the results obtained are shown in Table X, in the case of the gel corresponding to Table III. The volume of the particles has been expressed in relation to the final volume of the

³ *Proc. Ind. Acad. Sci.*, 1937, 5, 138.

particles when the gelation is complete and the results are given in the last column of Table X.

TABLE X

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
3	1.11	0.3	0.27	0.03	0.07
8	1.06	1.0	0.94	0.06	0.24
10	1.05	1.6	1.53	0.07	0.39
15	1.07	2.4	2.25	0.15	0.58
20	1.09	3.0	2.75	0.25	0.64
25	1.12	3.6	3.22	0.38	0.83
30	1.17	4.2	3.60	0.60	0.92
35	1.18	4.6	3.90	0.70	1.00
60	1.34	5.2	3.90	1.30	1.00

(a) *Changes in the anisotropy scattering during gelation.*—The contribution of the anisotropy scattering to the total scattering for silicic acid gels is comparatively smaller than those in gels of thorium molybdate and arsenate. As in the case of thorium arsenate gels, the anisotropy scattering increases during gel-formation. This shows that the particles become more anisotropic during gelation. In the earlier stages of gel-formation the anisotropy scattering is very small, showing that the particles are nearly spherical.

(b) *Changes in the density scattering during gelation.*—As in the case of other gels, the density scattering increases with time. This increase in the density scattering points to the increase in the volume and a decrease in the number of particles during gelation. Thus gelation is a coagulation process.

(c) *Changes in the volume of the individual particles during gelation.*—The volume of the individual particles at different intervals of time during gelation in relation to the final volume increases during gelation (column 4, Table X). The final volume of the gel particles is about 15 times of that at the commencement of the gelation process.

(d) *Comparison of the final volumes of the gel particles.*—A relative value of the volume of the particles in the gels prepared by mixing different amounts of A and B is shown in Table XI. These values have been obtained by dividing the final values of the density scattering I_D by the concentration of silicic acid in grams per litre (given in column 3) and expressing these values relative to the volume of the particles of the gel corresponding to Table V. The excess of sodium silicate which may exert an influence on the final volume of the gel particles is given in the last column of the table.

TABLE XI

Gel corresponding to table No.	Amount of silicic acid formed	Concentration of silicic acid	Final value of density scattering	Relative volumes of the particles	Excess of sodium silicate present
I	g. 0.51	10.2	4.47	1.17	g. 0.71
II	0.46	9.2	4.39	1.28	0.79
III	0.41	8.2	3.90	1.27	0.87
IV	0.41	8.2	3.54	1.15	0.57
V	0.41	8.2	3.07	1.00	0.27
VI	0.41	8.2	4.01	1.31	0.87 & HCl

It will be seen that there are very little changes in the volume of the particles in the gels formed by mixing different amounts of (A) and (B).

(e) *The mechanism of the formation of the gel.*—From the results obtained, the following can be inferred regarding the process of formation of silicic acid gels. When the two solutions of sodium silicate and ammonium acetate are mixed, a colloidal solution of silicic acid is formed. The colloidal silicic acid coagulates and the particles also get hydrated, the two processes running concurrently. After some time the whole mass sets to a gel. During gelation, in addition to the increase in size, there is also an increase in anisotropy in shape or/and structure of the coagulum resulting in an increase in the value of ρ_v and the anisotropy scattering I_A .

5. The applicability of the relation connecting ρ_v , ρ_h and ρ_u

The applicability of the relation $\rho_u = \left(1 + \frac{1}{\rho_h}\right) / \left(1 + \frac{1}{\rho_v}\right)$ connecting ρ_v , ρ_h and ρ_u theoretically deduced by R. S. Krishnan has been examined in the case of silicic acid gels by comparing the observed values of ρ_u with those calculated from the above relation using the final observed values of ρ_v and ρ_h , that is, the values at the completion of the gelation process. The results obtained are shown in Table XII.

TABLE XII

Gel corresponding to table No.	Final observed values of			
	ρ_h	ρ_v	ρ_u (obs.)	ρ_u (cal.)
I	68	8.2	15.5	18.7
II	70	8.4	15.5	18.8
III	70	8.2	13.3	18.4
IV	78	8.3	14.7	17.5
VI	70	8.2	14.3	18.4

The observed and calculated values of ρ_u fairly agree with each other. It can be therefore inferred that Krishnan's relation holds good fairly for the gels investigated.

Summary and Conclusions

The changes in the intensity and depolarization of the light transversely scattered by silicic acid gels during and after their formation have been investigated.

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 is less than the wavelength of light. An approximate estimate of the size of the particles has been made by comparing the intensities of light scattered at 45° and 135° to the incident light. It has been found that the size of the particles is about $\frac{1}{4}\lambda$. It has been pointed out that hydration can produce no change in the intensity of 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 less than the wavelength of light the density and anisotropy scatterings have been separately calculated from the observed total scattering, and their changes during gelation investigated. As in the case of other gels, the density scattering increases during gel-formation thereby showing that gelation is analogous to coagulation.

The anisotropy scattering is small compared with the density scattering in the early stages of gel-formation (about 1/9th). It increases during gel-formation and becomes about a third of the density scattering. The increase in the anisotropy scattering shows that the gel particles become more anisotropic during gelation.

The volume of the gel-particles at different intervals of time during gelation has been expressed in relation to the final volume of the gel-particles. The results show that the particles increase by about 15 times during gel-formation.

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

It has been inferred by comparing the observed and calculated values of ρ_u that the relation $\rho_u = \left(1 + \frac{1}{\rho_h}\right) / \left(1 + \frac{1}{\rho_v}\right)$ holds good fairly in the case of silicic acid gels.

The process of formation and the effect of different amounts of the gel-forming constituents on the formation of silicic acid gels as revealed by this investigation have been discussed in detail.

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